ESR spectra and electronic structure of the $C_{120}{}^{\cdot +}$ radical cation and the paramagnetic $C_{120}O^{2+}$ dication and $C_{120}O^{2-}$ dianion

S. P. Solodovnikov, E. G. Gal'pern, I. V. Stankevich, and A. L. Chistyakov*

A. N. Nesmeyanov Institute of Organoelement Compounds, Russian Academy of Sciences,
28 ul. Vavilova, 117813 Moscow, Russian Federation.
Fax: +7 (095) 135 5085. E-mail: stan@ineos.ac.ru

Electronic structure of the $C_{120}{}^{\cdot +}$ radical cation and the paramagnetic $C_{120}O^{2+}$ dication and $C_{120}O^{2-}$ dianion in the triplet state was calculated by the MNDO/PM3 method in the valence approximation. The density distributions of the unpaired electrons in these systems were found and the ESR spectra of the above species were interpreted.

Key words: ESR spectra, radical cations, hyperfine structure; triplet species, fine structure; fullerene dimers, molecular and electronic structure; quantum-chemical calculations, MNDO/PM3 method.

Syntheses of dimers, oligomers, and polymers based on fullerene C_{60} have stimulated investigations of the molecular and electronic structure of the derivatives of these novel carbon compounds[1—3] and their radical anions and cations.[4—7] Recently, the ESR spectra of paramagnetic species $C_{120}{}^{+}$,[4] $C_{140}{}^{+}$,[5] and $C_{120}O^{2+}$ [6] have been studied. The ESR data for the $C_{120}O^{2-}$ dianion in the triplet state have been reported.[7]

Radical cations $C_{120}{}^{\cdot +}$ and $C_{140}{}^{\cdot +}$ were synthesized using concentrated H_2SO_4 as both oxidant and solvent,[4—6] while the $C_{120}O^{2-}$ dianion was generated in the electrochemical reduction of $C_{120}O$ in *o*-dichlorobenzene using tetrabutylammonium perchlorate as electrolyte.[7] The ESR spectrum of the $C_{120}{}^{+}$ cation is characterized by three constants of hyperfine interaction (HFI) with ^{13}C nuclei (a_1 = 0.175 mT, a_2 = 0.100 mT, and a_3 = 0.030 mT).[4] It should be noted that close values of constants of HFI with ^{13}C nuclei have been observed recently[8] in ESR spectra of radical anions of mono- and bisfunctional fullerene derivatives $C_{60}[C(COOEt)_2]_n{}^{\cdot -}$ (n = 1, 2).

The fullerene fragments of C_{120} and $C_{60}[C(COOEt)_2]$ molecules have 58 π-electrons each and are structurally close. The constants of HFI with ^{13}C nuclei in the $C_{120}{}^{\cdot +}$ radical cation and $C_{60}[C(COOEt)_2]^{\cdot -}$ radical anion indicate that the density distribution of the unpaired electrons in the polyhedral fragments of these systems appreciably differ from the spherically symmetric distribution observed in the cation and anion of fullerene C_{60}.

The ESR spectra of the $C_{120}O^{2+}$ dication and $C_{120}O^{2-}$ dianion correspond to the triplet state of these species and are characterized by fine structure constants D of 2.95 mT [6] and 1.3 mT,[7] respectively. The effective distance (r) between the unpaired electrons, calculated using the point model of dipole-dipole interaction ($D = 3g^2\beta^2/(2r^3)$),[9] where g is the spectroscopic splitting factor and β is the Bohr magneton), is 7.8 Å in the $C_{120}O^{2+}$ dication and 13 Å in $C_{120}O^{2-}$ dianion. If in the first case the r value is close to the distance between the centers of the polyhedral fragments (8.5 Å), in the second case it approaches the linear size of the molecule (16 Å).

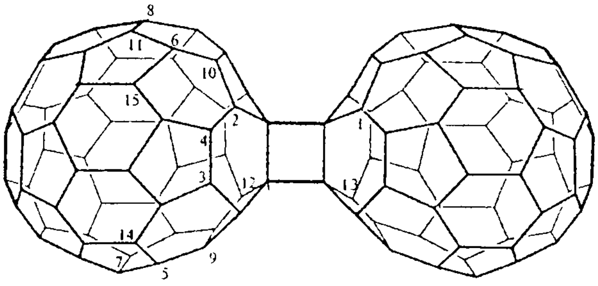

Fig. 1. Structure of σ-framework of radical cation **1**. The atoms with spin populations higher than 0.01 au are numbered.

When analyzing the ESR spectra of radical cations and anions of the fullerene C_{60} derivatives discussed above, the problem arises of the structure of the molecular orbitals (MO) on which the unpaired electrons are localized. To solve this problem, in this work we performed quantum-chemical studies of the density distribution of the unpaired electron in the $C_{120}{}^{\cdot +}$ radical cation (**1**, Fig. 1) and in the $C_{120}O^{2+}$ dication (**2**, Fig. 2) and $C_{120}O^{2-}$ dianion (**3**, see Fig. 2) in the triplet state.

