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# Electrochemical reduction and oxidation of fullerenopyrrolidines* and the ESR spectra of paramagnetic intermediates

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Electroreduction and electrooxidation of monosubstituted *N*-methyl[60]fullerenopyrrolidines were studied by cyclic voltammetry and potentiostatic microelectrolysis in the cavity of an ESR spectrometer. Stepwise reversible transfer of three electrons to the fullerenopyrrolidine molecule results in the formation of stable radical anions (according to ESR, $g = 2.0000$, $\Delta H = 0.8$ G), dianions, and radical trianions (according to ESR, $g = 2.0015$, $\Delta H = 1.5$ G). The reduction potentials vary over narrow limits depending on the nature of the substituents in the pyrrolidine fragment of the compounds. Electrooxidation is irreversible and occurs in either one or two steps. For compounds containing the aniline, indole, or phenol fragment, the first step is associated with oxidation of these fragments and only after that, is the fullerenopyrrolidine core oxidized. Oxidation of the pyrrolidine fragment is substantially more difficult than that of tertiary amines.

**Key words:** fullerenes, fullerenopyrrolidines, electrochemistry, radical anions, dianions, radical trianions, ESR spectroscopy, quantum chemical calculations.

An important feature of fullerene molecules is the capability of easy, stepwise, and reversible addition of several electrons without destruction of the fullerene cage. Similar properties are found for monosubstituted derivatives of $C_{60}$ fullerene. Thus reversible transfer of six electrons has been described for fullerene and transfer of five electrons has been reported for fullerenopyrrolidines.[1,2] The salts of fullerenes with metal ions are rather stable and can be prepared in a pure state; superconducting $M_3C_{60}$ derivatives (M is an alkali metal) can be cited as examples.[3] The anionic intermediates, namely, radical anions (RA), dianions (DA), and radical trianions (RTA), are quite stable[4] even in the presence of phenol. This points to the possibility of delocalization of electron density in the highly conjugated spherical $C_{60}$ molecule.

Good prospects of indirect electroorganic synthesis using mediators, *i.e.*, electron transferring agents, were demonstrated by studies carried out for many years. In electroreduction (ER) of organic compounds, molecules that are reduced reversibly to give RA are often used as mediators.[5] As a rule, these molecules transfer one electron and their RA are stable only in strictly aprotic media. However, in many cases, ER must be carried out in the presence of proton donors using an efficient transferring agent for several electrons.[6] In realization of these processes, fullerenes and their derivatives may exhibit high efficiency as electron transferring agents.

Electroreduction in the series of functionally substituted fullerenes follows a specific pattern: the transfer of two, three, or four electrons per molecule results in anionoid elimination of the substituent to give the fullerene anion, while subsequent oxidation gives $C_{60}$ fullerene. Thus the two-electron ER of dicarbethoxymethano[60]fullerene and phosphorylated methano[60]fullerenes results in slow elimination of the methane fragment, which is substantially accelerated upon transfer of three electrons (retro-Bingel reaction).[7—9] The [2+3]-retro-reaction takes place[10] upon transfer of four electrons to the fullerenopyrrolidine molecule containing *p*-benzoquinone and NH groups (two electrons to each of fullerene and *p*-benzoquinone). No retro-reaction takes place in the reduction of a similar N-methyl derivative even on transfer of five electrons. This implies that substituted fullerenopyrrolidines containing no NH proton are stable in the course of ER. Electrochemical retro-reactions represent a distinctive feature of functionally substituted fullerenes and require detailed investigation because the reductive cleavage of C—C bonds is uncharacteristic of conventional organic compounds. The retro-reaction can be used to develop a scheme for the synthesis of new fullerene derivatives that are difficult to prepare; the scheme would include preliminary introduction of a pro-

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* The name fulleropyrrolidines sometimes used in the literature was changed on editing for fullerenopyrrolidines in accordance with the IUPAC rules and *Chemical Abstracts* nomenclature.

