Fulleropyrrolidine-containing sterically hindered phenol. Synthesis, structure, and properties

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Fulleropyrrolidine containing a sterically hindered phenolic fragment was synthesized by the reaction of fullerene C_{60} with *N*-methylglycine and 3,5-di-*tert*-butyl-4-hydroxybenzaldehyde. Electrochemical reduction of fulleropyrrolidine-containing phenol **1** and the corresponding phenoxide ion proceeded stepwise to form stable radical anions, dianions, and trianions. The radical anion (g = 2.0000) and the phenoxyl radical (g = 2.0045) obtained by chemical oxidation with lead dioxide were identified by ESR spectroscopy. The electron affinity of fulleropyrrolidine was estimated at 2.58 eV. For the phenoxide ion, the electrochemical gap was determined ($\Delta E = E_{\rm I}^{\rm ox} - E_{\rm I}^{\rm red}$ = 0.47 V). The heats of formation and the energies of the frontier orbitals of fulleropyrrolidine and its transformation products were evaluated by the PM3 method.

Key words: fullerenes, fulleropyrrolidines, electrochemistry, ESR spectroscopy, electronic structure, quantum-chemical calculations.

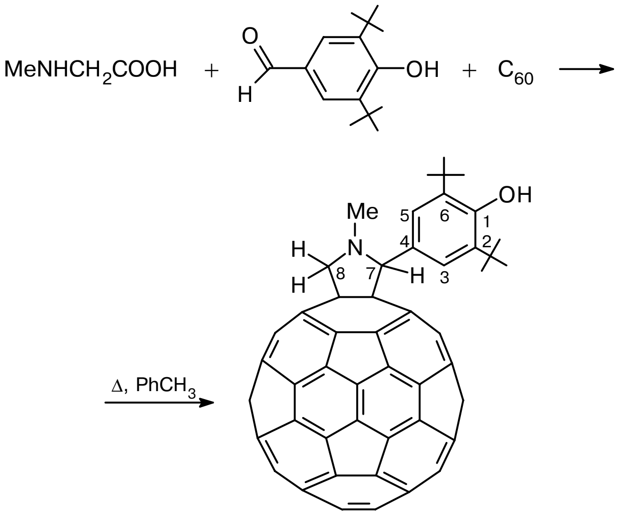
The availability of fullerene C_{60} [1] gave impetus to a search for new functionally substituted fullerene derivatives promising in studies of biological properties.[2,3] These hopes are associated with the fact that the fullerene core readily interacts with different electron donors,[4,5] is excited with light, and accepts an electron to form the radical anion.[6] A search for new fullerene derivatives containing the so-called "pharmacophore" groups is of most interest. In the present study, we describe the synthesis of a representative of the previously unknown type of fullerene C_{60} derivatives containing a fragment of a sterically hindered phenol, which finds application as a component of medicines used in the treatment of tumor diseases.[7,8]

Results and Discussion

The fullerene core was functionalized by the reaction of fullerene C_{60} with 3,5-di-*tert*-butyl-4-hydroxybenzaldehyde and *N*-methylglycine (Scheme 1) on heating in toluene according to a general procedure for the synthesis of fulleropyrrolidines.[9,10]

Column chromatography on SiO_2 afforded compound **1**. Its structure was established by spectral methods and its composition was confirmed by the data from elemental analysis. The IR spectra of compound **1** have absorption bands typical of the fullerene core[11] (526.6, 572.8, 1178.5, and 1429.9 cm^{-1}) and the absorption band at 3652 cm^{-1} belonging to vibrations of the OH group of the phenolic fragment, which are consistent with the suggested structure **1**.

Scheme 1



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The electronic absorption spectrum of a solution of compound **1** in a 10 : 2 THF—$CHCl_3$ mixture has intense absorption bands at 258, 328, and 431 nm and weak bands (shoulders) at 460, 540, and 714 nm. The absorption band at 431 nm is characteristic of 6,6-adducts and is present in the spectra of virtually all fulleropyrrolidines.[3,9]

The ^{1}H NMR spectrum of compound **1** shows signals for the protons of the *tert*-butyl groups (δ 1.41), the

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N-methyl group (δ 2.86), and the CH_2 group (δ 4.98 and 4.28). The proton of the CH group of the pyrrolidine ring has a resonance signal at δ 4.87. The protons of the aromatic ring are manifested as two signals at δ 7.11 and 7.14. The proton of the OH group gives a signal at δ 5.14.

