

ELECTRONIC STRUCTURE OF C₆₀ DERIVATIVES AT π-CONJUGATION BREAKING IN MODELS C₆₀H₂, C₆₀-C₂H₄, C₆₀-C₅H₇N, C₆₀-C-(CH₃)₂, AND C₅₉

*O.L. Pavlenko, M.P. Kulish, O.P. Dmytrenko, A.M. Zarytska,
V.A. Sendiuk, O.D. Kachkovsky¹*

*Taras Shevchenko National University of Kyiv, Kyiv, Ukraine,
tel. +38(044)526-05-12;*

¹*Institute of Bioorganic Chemistry and Petrochemistry, NAS of Ukraine, Kyiv, Ukraine,
tel. +38(044) 558-53-88,*

E-mail: olpavl57@gmail.com

The quantum-chemical calculations were applied for study of changes in the electron structure occurring in fullerene derivatives C₆₀-H₂, C₆₀-C₂H₄, C₆₀-C₅H₇N, C₆₀-C-(CH₃)₂, and C₅₉ molecules, which are convenient model objects with a covalent attachment of various types of ligands and also in fullerene C₅₉ formed by radiation irradiation and accompanied by break of π-conjugation in fullerenes C₆₀. Maximum of alternation of the atomic charges of the fullerene molecule is observed near place of the connection of functional groups and the radiation damage. Breaking of the conjugation leads to lowering of C₆₀ symmetry and splitting of degenerated electronic levels, lowering of energy gap, transition of HOMO-LUMO in the absorption spectra becomes allowed and other transitions shifted.

INTRODUCTION

Fullerenes C₆₀ are used in many scientific fields: medicine, nanobiotechnology, molecular electronics, nonlinear optics, atomic energetics and others due to specifics of their electronic structure, spectral properties, resulted from unique symmetry of the molecule. This is due to specific electronic structure and their symmetry spectral properties, especially, its lowest triplet state (*T*₁) [1–4]. High symmetry produces extremely high density of electronic states. From an experimental point of view this implies that high resolution spectra are required to properly distinguish the electronic structure. For the synthesis of compounds with novel properties fullerenes C₆₀ are modified by coupling them to different types of functional groups. The most sensitive to this rearrangement is the electronic structure of the C₆₀ and one can expect a reorganization in the experimental absorption spectra.

In this paper, we consider electronic structure of few compounds: the C₆₀H₂ one has the most polarized C-H bonds as a result of the connection of hydrogen atoms, that almost completely transfer the electron density for the bond formation. In model C₆₀-C₂H₄ due to location of carbon atoms between C₆₀ and hydrogen atoms, the polarization is less, as well as in models C₆₀-C₅H₇N, which are often used as a bridge with covalent bonding. [5]. Another considered model is C₆₀-C-(CH₃)₂, which has a bridge as in the functionalized fullerene pcbm (phenyl-C61-butyric acid methyl ester) used in photovoltaics. And finally, we consider model C₅₉ that can be formed in case of highenergetic irradiation [6–10], is stable and can be basic element for formation of polymerized fullerenes [11] that had been proclaimed as the hardest material and undergoes to the break of π-conjugation due to absence of one carbon atom.

MATERIALS AND METHODS

In order to study geometry of the molecules C₆₀H₂, C₆₀-C₂H₄, C₆₀-C₅H₇N, C₆₀-C-(CH₃)₂, and C₅₉, at the first stage we have performed optimization of geometry using density functional theory (DFT), (Gaussian '09) [12]. For further understanding of electron structure and its manifestation in the the spectrum electron transition characteristics were calculated by the non-empirical (TD/DFT/6-31G(d, p)/CAM-B3LYP) method and semi-empirical ZINDO method. Of course, there is no perfect coincidence of the calculated and experimental data, which is typical for this approach; however it is enough for correct analysis of the electron transitions nature [13].

RESULTS AND DISCUSSION

Fig. 1 shows optimized geometry of C₆₀ derivatives with -H₂ group, molecule, in which two hydrogen atoms are connected to the fullerene due to the break of double bonds, C₆₀-C₂H₄ – the case of connection of two carbon atoms with hydrogen, C₆₀-C₅H₇N, and C₆₀-C-(CH₃)₂. In such molecules, two carbon atoms near break of double bond have *sp*³-type of conjugation, in contrast to the carbon atoms in the C₆₀ molecule with *sp*²-hybridization. The important property of the fullerene that determines the electron properties and potential for formation of bonds between the molecules is the alternation of bonds: each carbon atom is connected to the two nearest neighbors by two single (length (1.455±0.005) Å [6–6]–connection and one double bond [5–6] – connection length (1.391±0.009) Å), which is associated with the peculiarities of the population of molecular orbitals.