Calculation procedure

Calculations were performed in the valence approximation by the semiempirical quantum-chemical MNDO/PM3 method[10] on a DEC 3000 AXP-400X workstation using the

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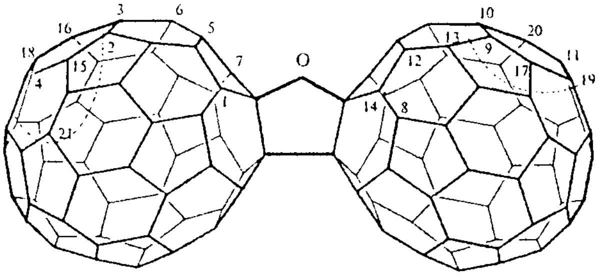

Fig. 2. Structure of σ-framework of dication **2** and dianion **3** in the triplet state. The atoms with spin populations higher than 0.035 au for **2** and 0.05 au for **3** are numbered.

Table 1. Spin populations on atoms (ρ) calculated by the MNDO/PM3 method and constants of HFI with ^{13}C nuclei (*a*) in the $C_{120}^{\cdot +}$ radical cation

Atom*	ρ /au**	*a* /mT	Atom*	ρ /au**	*a* /mT
C(1)	0.14	0.42	C(9)	0.02	0.003
C(2)	0.14	0.22	C(10)	0.02	0.20
C(3)	0.13	0.22	C(11)	0.02	0.05
C(4)	0.13	0.02	C(12)	0.01	0.03
C(5)	0.05	0.11	C(13)	0.01	0.03
C(6)	0.05	0.08	C(14)	0.01	0.04
C(7)	0.03	0.09	C(15)	0.01	0.04
C(8)	0.03	0.06			

* The numbering of atoms is shown in Fig. 1.

** The ρ values equal to or larger than 0.01 au are listed.

GAMESS program package.[11] Systems with open electron shells were studied in the framework of the ROHF scheme. The calculations were performed taking into account that the C_{60} dimers were formed as a result of [2+2]-cycloaddition reaction. This reaction proceeds with involvement of either bonds common to two adjacent six-membered cycles (6,6-bonds) or bonds common to adjacent five-membered and six-membered cycles (5,6-bonds).

Among fullerene C_{60} dimers formed as a result of [2+2]-cycloaddition on 6,6/6,6; 6,6/5,6; and 5,6/6,5-bonds, we chose the most stable 6,6/6,6-isomer[1,12] with D_{2h} symmetry, whose structure corresponds to the experimental data.[13] In such a C_{120} cluster, two C_{60} monomers are bonded through the four-membered cycle. One 6,6-bond of each of the C_{60} molecules (see Fig. 1) participates in the formation of this cycle. Calculations of the density distribution of the unpaired electron in the $C_{120}^{\cdot +}$ radical cation were performed ignoring a possible effect of the SO_3^- counterion.

To calculate the MO of the $C_{120}O^{2+}$ dication and $C_{120}O^{2-}$ dianion, we chose the most stable isomer with C_{2v} symmetry.[14] Simulation of the density distributions of the unpaired electrons in $C_{120}O^{2+}$ and $C_{120}O^{2-}$ species was carried out ignoring the presence of SO_3^- anions and tetrabutylammonium cations, respectively.

Results and Discussion

Radical cation $C_{120}^{\cdot +}$. The populations of the unpaired electron on carbon atoms of the $C_{120}^{\cdot +}$ radical cation (the numbering of atoms is shown in Fig. 1) and the constants of HFI with ^{13}C nuclei, estimated using the parameters of equations that describe HFI in planar π-electron radicals, are shown in Table 1.[15] Such a procedure for estimating is, to some extent, based on the results[16] of analysis of the constants of HFI with ^{13}C nuclei in the $C_{60}CMe_3^{\cdot}$ radical.

Mention has been made[16] that the HFI with ^{13}C nuclei does not differ appreciably from that characteristic of planar π-electron radicals. Our calculations showed that an asymmetric structure corresponds to the energy minimum in the case of radical cation $C_{120}^{\cdot +}$. This is reflected in the density distribution of the unpaired electron. From the data listed in Table 1 it follows that this distribution is asymmetric and the populations are mostly (0.80 au) localized on only 15 carbon atoms, the greatest part of which belongs to one of the C_{60} fragments (see Fig. 1). The remaining populations (0.20 au) are distributed over 105 carbon atoms. The above populations of the unpaired electron correspond to one of the asymmetric structures. It is obvious that an energetically equivalent state should also exist, in which the unpaired electron is mostly localized on atoms of the other part of the cation.