The ^{13}C NMR spectra of compound **1** have ^{13}C signals of the fullerene core and the attached fragment. It should be noted that the signals of the latter are observed in the ^{13}C NMR spectra at δ 125—130 and δ 156 (the aromatic ring), δ 40—75 (the C atoms bound to the N atom of the pyrrolidine fragment), and δ 29—34 (the carbon atoms of the *tert*-butyl groups). The ^{13}C chemical shifts of the sp^3-hybridized C atoms of the fullerene core are detected at δ 68.33 and 77.29, which is typical also of other fulleropyrrolidines.[9] The signals for virtually all sp^2-hybridized C atoms of the fullerene core of compound **1** are observed in the region δ 135—153. In our opinion, this indicates that the nonsymmetrical substituent has a pronounced effect on the electronic structure of the fullerene core resulting in distortion of its geometry.

The properties of compound **1** were studied by cyclic voltammetry and ESR spectroscopy using electrochemical generation of radical anions, which provided information on the character of electron transfer processes. Electrochemical reduction and oxidation of compound **1** were examined in a 2 : 1 toluene—DMF mixture against 0.1 *M* Et_4NBF_4 using a glassy-carbon electrode and in a 3 : 1 *o*-dichlorobenzene—DMF mixture against 0.1 *M* Bu_4NBF_4 using glassy-carbon and Pt electrodes.

Three reduction peaks were obtained both for compound **1** and fullerene C_{60} in a toluene—DMF solution (Fig. 1). However, these peaks for compound **1** are shifted to more negative potentials (Table 1) due, apparently, to a decrease in the electron affinity caused by the attachment of the pyrrolidine fragment to the fullerene core. The transfer of the first two electrons giving rise to the radical anion and the dianion, respectively, is reversible, *viz.*, the corresponding oxidation peaks appeared in the cyclic voltammograms upon reversal of the potential (see Fig. 1). The transfer of the third electron and the formation of the trianion occurs at potentials close to the decomposition potential of the supporting electrolyte. Apparently, the superposition of reduction currents of the supporting electrolyte is responsible for the facts that the oxidation peak of the trianion is absent from the cyclic voltammograms and the third reduction peak is formally irreversible.

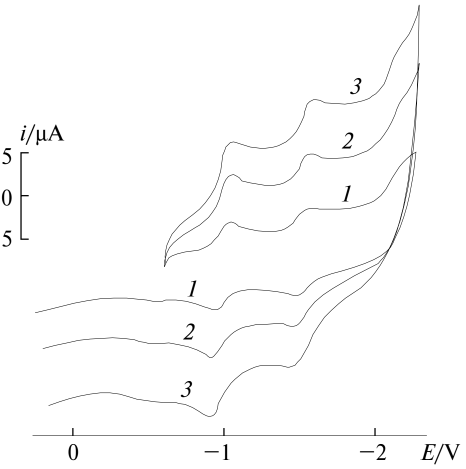


Fig. 1. Cyclic voltammograms of fulleropyrrolidine **1** in a toluene—DMF (2 : 1)/0.1 *M* Et_4NBF_4 mixture on a glassy-carbon electrode at 15 °C obtained at different rates of the potential scan: 20 (*1*); 50 (*2*); and 100 mV s^{-1} (*3*); the measurements were performed relative to Fc/Fc^+.