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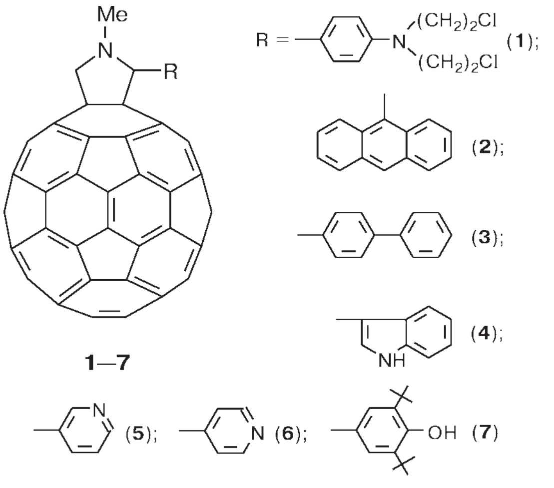
tective nucleofugal group and electrochemical removal of this group after functionalization.

In this communication, we report the results of a study of ER of fullerenopyrrolidines **1—6**, whose structures are shown below, carried out by cyclic voltammetry (CV) and potentiostatic microelectrolysis in the cavity of an ESR spectrometer and the results of PM3 semiempirical calculations.



## Experimental

A 99.5%-purity $C_{60}$ fullerene sample was used (HPLC data on a Gilson chromatograph with a UV detector, a column with $C_{18}$ reverse phase (Partisil-5 ODS-3), elution with a toluene—MeCN mixture, 1 : 1). Organic solvents were distilled and dried prior to use. All operations were carried out under argon.

Electrochemical reduction and oxidation of compounds **1—6** was carried out in *o*-dichlorobenzene—MeCN (2 : 1) and *o*-dichlorobenzene—DMF (3 : 1) mixtures. The supporting electrolytes used were $Et_4NBF_4$ (0.1 mol $L^{-1}$) and $Bu_4NBF_4$ (0.1 mol $L^{-1}$) recrystallized from MeCN. The CV curves were recorded using a PI-50-1 potentiostat with an H-307/2 XY-recorder. A disc Pt electrode ($d$ = 0.5 mm) sealed in glass and a disc glass carbon electrode ($d$ = 2 mm) pressed in Teflon served as the working electrodes. The electrodes were polished prior to each measurement. The potentials were measured *vs.* the standard potential of the $Fc/Fc^+$ redox system using an $Ag/AgNO_3$ silver reference electrode (0.01 mol $L^{-1}$) in MeCN. The dissolved oxygen was removed by bubbling argon or nitrogen through the solution. The measurements were carried out at 22 °C.

ESR spectra were recorded using a setup comprising an SE/X-2544 (Radiopan) ESR spectrometer, a potentiostat, and an electrochemical cell, which allowed electrogeneration of paramagnetic species in the cavity of the ESR spectrometer. A Pt plate served as the working electrode, a Pt wire was the auxiliary electrode, and an Ag wire served as the reference electrode. Solutions were deaerated by the freezing—evacuation—unfreezing (22 °C) cycle repeated three times.

The synthesis of compounds **1—4** will be described elsewhere.* Substituted fullerenes **5**,[1] **6**,[11] and **7** [4] were synthesized by previously reported procedures. Quantum-chemical calculations[12] were performed by the PM3 method (GAMESS program package).

**Table 1.** Reduction potentials ($E_{(1/2)}^{\text{red}}$) of $C_{60}$ fullerene and fullerenopyrrolidines **1—7** at a platinum (Pt) and glass carbon (GC) electrodes[a] from CV data

| Compound | Working electrode | $E_{(1/2),1}^{\text{red}}$ | $E_{(1/2),2}^{\text{red}}$ | $E_{(1/2),3}^{\text{red}}$ |
|---|---|---|---|---|
| | | | V | |
| $C_{60}$ | Pt | −0.96 | −1.40 | −1.93 |
| | GC[b] | −0.96 | −1.40 | −1.93 |
| **1** | Pt | −1.04 | −1.48 | −2.06 |
| | GC[b] | −1.05 | −1.48 | −2.05 |
| **2** | Pt | −1.03 | −1.47 | −2.04 |
| | GC | −1.04 | −1.47 | −2.03 |
| **3** | Pt | −1.02 | −1.47 | −2.03 |
| | GC | −1.03 | −1.47 | −2.04 |
| **4** | Pt | −1.04 | −1.47 | −2.06 |
| | GC | −1.05 | −1.48 | −2.09 |
| **5** | Pt | −1.04 | −1.47 | −2.04 |
| | GC | −1.04 | −1.48 | −2.04 |
| **6** | Pt | −1.04 | −1.46 | −2.03 |
| | GC | −1.04 | −1.46 | −2.03 |
| **7** [c] | Pt | −1.04 | −1.47 | −2.05 |
| | GC | −1.05 | −1.50 | −2.10 |