Dynamic transitions of the SO_3^- counterion between the fullerenyl fragments of the $C_{120}^{\cdot +}$ radical cation can lead to delocalization of the unpaired electron over the entire molecule. It should be noted that, previously,[4] HFI with ^{13}C nuclei in C_{120}^{+} was observed at an elevated temperature (330 K) and the total intensity of the components of hyperfine structure (HFS) due to HFI with ^{13}C nuclei corresponded to the distribution of the unpaired electron over ~30 carbon atoms. This means that in fact the unpaired electron is delocalized over both fullerenyl fragments and, hence, the calculated values of populations and HFI constants should be halved when comparing them with experimental data. Mention should be made that for the $C_{60}[C(COOEt)_2]^{\cdot -}$ radical anion, the constant of HFI with ^{13}C nuclei is 0.09 mT and that the number of atoms participating in the interaction with the unpaired electron is 15.[8]

The appreciable nonuniformity of the distribution of the unpaired electron over the fullerenyl fragment and the shift of the electron density toward the cyclobutane bridge are the most important results obtained in our calculations.

The calculated and measured values of HFI constants are of the same order of magnitude and there is little point in performing a detailed comparison of their values. It should be noted that the measured values of HFI constants are most likely averaged over groups of approximately equivalent atoms rather than being the true values corresponding to particular groups of equivalent atoms. This conclusion is confirmed by the fact that the width of the components of HFS due to HFI with ^{13}C nuclei is much larger than that of the central line that contains no HFS components.

The high electron density on the C(1) atom in the right fullerenyl fragment (see Fig. 1) is a consequence of asymmetry of the structure of the calculated $C_{120}^{\cdot +}$ radical cation. In the case of migration of the SO_3^- anion and delocalization of the unpaired electron over the entire molecule the distribution should become symmetrized.

Dication $C_{120}O^{2+}$. The calculated populations of the unpaired electrons on the atoms of the $C_{120}O^{2+}$ dication in the triplet state are listed in Table 2. As follows from the data listed in Table 2 and shown in Fig. 2, these populations are localized for the most part in the "northern" (upper) hemispheres of the polyhedral fragments of the dication. At the same time, mention should be made of the approximately symmetric density distribution of the unpaired electrons about the twofold symmetry axis passing through the O atom perpendicular to the C—C bond connecting the two C_{60} fragments. The distribution obtained is in qualitative agreement with the value of the effective distance between the unpaired electrons (7.8 Å). Most likely, the contribution of the populations of the unpaired electrons on the atoms located between the planes perpendicular to the horizontal symmetry axis of the $C_{120}O^{2+}$ dication and passing through the "centers" of the fullerenes to the *D* value is appreciably larger than that of the densities of the unpaired electrons on the atoms located outside these planes.

Dianion $C_{120}O^{2-}$. The calculated spin populations on the atoms in the $C_{120}O^{2-}$ dianion are also listed in Table 2. As can be seen, the spin density distribution in this dianion is also asymmetric. The highest spin populations are localized on the atoms located in the fragments marked by dashed lines in Fig. 2, which is in agreement with an increase in the effective distance between the unpaired electrons in the dianion (up to 13 Å) as compared to the dication.

Table 2. Spin populations on atoms (ρ) of the $C_{120}O^{2+}$ dication and $C_{120}O^{2-}$ dianion in the triplet state, calculated by the MNDO/PM3 method

$C_{120}O^{2+}$		$C_{120}O^{2-}$	
Atom[a]	ρ/au[b]	Atom[a]	ρ/au[c]
C(2)	0.137	C(15)	0.108
C(8)	0.123	C(11)	0.106
C(3)	0.123	C(4)	0.104
C(9)	0.136	C(10)	0.098
C(4)	0.071	C(16)	0.065
C(10)	0.071	C(17)	0.071
C(5)	0.092	C(18)	0.062
C(11)	0.092	C(19)	0.051
C(6)	0.056	C(21)	0.060
C(12)	0.056		
C(7)	0.035		
C(13)	0.035		
C(1)	0.085		
C(14)	0.085		

[a] The numbering of atoms is shown in Fig. 2.

[b] The ρ values equal to or larger than 0.035 au are listed.

[c] The ρ values equal to or larger than 0.05 au are listed.

Thus, the spin density distributions in the $C_{120}O^{2+}$ dication and $C_{120}O^{2-}$ dianion are in qualitative agreement with the effective distances between the unpaired electrons, calculated using the point model of dipole-dipole interaction. Strictly speaking, since this model gives no reasonable idea of the true distribution of the unpaired electrons in the case of paramagnetic systems containing a large number of conjugated bonds, quantum-chemical calculations acquire particular significance.

* * *

The above comparison of the results of calculations with the experimental data has demonstrated their good agreement. This makes it possible to draw a conclusion that the ESR spectral parameters of paramagnetic species C_{120}^{+}, $C_{120}O^{2+}$, and $C_{120}O^{2-}$ are mostly determined by electronic factors and that the effects of solvation, formation of ion pairs, and temperature are insignificant. Of fundamental importance is theoretical confirmation of substantial violation of spherical symmetry of the spin density distribution on the C_{60} fragments in the $C_{120}^{\cdot +}$ radical cation. Comparison of the parameters of ESR spectra with the results of calculations shows the efficiency of using the MNDO/PM3 method in the simulation of the electronic structure of paramagnetic species generated from dimers of fullerene C_{60} and their derivatives.

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