It should be noted that electroreduction of compound **1** did not proceed in this medium in the observ-

Table 1. Potentials* of the reduction and oxidation peaks of fulleropyrrolidine **1** and fullerene C_{60}

Compound	$c \cdot 10^3$/mol L^{-1}	Solvent	Supporting electrolyte	Electrode	$[Et_4NOH]$ /mol L^{-1}	$E_{p,1}^{red}$	$E_{p,2}^{red}$	$E_{p,3}^{red}$	$E_{p,1}^{ox}$	$E_{p,2}^{ox}$
						V				
C_{60}	0.2	PhMe—DMF (2 : 1)	0.1 *M* Et_4NBF_4	Glassy-carbon	—	−0.79	−1.30	−1.83	—	—
1	0.2	PhMe—DMF (2 : 1)	0.1 *M* Et_4NBF_4	Glassy-carbon	—	−0.90	−1.43	−2.08	—	—
					$5 \cdot 10^{-3}$	−0.90	−1.40	−2.05	—	—
C_{60}	1	*o*-DCB**—DMF (3 : 1)	0.1 *M* Bu_4NBF_4	Glassy-carbon	—	−0.96	−1.41	−1.91	—	—
				Pt	—	−0.96	−1.41	−1.91	—	—
1	1	*o*-DCB**—DMF (3 : 1)	0.1 *M* Bu_4NBF_4	Glassy-carbon	—	−1.05	−1.50	−2.10	—	—
					$1 \cdot 10^{-2}$	−0.93	−1.41	−2.06	—	—
						(−1.09)	(−1.56)			
				Pt	—	−1.04	−1.47	−2.05	—	—
					$1 \cdot 10^{-2}$	−0.99	−1.45	−2.04	—	—
						(−1.27)	(−1.58)		−0.52	−0.32

* The potentials were measured at 25 °C relative to the Fc/Fc^+ electrode with the use of Ag/0.01 *M* $AgNO_3$ as the reference electrode; *V* = 20 mV s^{-1}.

** *o*-Dichlorobenzene.

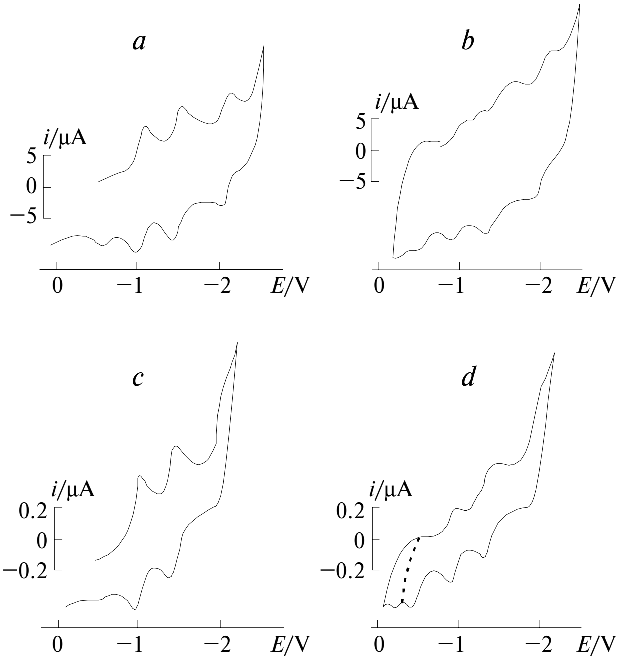


Fig. 2. Cyclic voltammograms of fulleropyrrolidine **1** ($1 \cdot 10^{-3}$ mol L^{-1}) in a *o*-dichlorobenzene—DMF (3 : 1)/0.1 *M* Bu_4NBF_4 system on glassy-carbon (*a*, *b)* and platinum (*c*, *d*) electrodes in the absence (*a*, *c*) and in the presence (*b*, *d*) of 0.01 *M* Et_4NOH at 22 °C; the rate of the potential scan was 100 mV s^{-1}.

able potential region (≤0.73 V). Taking into account the low solubility of compound **1** ($\leq 5 \cdot 10^{-4}$ mol L^{-1}) in toluene and DMF, the results obtained demonstrate that the toluene—DMF/0.1 *M* Et_4NBF_4 system is not optimum for studying electrochemical reactions of compound **1**. The latter and fullerene C_{60} are somewhat more soluble in a 3 : 1 *o*-dichlorobenzene—DMF mixture.* In this medium in the presence of 0.1 *M* Bu_4NBF_4, the decomposition potential of the supporting electrolyte is shifted to more negative values, and hence, four reduction peaks of C_{60} and three pronounced reduction peaks of compound **1**, which are not distorted by reduction processes of the supporting electrolyte, are observed in the experiments with the use of a glassy-carbon electrode. According to the data from cyclic voltammetry, all peaks are reversible (Fig. 2). These peaks are equal in height and each peak corresponds to single-electron transfer.