[a] $Bu^n_4NBF_4$ (0.1 mol $L^{-1}$), *o*-dichlorobenzene—DMF (3 : 1), 25 °C, potential sweep rate 100 mV $s^{-1}$. The potentials were measured *vs.* the $Fc/Fc^+$ electrode with the $Ag/AgNO_3$ reference electrode (0.01 mol $L^{-1}$). The $E_{1/2}$ values were found as the half-sum of the potentials of the reduction peaks and the corresponding oxidation peaks of the reduction products formed: $E_{(1/2)}^{\text{red}} = (E_p^{\text{red}} + E_p^{\text{ox}})/2$.

[b] The fourth reduction peak can be recorded ($E_p$ = −2.43 V).

[c] Data from Ref. 4.

## Results and Discussion

The CV curves for fullerenopyrrolidines **1—6** recorded with Pt and glass-carbon electrodes in the *o*-dichlorobenzene—DMF system (3 : 1, v/v*) with 0.1 *M* $Bu^n_4NBF_4$ as the supporting electrolyte, like the curve for compound **7** studied previously,[4] exhibit three reversible single-electron reduction peaks. The potentials are somewhat shifted toward negative values with respect to the corresponding peaks for $C_{60}$ fullerene (Table 1).

Typical CV curves for different potential sweep rates are shown in Fig. 1. Reduction potentials virtually do not depend on the nature of the substituents in the pyrrolidine ring or on the electrode material. The results indicate that all three electrons were transferred onto the fullerene sphere and that the resulting fullerenopyrrolidine RA, DA, and RTA are stable on the voltammetric time scale. High stability of the anionic intermediates is also confirmed by

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* Here and below, volume ratios are given.

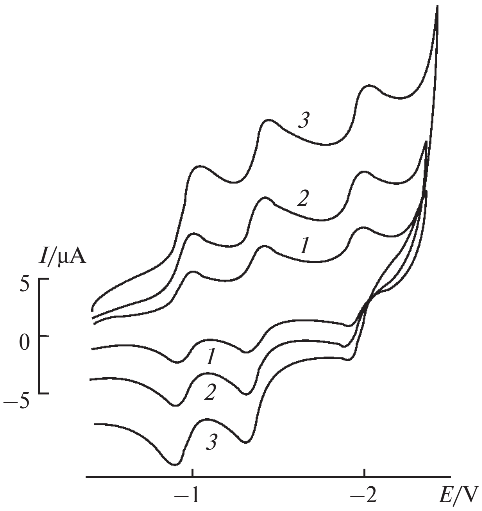

**Fig. 1.** Cyclic voltammograms of a solution of fullerenopyrrolidine **5** ($10^{-3}$ mol $L^{-1}$) in the *o*-dichlorobenzene—DMF (3 : 1)/0.1 *M* $Bu_4NBF_4$ system at a glass-carbon electrode at different potential sweep rates: 20 (*1*), 50 (*2*), and 100 mV $s^{-1}$ (*3*).

the data of ESR spectroscopy used in combination with CV. In this case, CV curves were recorded at a low potential sweep rate (2 or 5 mV $s^{-1}$) at a helical Pt electrode with a large surface area in a special cell directly in the cavity of the ESR spectrometer with synchronous recording of ESR spectra. The same pattern was observed for each of compounds **1**—**6**. No paramagnetic species can be detected by ESR in the initial solution without application of a potential or when the potential varies from 0 V to the beginning of the first ER step. When the potential of the first cathodic peak is attained, a signal for the fullerenopyrrolidine RA ($\mathbf{FP}^{\bullet-}$) is recorded as a single line with a *g* factor of 2.0000 and the width $\Delta H = 0.8$ G (Fig. 2, *a*). The signal intensity increases when the first-peak maximum is attained due to electrochemical generation of RA directly at the electrode. A gain in intensity also takes place at potentials corresponding to the initial section of the second peak, which is due to the homogeneous reaction of the DA ($\mathbf{FP}^{2-}$) with the remaining initial neutral fullerenopyrrolidine molecules **FP**:

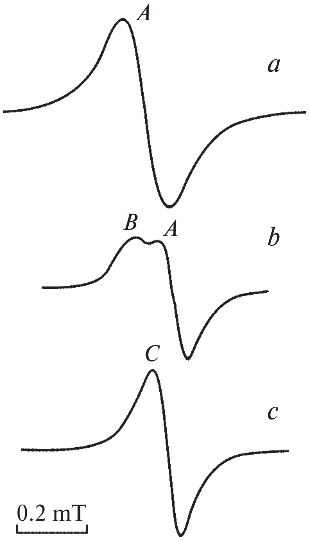

**Fig. 2.** ESR spectra of paramagnetic intermediates generated by electroreduction of a solution of fullerenopyrrolidine **5** ($10^{-3}$ mol $L^{-1}$) in the *o*-dichlorobenzene—DMF (3 : 1)/0.1 *M* $Bu_4NBF_4$ system at a helical Pt electrode in a cavity of the ESR spectrometer at the first- (*a*), second- (*b*), and third-peak (*c*) potential.

$$\mathbf{FP}^{2-} + \mathbf{FP} \rightleftharpoons 2\,\mathbf{FP}^{\bullet-}.$$

This reaction is reversible ($K_p$ is the equilibrium constant) but the equilibrium is markedly shifted toward the RA:

$$K_p = [\mathbf{FP}^{\bullet-}]^2/[\mathbf{FP}][\mathbf{FP}^{2-}] =$$

$$= \exp[(E_{(1/2),1}^{\text{red}} - E_{(1/2),2}^{\text{red}})nF/RT] = (1\text{—}4)\cdot 10^7,$$

where $E_{(1/2),1}^{\text{red}}$ and $E_{(1/2),2}^{\text{red}}$ are the potentials of the first and second reduction peaks (see Notes to Table 1).

As the potential shifts to negative values along the second reduction peak, *i.e.*, the $\mathbf{FP}^{2-}$ dianion is accumulated, the concentrations of fullerenopyrrolidine and the corresponding RA decrease, and the RA signal intensity in the ESR spectrum decreases. This is accompanied by appearance and growth of a new signal (Fig. 2, *b*, line *B*), whose *g*-factor increases (from 2.0003 to 2.0008) as electrolysis goes on. The nature of the paramagnetic species responsible for line *B* (see Fig. 2, *b*) is not entirely clear. This might be an RA dimer.[4] Prolonged electrolysis leads to fuller reduction of fullerenopyrrolidines to the DA and to attenuation of both lines down to disappearance. At potentials of the third peak, a signal for the RTA of fullerenopyrrolidines ($\mathbf{FP}^{\bullet 3-}$) appears in the ESR spectrum in a lower fields ($g = 2.0015$, $\Delta H = 1.5$ G) with respect to the RA signal (Fig. 2, *c*, line *C*). During electrolysis, the intensity of the $\mathbf{FP}^{\bullet 3-}$ signal also increases to reach a limiting value. During the reverse potential sweep, the intensity of the RTA signal decreases after the oxidation potential of $\mathbf{FP}^{\bullet 3-}$ has been reached, and, finally, this signal completely vanishes. At the potentials of DA oxidation, line *B* is the first to appear, while line *A* corresponding to the RA is the next. The intensity of these signals increases, but at the oxidation potentials of the RA, the intensity decreases. These signals completely vanish at more anodic potentials. No other paramagnetic species have been detected in noticeable amounts over the whole range of potentials studied.

Under conditions of prolonged electrolysis at a controlled potential of the third peak, the ESR spectrum contains only the line due to the RTA. After switching off the potential, the intensity of the RTA lines decreases as they react with the residual fullerenopyrrolidine until the lines disappear. Simultaneously, line *B* appears (see Fig. 2, *b*) and undergoes similar transformations with time, namely, its intensity decreases and, simultaneously, a signal for the fullerenopyrrolidine **1—6** RA appears and grows in the higher-field region, so that the resultant signal corresponds to line *A* (see Fig. 2).