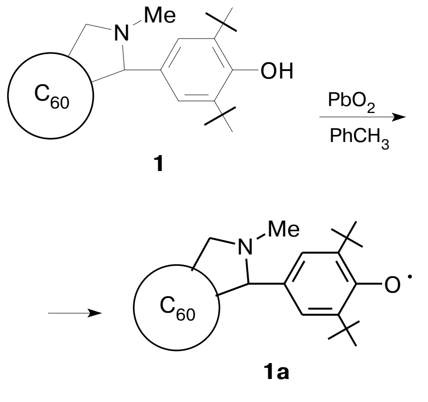
Reduction of compound **1** in an electrochemical cell directly in a resonator of an ESR spectrometer at the potentials of the first wave proceeded analogously to that of other fullerene derivatives[9] and was accompanied by the appearance of a signal of a radical anion of compound **1** characterized by $g = 2.0000$ and the line width of ~0.75 G at 290 K. In the course of electrolysis at the potentials of the first wave, the signal with $g = 2.0004$, which can be assigned to the dimeric radical anion $(\mathbf{1})_2^{\bullet -}$, appeared in the ESR spectrum along with the signal of the radical anion. Reduction at the potentials of the second wave corresponding to the formation of the dianion led to a decrease in the intensity of the signal of the radical anion and (to a lesser degree) to a decrease in the intensity of the signal of dimeric paramagnetic products. Switching-off of the potential was accompanied by an increase in the intensity of the ESR signal due to the reaction of the dianion with the initial molecule **1** to form two radical anions.

$$\mathbf{1}^{2-} + \mathbf{1} \longrightarrow 2\,(\mathbf{1}^{\bullet -})$$

Oxidation of compound **1** in this medium was not observed in the potential range under examination ≤+0.73 V. The fact that the fullerene fragment was not oxidized under these conditions seems to be quite reasonable because it is known[4] that it is rather difficult to abstract an electron from fullerene C_{60}. However, the fact that neither the pyrrolidine moiety nor the phenolic fragment were oxidized under these conditions is unexpected.

Oxidation of compound **1** by lead dioxide in toluene under an atmosphere of argon at 25 °C according to a procedure reproted previously[12] (Scheme 2) afforded phenoxyl radical **1a** characterized by $g = 2.0045$ and the line width of ~0.4 G with characteristic splitting caused by two *meta*-protons of the phenyl ring ($a_{2H} = 1.8$ G), the protons at the C(7) atom ($a_H = 4.7$ G), and the ^{14}N nucleus ($a_N = 0.9$ G) (Fig. 3).

Scheme 2



The rather high stability of phenoxyl radical **1a** allowed us to detect satellite lines in the ESR spectrum and to assign them to ^{13}C isotopes: $a^4{}_{^{13}C} = +13.8$ G, $a^1{}_{^{13}C} = -9.6$ G, and $a^{3,5}{}_{^{13}C} = -8.6$ G. The signs of these hyperfine splitting constants were chosen based on the effect of broadening of the low-field/high-field components of the satellite hyperfine splitting.[13,14]

Radical anions of organic compounds are generally protonated by phenols.[15] In the reduction of compound

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* Hereinafter, all experimental data and the discussion of the results refer to the *o*-dichlorobenzene—DMF (3 : 1)/0.1 *M* Bu_4NBF_4 system.

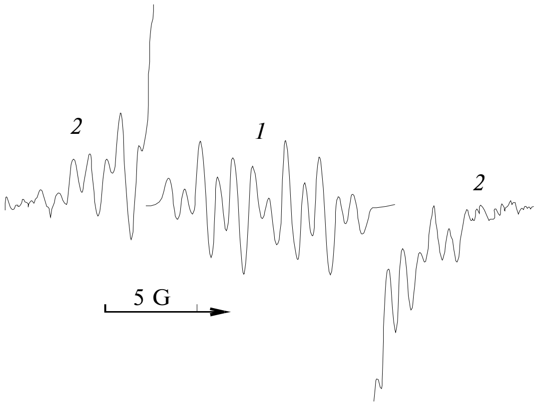
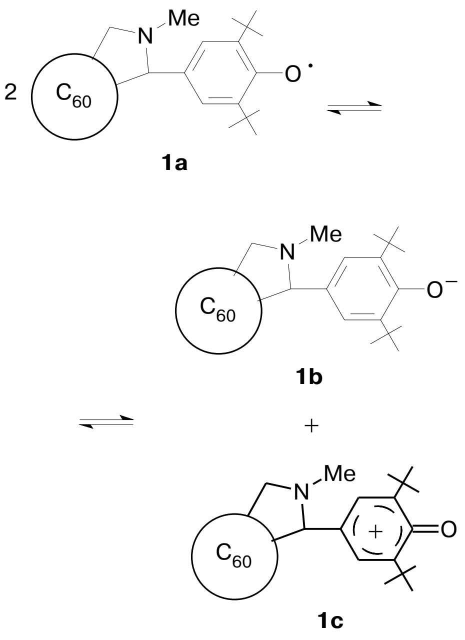


Fig. 3. ESR spectrum of phenoxyl radical **1a** in a solution in toluene at the amplifications of $2 \cdot 10^3$ (*1*) and $2 \cdot 10^5$ (*2*) at 303 K; the microwave power was decreased to 20 eV; the modulation amplitude was 0.032 mT.

1, the phenolic fragment could serve as a proton donor with respect to the radical anions of fullerene generated upon electrochemical reduction. The reversibility of three one-electron reduction peaks indicates that neither anion radicals nor even more basic dianions and trianions of compound **1** undergo autoprotonation. This is also evidenced by the fact that the oxidation peak of fullerene-containing phenoxide ion **1b** (Scheme 3) is absent on the reverse branch of the cyclic voltammograms obtained upon potential reversal of the limiting current of the third wave. The reversible oxidation peak of the phenoxide anion ($E_{p,1}{}^{ox} = -0.52$ V) is manifested only in the presence of a base generated electrochemically at the decomposition potential of the supporting electrolyte (see Fig. 2, *a* and *c*) and upon oxidation of the initial compound **1** in the presence of a tenfold excess of tetraethylammonium hydroxide. By analogy with the properties of sterically hindered phenols,[16] it can be suggested that reversilble one-electron oxidation of the fullerene-containing phenoxide ion giving rise to the phenoxyl radical occurred in the case under consideration. The latter was oxidized to the phenoxonium ion at the potentials of the second irreversible oxidation peak ($E_{p,2}{}^{ox} = -0.32$ V). The similarity of the potentials of two oxidation peaks ($\Delta E_p{}^{ox} = 0.20$ V) indicates that the phenoxyl radical can undergo disproportionation to form phenoxide ion **1b** and phenoxonium ion **1c**. The latter undergoes irreversible transformations.

Scheme 3



Radical **1a** was not detected upon electrooxidation on a Pt electrode directly in a resonator of an ESR spectrometer due, apparently, to disproportionation of **1a** and deep passivation of the electrode, which inhibits oxidation. This conclusion was confirmed by the results of electrochemical oxidation of 2,4,6-tri-*tert*-butylphenol, which is known to form a stable phenoxyl radical.[15] Under analogous conditions, no phenoxyl radical could either be detected for this compound by ESR spectroscopy, although the reversible oxidation peak was observed by cyclic voltammetry.