Thus, the set of results obtained by two methods shows that the RA, DA, and RTA generated from fullerenopyrrolidines **1—6** upon ER at the first, second, and third cathodic peak potentials are quite stable in the *o*-dichlorobenzene—DMF (3 : 1) medium and do not undergo noticeable irreversible transformations for at least 10—20 min.

Then it was shown that the replacement of DMF (one component of the supporting electrolyte) by MeCN (*o*-dichlorobenzene—MeCN, 2 : 1) does not change the pattern of fullerenopyrrolidine ER at a platinum electrode. CV studies showed that in this medium, too, the consecutive reversible transfer of three electrons results in the formation of stable RA, DA, and RTA, respectively (Table 2).

The results obtained are consistent[13,14] with published data on ER of other fullerenopyrrolidines giving the corresponding RA [15—17] and indicate that the transfer of one, two, and even three electrons in these media does not induce elimination of substituents, observed for methanofullerenes.[7—9] The influence of the pyrrolidine fragment is reduced to hampering the electron transfer to the fullerene sphere. This effect is of the same order as that involved in the ER of phosphorylated methanofullerenes,[8,9] and appears to be mainly related to some violation of conjugation and symmetry in the fullerene molecule. This is indicated by ESR data. According to our and published results,[18] the ESR spectrum of the RA derived from $C_{60}$ fullerene exhibits a very broad line with $\Delta H$ ~70 G, whereas in the case of the methano- and pyrrolidinofullerenes, it is much narrower ($\Delta H$ ~1 G).

**Table 2.** Reduction ($E_{(1/2)}^{\text{red}}$) and oxidation ($E_{\text{p}}^{\text{ox}}$) potentials of $C_{60}$ fullerene and fullerenopyrrolidines **1**, **3—5**, **7** from CV data at a Pt electrode

| Compound | $E_{(1/2),1}^{\text{red}}$ | $E_{(1/2),2}^{\text{red}}$ | $E_{(1/2),3}^{\text{red}}$ | $E_{\text{p},1}^{\text{ox}}$ | $E_{\text{p},2}^{\text{ox}}$ |
|---|---|---|---|---|---|
| | V | | | | |
| $C_{60}$ | −1.01 | −1.36 | −1.87 | — | 1.31 |
| **1** | −1.17 | −1.57 | −2.06 | 0.82 | 1.31 |
| **3** | −1.16 | −1.58 | −2.04 | — | 1.27 |
| **4** | −1.12 | −1.52 | −2.04 | 0.77 | 1.35 |
| **5** | −1.16 | −1.60 | −2.12 | — | 1.33 |
| **7** | −1.14 | −1.55 | — | 0.81 | 1.32 |

*Note.* In the *o*-dichlorobenzene—MeCN (2 : 1)/0.1 *M* $Et_4NBF_4$ medium.
$E_{(1/2)}^{\text{red}} = (E_{\text{p}}^{\text{red}} + E_{\text{p}}^{\text{ox}})/2$.

Previously,[19] it was shown that in fullerenopyrrolidines containing a pyridine fragment (see, for example, compounds **5**, **6**), the presence of fullerene substantially decreases the nucleophilicity of the pyrrolidine N atom, so that quaternization involves the pyridine nitrogen. Thus, the fullerene shell of fullerenopyrrolidines shields the N atom and/or acts as a strong electron acceptor. These factors should hamper the abstraction of an electron from the nitrogen lone electron pair (LEP), and, hence, the potential of this process should be much higher than those for aliphatic tertiary amines. To make sure that this is really so, we studied the electrochemical oxidation of fullerenopyrrolidines.