It is noteworthy that the addition of a tenfold excess of Et_4NOH leads to the appearance of oxidation peaks of compound **1** as well as to a change in the morphology of the cyclic voltammograms of reduction. This is manifested in splitting of the first two signals, and a total of five reduction steps are observed in the cyclic voltammogram. Additional peaks were observed at different potentials on Pt and glassy-carbon electrodes (see Fig. 2). The dependence on the electrode material is indicative of the absorption nature of these peaks. At the same time, the reverse branches of the cyclic voltammograms recorded on both electrodes are identical in character. Thus, three steps corresponding to oxidation of the trianion, the dianion, and the radical anion are observed. These peaks are virtually identical in intensities and potentials with the corresponding oxidation peaks obtained in the absence of Et_4NOH. Hence it follows that not only absorption, but also other factors are responsible for the appearance of the additional signals. Apparently, aggregation of poorly soluble compound **1** under conditions of electrolysis is one of these factors.

For various reaction series, the oxidation potentials ($E_{p,1}{}^{ox}$) measured in Volts linearly depend on the ionization potentials (IP_1) measured in electron-Volts or the reduction potentials ($E_{p,1}{}^{red}$) linearly depend on the electron affinity (*EA*), the slope coefficient (*a*) being close to 0.9.[17—20]

$$E_{P,1}{}^{ox} = aIP_1 + \text{const}_1$$

$$E_{P,1}{}^{red} = aEA + \text{const}_2$$

Taking into account a high degree of delocalization of the excess electron at the C atoms of the fullerene core and a weak dependence of the reduction potentials on the nature of the substituents, it can be assumed that for a seires of fullerene C_{60} derivatives, $a \approx 1.0$ and the difference between the reduction potentials of C_{60} and compound **1** corresponds to the difference between *EA* for these compounds.

$$E^{\text{red}}(C_{60}) - E^{\text{red}}(\mathbf{1}) = EA(C_{60}) - EA(\mathbf{1})$$

The electron affinity of C_{60} is 2.67 eV,[4] and, consequently, the electron affinity of compound **1** is 2.58 eV.

For phenoxide ion **1a** $(\mathbf{1} - \text{H})^-$, we determined the electrochemical gap $\Delta E = (E^{\text{ox}} - E^{\text{red}}) = 0.47$ V, which has the meaning of the energy gap $(E_{\text{HOMO}} - E_{\text{LUMO}})$ for the phenoxide ion solvated in this medium. This gap is small and is virtually equal to the difference between the potentials of the transfer of the first and second electrons to the molecule of compound **1**, which indicates the high reactivity of phenoxide ion **1a** in redox reactions.

Previously,[21,22] it has been reported that the transfer of two or more electrons to the methanofullerene molecule leads to the cleavage of the bonds between the *exo* C atoms and the fullerene core to form anions of free C_{60} (the retro-Bingel reaction). Analogous elimination of the group bound to fullerene proceeding upon transfer of four electrons to the NH-pyrrolidinofullerene molecule[21] has been also described.[23] In studies of properties of compound **1**, elimination of the attached fragment did not occur within the time scale of voltammetric measurements (tens of seconds) neither upon oxidation nor upon reduction accompanied by the transfer of three electrons.

Therefore, our results demonstrate that compound **1** is rather stable in redox reactions and exhibits a combination of properties of fullerene C_{60} and sterically hindered phenol. At the same time, phenoxide ion **1b** is rather readily oxidized to form a stable phenoxyl radical and it also readily accepts electrons giving rise to stable radical anions, dianions, and trianions.

The redox properties of compound **1** are confirmed by quantum-chemical calculations of the electronic structures of its molecule and of some conversion products. Actually, calculations by the PM3 method (the GAMESS program package)[24,25] demonstrated that the phenolic fragment should more readily lose an electron upon oxidation of this compound, whereas the fullerene core should more readily accept an electron upon reduction. This can be readily seen from Fig. 4 presenting maps of populations of the highest occupied and lowest unoccupied molecular orbitals for compound **1**. It can be seen that LUMO and HOMO are accumulated at the fullerene core and the phenolic fragment, respectively (see Fig. 4).

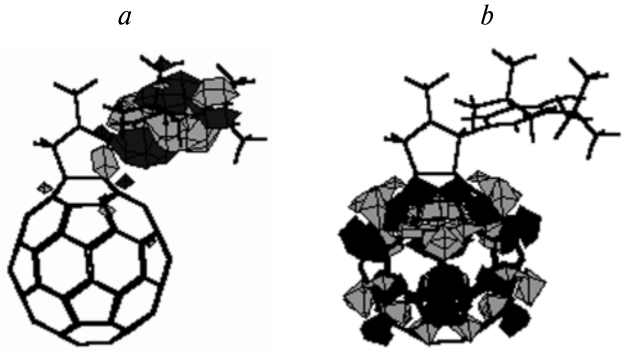


Fig. 4. Distribution of the frontier orbitals in molecule **1**: HOMO, −8.97 eV (*a*); and LUMO, −2.77 eV (*b*).

The results of calculations (see Table 2) show that the heats of formation of the anions of compound **1** are lower, whereas the heats of formation of the phenoxyl radical and, in particular, of the radical cation, are higher than that of neutral compound **1**. It has already been noted that compound **1** containing the pyrrolidine and phenolic fragments is difficult to oxidize probably due to the electron-withdrawing properties of the fullerene core. The results of calculations demonstrate that the charge transfer from the pyrrolidine fragment to the fullerene core actually takes place in molecule **1** (see Table 2). Interestingly, the negative charge is localized on the fullerene core in the case of formation of radical anion $\mathbf{1}^{\cdot -}$, whereas in the case of formation of radical cation $\mathbf{1}^{\cdot +}$, the positive charge is distributed over the whole molecule although its major portion is localized on the fullerene fragment.

Table 2. Heats of formation (ΔH), energies (E) of the frontier orbitals, and charges (Q) on the fragments of molecule **1** and its transformation products (PM3)

Compound	ΔH /kcal mol^{-1}	E/eV		Q_{ful}*	Q_{pyr}**	Q_{phen}***
		HOMO	LUMO		a.u.	
1	729.32	−8.97	−2.77	−0.1121	0.1340	−0.0218
$\mathbf{1}^{\cdot -}$	659.70	−1.46	0.170	−1.0448	0.0866	−0.0418
$\mathbf{1a}^{\cdot}$	762.97	−5.35	−2.86	−0.0948	0.1284	−0.0339
$\mathbf{1}^{\cdot +}$	928.90	−10.28	−6.26	0.7820	0.2134	−0.0038

* Total charge.

** The charge on the pyrrolidine fragment.

*** The charge on the fullerene core

Therefore, the results of studies of the fulleropyrrolidine-containing sterically hindered phenol **1**, which was synthesized for the first time, by cyclic voltammetry, ESR spectroscopy, and quantum-chemical calculations suggest that this compound is highly reactive in deactivation of different radical species serving both as an electron acceptor and donor and, consequently, it can be used as an antioxidant and a radical scavenger.

Experimental

We used fullerene C_{60} with 99.5% purity (according to the HPLC data obtained on a Gilson instrument equipped with an UV detector and a C_{18} reversed-phase column (Partisil-5 ODS-3) using a toluene—MeCN mixture (1 : 1, v/v) as the eluent). Organic solvents were dried and distilled before use. All chemical operations were carried out under an atmosphere of argon. The UV spectra were recorded on a Specord M-40 spectrophotometer in THF—$CHCl_3$ (10 : 2). The IR spectrum was measured on a Bruker Vector 22 Fourier spectrometer (in KBr pellets). The ^1H,^{31}P, and ^{13}C NMR spectra were recorded on Bruker WM-250 (250 MHz for ^1H) and Bruker MSL 400 (100.57 MHz for ^{13}C and 400.00 MHz for ^1H) spectrometers in $CDCl_3$ with Me_4Si as the internal standard.

Electrochemical reduction and oxidation of compound **1** were carried out in 2 : 1 toluene—DMF and 3 : 1 *o*-dichlorobenzene—DMF mixtures using Et_4NBF_4 (0.1 mol L^{-1}) and Bu_4NBF_4 (0.1 mol L^{-1}) as the supporting electrolytes; the salts were purified by recrystallization from acetonitrile.