In the *o*-dichlorobenzene—DMF/0.1 *M* $Bu_4NBF_4$ medium, the accessible anodic region of potentials is rather narrow (≤0.7 V), therefore the oxidation peaks for the compounds under study cannot be recorded by CV. Meanwhile, the potential range accessible experimentally in the *o*-dichlorobenzene—MeCN (2 : 1)/0.1 *M* $Et_4NBF_4$ medium is much wider and clear irreversible oxidation peaks can be observed for all compounds. The peak potentials ($E_\text{p}$) are presented in Table 2; for comparison, the oxidation potential of $C_{60}$ fullerene is also given. The oxidation potential of fullerenopyrrolidine **5** ($E_\text{p}$ = 1.33 V) virtually coincides with the oxidation potential of fullerene ($E_\text{p}$ = 1.31 V). Since pyridine is oxidized with greater difficulty ($E_\text{p}$ = 1.67 V in MeCN),[20] oxidation of compound **5** implies transfer of an electron from the highest occupied MO (HOMO), the major contribution to whose energy is made by the fullerenopyrrolidine cage. Oxidation of the cage in compounds **1**, **4**, and **7** takes place at second-peak potentials (see Table 2). The first-peak potentials, which are markedly displaced to lower values (by 0.51—0.52 V), correspond to the oxidation of substituents: substituted aniline in compound **1** ($E_\text{p}$ = 0.82 V), indole in compound **4** ($E_\text{p}$ = 0.77 V), and phenol in compound **7** ($E_\text{p}$ = 0.81 V). Compound **3** gives rise to only one oxidation peak slightly shifted to lower potentials with respect to the $C_{60}$ oxidation peak. Apparently, in this case, the oxidation peak of the fullerenopyrrolidine cage is superimposed by the peak of the diphenyl group, which is oxidized in the same potential range.[20]

The available data do not allow one to find out exactly which fragment of the fullerenopyrrolidine cage, the LEP of the pyrrolidine nitrogen or the fullerene cage is the direct reaction center during oxidation of compounds **1**, **3—5**, and **7**. However, it can be stated unambiguously that the potential of electron transfer from the nitrogen LEP is ≥1.27 V. This is much greater than the oxidation potentials of tertiary amines[20] (for example, for *N*,*N*-dimethylbenzylamine, $Me_3N$, and $Et_3N$, the $E_\text{p}$ values are 0.56, 0.67, and 0.51 V, respectively). Thus it can be seen that the fullerene cage in fullerenopyrrolidines substantially hampers the electron detachment from the pyrrolidine nitrogen.

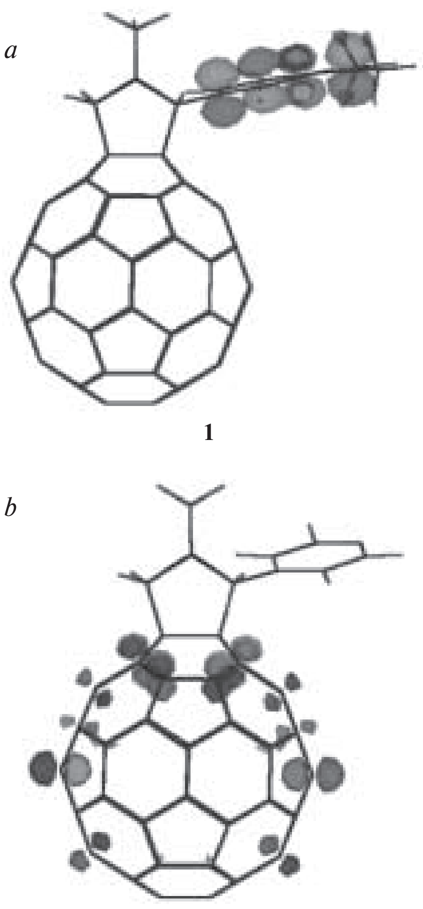

**Fig. 3.** Distribution maps of the higher occupied molecular orbitals in molecules **1** (*a*) and **6** (*b*) (the energies are –8.54 and –9.20 eV, respectively).