The cyclic voltammograms were obtained on a PI-50-1 potentiostat using a two-coordinate H 307/2 automatic recorder. A 0.5-mm disk Pt electrode sealed into glass and a 2-mm disk glassy-carbon electrode pressed into Teflon were used as the working electrodes. Before each measurement, the electrodes were polished off mechanically. The potentials were measured relative to the standard potential of the ferrocene/ferrocenium ion (Fc/Fc^+) redox system with the use of a reference electrode ($Ag/AgNO_3$; 0.01 mol L^{-1}) in MeCN. Dissolved oxygen was removed by bubbling argon or nitrogen through a solution. The measurements were carried out at 22 °C.

Studies by the electrolysis—ESR method were carried out using an instrument combining an SE/X-2544 ESR spectrometer (Radiopan), a potentiostat, and an electrochemical cell, which made it possible to perform the electrochemical process directly in the resonator of the ESR spectrometer. A Pt plate was used as the working electrode, Pt wire was used as the auxiliary electrode, and Ag wire was used as the reference electrode. The solutions were deaerated by the freezing—evacuation—thawing procedure repeated three times. The experiments were carried out at 22 °C.

***N*-Methyl-3,4-[60]-fullero-5-(3,5-di-*tert*-butyl-4-hydroxyphenyl)pyrrolidine (1).** A mixture of fullerene C_{60} (0.144 g, 0.2 mmol), *N*-methylglycine (0.0534 g, 0.6 mmol), and 3,5-di-*tert*-butyl-4-hydroxybenzaldehyde (0.094 g, 0.4 mmol) in toluene (100 mL) was refluxed under argon for 8 h. The reaction mixture was washed with water (2×30 mL), concentrated *in vacuo*, and chromatographed on a column with SiO_2. Elution with hexane afforded unconsumed C_{60} in a yield of 0.048 g. Compound **1** was isolated using a 1 : 1 hexane—toluene mixture. After removal of the solvent, compound **1** was obtained as a dark-brown powder in a yield of 0.053 g (41.5% with respect to unconsumed C_{60}), m.p. >300 °C. Found (%): C, 95.59; H, 2.89; N, 1.51. $C_{77}H_{27}NO$. Calculated (%): C, 94.19; H, 2.75; N, 1.43. UV (THF/$CHCl_3$, 10 : 2), λ_{max}/nm (ε): 258 (45000), 328 (13000), 431 (1800), 540 (sh, 600), 714 (280). IR (KBr), ν/cm^{-1}: 526.6; 1120.6; 1151.8; 1429.9; 1633.7; 2365.9; 2775.1; 2945.5; 3652.1. ^1H NMR ($CDCl_3$), δ: 1.41 (18 H); 2.86 (3 H); 4.28 (d, 1 H, *J* = 9.0 Hz); 4.87 (1 H); 4.99 (d, 1 H, *J* = 9.0 Hz); 5.14 (1 H); 7.11 (1 H); 7.14 (1 H). ^{13}C NMR ($CDCl_3$), δ: 30.07; 33.82; 39.42; 68.33; 69.65; 77.29; 83.55; 125.63; 126.88; 127.91; 128.60; 135.34; 135.37; 135.38; 135.47; 135.49; 136.10; 138.81; 139.22; 139.63; 139.78; 141.06; 141.21; 141.25; 141.40; 141.58; 141.66; 141.71; 141.74; 141.80; 141.86; 142.13; 142.15; 142.24; 142.55; 142.72; 143.94; 144.25; 144.31; 144.66; 144.80; 144.95; 144.97; 145.01; 145.03; 145.05; 145.17; 145.34; 145.45; 145.64; 145.66; 145.68; 145.76; 145.82; 145.85; 146.09; 146.36; 146.61; 146.62; 153.15; 153.43; 153.55; 153.92; 155.98.

Compound **1** (a toluene solution) was oxidized to phenoxyl radical **1a** with an excess of lead dioxide directly in an ESR cell without isolation according to a procedure reported previously.[12]

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