**Table 3.** Heats of formation ($\Delta H_f$/kcal mol$^{-1}$), the energies of frontier orbitals (the higher occupied (HOMO) and lower unoccupied MO (LUMO)), charges ($Q$) on the atoms of the fullerene ($Q_{ful}$), pyrrolidine ($Q_{pyr}$), and attached ($Q_{frag}$) fragments of fullerenopyrrolidines **1—7** and $C_{60}$ fullerene

| Compound* | $\Delta H_f$ | $E$/eV | | $Q_{full}$ | $Q_{pyr}$ | $Q_{frag}$ |
|---|---|---|---|---|---|---|
| | | HOMO | LUMO | | au | |
| $\mathbf{1}^0$ | 807.67** | –8.54 | –2.76 | –0.1134 | –0.0006 | 0.1134 |
| $\mathbf{1}^{\cdot -}$ | 740.29** | — | — | –1.0458 | –0.0199 | 0.0655 |
| $\mathbf{1}^{\cdot +}$ | 978.42** | — | — | –0.0276 | 0.2808 | 0.7459 |
| $\mathbf{2}^0$ | 857.45 | –8.31 | –2.78 | –0.1029 | 0.0622 | 0.0412 |
| $\mathbf{2}^{\cdot -}$ | 789.32 | — | — | –1.0379 | 0.0496 | –0.0166 |
| $\mathbf{2}^{\cdot +}$ | 1038.67 | — | — | –0.0157 | 0.2495 | 0.7719 |
| $\mathbf{3}^0$ | 835.51 | –8.98 | –2.78 | –0.1166 | 0.0392 | 0.0739 |
| $\mathbf{3}^{\cdot -}$ | 767.67 | — | — | –1.0379 | 0.0145 | 0.0238 |
| $\mathbf{3}^{\cdot +}$ | 1032.40 | — | — | –0.0219 | 0.2495 | 0.7719 |
| $\mathbf{4}^0$ | 828.87 | –8.57 | –2.74 | –0.1175 | –0.0094 | 0.1280 |
| $\mathbf{4}^{\cdot -}$ | 762.03 | — | — | –1.0519 | –0.0301 | 0.0815 |
| $\mathbf{4}^{\cdot +}$ | 1006.91 | — | — | –0.0065 | 0.2969 | 0.7098 |
| $\mathbf{5}^0$ | 818.43 | –9.17 | –2.82 | –0.1005 | 0.0129 | 0.1055 |
| $\mathbf{5}^{\cdot -}$ | 749.69 | — | — | –0.9150 | –0.0291 | 0.0635 |
| $\mathbf{5}^{\cdot +}$ | 1023.61 | — | — | 0.8029 | 0.0343 | 0.1629 |
| $\mathbf{6}^0$ | 818.56 | –9.20 | –2.85 | –0.0973 | 0.0732 | 0.0240 |
| $\mathbf{6}^{\cdot -}$ | 749.36 | — | — | –1.0297 | 0.0467 | –0.0156 |
| $\mathbf{6}^{\cdot +}$ | 1024.45 | — | — | 0.8065 | 0.1148 | 0.0783 |
| $\mathbf{7}^0$ | 729.32 | –8.97 | –2.77 | –0.1121 | 0.1340 | –0.0218 |
| $\mathbf{7}^{\cdot -}$ | 659.70 | — | — | –1.0448 | 0.0866 | –0.0418 |
| $\mathbf{7}^{\cdot +}$ | 928.90 | — | — | 0.7820 | 0.2134 | 0.0038 |
| $C_{60}$ | 811.75 | –9.48 | –2.89 | — | — | — |
| $C_{60}{}^{\cdot -}$ | 740.58 | — | — | — | — | — |
| $C_{60}{}^{\cdot +}$ | 1023.26 | — | — | — | — | — |

* The subscript "0" marks neutral molecules.

** The calculations were carried out for compound **1**, containing the $NMe_2$ group instead of $N(CH_2CH_2Cl)_2$.

The redox behavior of compounds **1—7** characterized above are in reasonable agreement with the results of quantum-chemical investigations of the electronic structures of these substances and the products of their single-electron oxidation or reduction. Indeed, the PM3 calculations carried out for the gas phase (the GAMESS program package[12]) showed that the nature of substituents in the pyrrolidine ring has a pronounced influence on the pattern of the fullerenopyrrolidine frontier orbitals. This can be easily seen in Fig. 3 in which the HOMO of compounds can be clearly distinguished. Upon the formation of RA $\mathbf{1}^{\cdot -}$—$\mathbf{7}^{\cdot -}$, the negative charge becomes concentrated on the fullerene shell, whereas in the case of radical cations $\mathbf{1}^{\cdot +}$—$\mathbf{7}^{\cdot +}$, the positive charge is distributed over the whole molecule. In compounds **1—4**, the charge is mainly located on the substituent, while in the case of **5—7**, it is mainly concentrated on the fullerene cage. This implies that in the gas phase, the fullerene cage can act as the reaction center in the single-electron reduction, while in the oxidation, this can be both the fullerene cage and the substituent. It was noted above that the difficulty of oxidation of the pyrrolidine fragment may be related to the electron-withdrawing properties of the fullerene cage in compounds **5** and **6**. Calculation showed that in neutral molecules of compounds **1—7**, the charge is transferred in fact from the pyrrolidine fragment to the fullerene nucleus (Table 3). Therefore, the fullerene cage is the most probable reaction center in the ionization of compounds **5** and **6** both in the gas phase and in solution.

The empirical and theoretical values of adiabatic ionization potentials $IP_a$ and electron affinities ($E_a$) for compounds **1—7** are compared in Table 4. The theoretical $IP_a$ and $E_a$ values were determined as the differences between the heats of formation of neutral molecules and radical cations or radical anions (see Table 3). Since geometry optimization was involved in the calculations, the results can be regarded as the adiabatic electron affinity and the adiabatic ionization potential. The HOMO and LUMO energies can also be taken as the theoretical $IP_a$ and $E_a$ values (see Table 3). The two ways of theoretical estimation of $IP_a$ and $E_a$ provide similar results. The $IP_a$ and $E_a$

**Table 4.** Adiabatic electron affinity ($E_a$) and adiabatic ionization potential ($IP_a$) of $C_{60}$ fullerene and fullerenopyrrolidines **1—7** solvated in the *o*-dichlorobenzene—MeCN (2 : 1)/0.1 *M* $Et_4NBF_4$ medium (experiment) and the theoretical values for the gas phase (calculation)

| Compound | Experiment | | Calculation | |
|---|---|---|---|---|
| | $E_a$ | $IP_a$ | $E_a$ | $IP_a$ |
| | eV | | | |
| $C_{60}$ | 4.17 | 6.64 | 3.09 | 9.18 |
| **1** | 4.01 | 6.15 | 2.93* | 7.41* |
| **2** | — | — | 2.96 | 7.87 |
| **3** | 4.02 | 6.60 | 2.95 | 8.55 |
| **4** | 4.06 | 6.10 | 2.90 | 7.73 |
| **5** | 4.02 | 6.66 | 2.98 | 8.91 |
| **6** | — | — | 3.00 | 8.94 |
| **7** | 4.04 | 6.14 | 3.02 | 8.67 |

* The calculations were carried out for compound **1** containing the $NMe_2$ group instead of $N(CH_2CH_2Cl)_2$.

values for solvated molecules of fullerenopyrrolidines **1—7** were also determined from their reduction and oxidation potentials against the absolute potential scale using a previously proposed procedure.[21] We proceeded from the fact that the standard potential of the $Fc/Fc^+$ system in the absolute potential scale is 5.18 V. For irreversible processes, we applied a correction for the subsequent chemical reaction (0.15 V).[21]

The calculated $IP_a$ and $E_a$ values for $C_{60}$ fullerene (7.61 and 2.65 eV) differ from experimental ones by 1.56 and 0.43 eV, respectively. Therefore, for compounds **1—7**, the calculated values are only rough estimates and cannot be compared quantitatively with the experimental $IP_a$ values of solvated molecules. Nevertheless, a number of qualitative conclusions can be made. In particular, the calculations show that the $E_a$ values of compounds **1—7** are virtually equal (2.90—3.02 eV), whereas the $IP_a$ values (7.7—9.2 eV) change appreciably similarly to the empirical series of $IP_a$ of solvated molecules. In addition, as can be seen from Table 4, the $E_a$ values of solvated fullerenopyrrolidines are much higher, while $IP_a$ are lower than those for nonsolvated molecules. This is due to fact that the solvation energies of the charged species formed upon electron transfer (radical anions and cations) are higher than those of the neutral initial compounds.

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