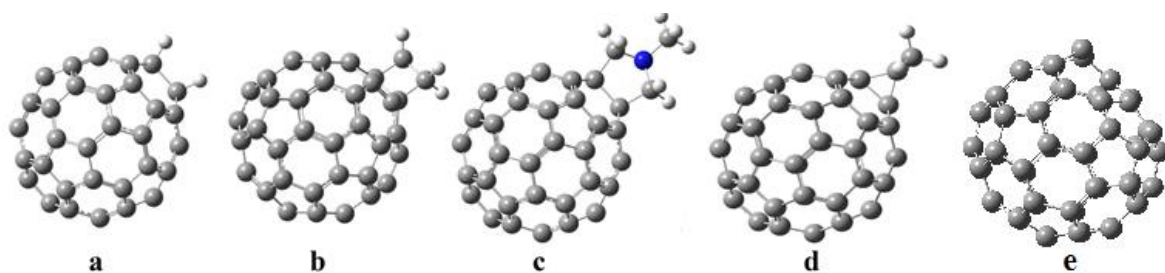


Fig. 1. Optimized geometry of $C_{60}H_2$ (a), $C_{60}-C_2H_4$ (b), $C_{60}-C_5H_7N$ (c), $C_{60}-C-(CH_3)_2$ (d), C_{59} (e)

Addition to fullerene molecule hydrogen atoms or bridges $-C_2H_4$, $-C_5H_7N$, and $C-(CH_3)_2$ leads to violation of this alternation near place of connection, the change in the geometry of the molecule and the decrease of its symmetry, which is directly proportional to changes in the lengths of the bonds, which is manifests itself in redistribution of charges, Fig. 2. Due to the high symmetry of the C_{60} molecule, the magnitudes of charges on each of the carbon atoms are zero.

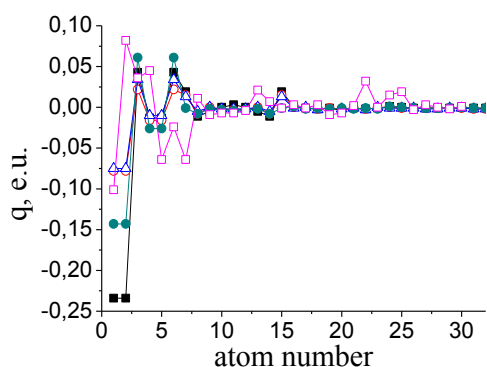


Fig. 2. The distribution of charges on the atoms according to the numbering: the first atoms are close to the chemical bonds, the far is atom the bigger is number of atoms for the molecules $C_{60}H_2$ (■), $C_{60}-C_2H_4$ (○), $C_{60}-C_5H_7N$ (Δ), $C_{60}-C-(CH_3)_2$ (●), and C_{59} (□)

It can be seen that covalent bonding of two hydrogen atoms causes the largest deviations of charges, especially in the place of the double bond break to -0.234 e.u., the smallest deviation is observed for the compound $C_{60}-C_5H_7N$, which is -0.075 e. u. As far as the distance from the chemical attachment, the magnitude of the deviations of charges is insignificant and decreases to almost zero values in the places opposite the bond for all considered structures.

Let's consider how the charge changes influence in the distribution of electronic levels. Fig. 3 shows the electronic structure of the investigated compounds near energy gap.

It is well known [4] and confirmed by our Hartree-Fock method calculations, Tabl. 1, that electronic levels of fullerene molecule C_{60} are degenerated due to high symmetry.

Table 1

Energetic characteristics of the structures

	E_{HOMO} , eV	E_{LUMO} , eV	Dipole m, D	Energy, a.u.
AMI				
C_{60}	-9.64	-2.95	0.00	1.55
$C_{60}H_2$	-9.26	-2.83	2.87	1.48
$C_{60}-C_2H_4$	-9.27	-2.81	3.34	1.51
$C_{60}-C_5H_7N$	-9.29	-2.84	2.75	1.51
$C_{60}-C-(CH_3)_2$	-9.28	-2.81	3.32	1.53
C_{59}	-9.16	-3.49	1.39	1.76
DFT				
C_{60}	-6.25	-3.38	0.00	-2285.6
$C_{60}H_2$	-5.66	-3.12	2.44	-2287.4
$C_{60}-C_2H_4$	-5.88	-3.24	3.14	-2364.2
$C_{60}-C_5H_7N$	-5.85	-3.21	3.85	-2458.8
$C_{60}-C-(CH_3)_2$	-5.91	-3.24	3.25	-2403.5
C_{59}	-5.76	-4.13	1.35	-2247.3

So the HOMO level is fivefold degenerated, while the LUMO level is threefold degenerated. In the case of hydrogen atoms are attached, two methyl groups and a nitrogen-containing pentagon in the $C_{60}H_2$, $C_{60}-C_2H_4$, and $C_{60}-C_5H_7N$ models, there is complete splitting of the levels near band gap. There is a narrowing of the energy gap due to the degeneration of levels. Mostly for $C_{60}H_2$ (a) and $C_{60}-C_5H_7N$ (c). The free levels rises up compared to the LUMO pure C_{60} , the largest offset - for the $C_{60}-H_2$. Filling of the gap occurs due to splitting of degenerated levels and levels of the connected atoms, that is confirmed by forms of molecular orbitals, Fig. 3. With the exception of the compound $C_{60}H_2$, where the orbital HOMO-2 is delocalized simultaneously on C_{60} and hydrogen atoms and HOMO for $C_{60}-C_2H_4$, which is delocalized on all atoms of the compound, the exception is for hydrogen atoms. Calculations of electron transitions confirm that for C_{60} HOMO-LUMO transition is forbidden on that points zero magnitude of the oscillator strength f_{osc} .

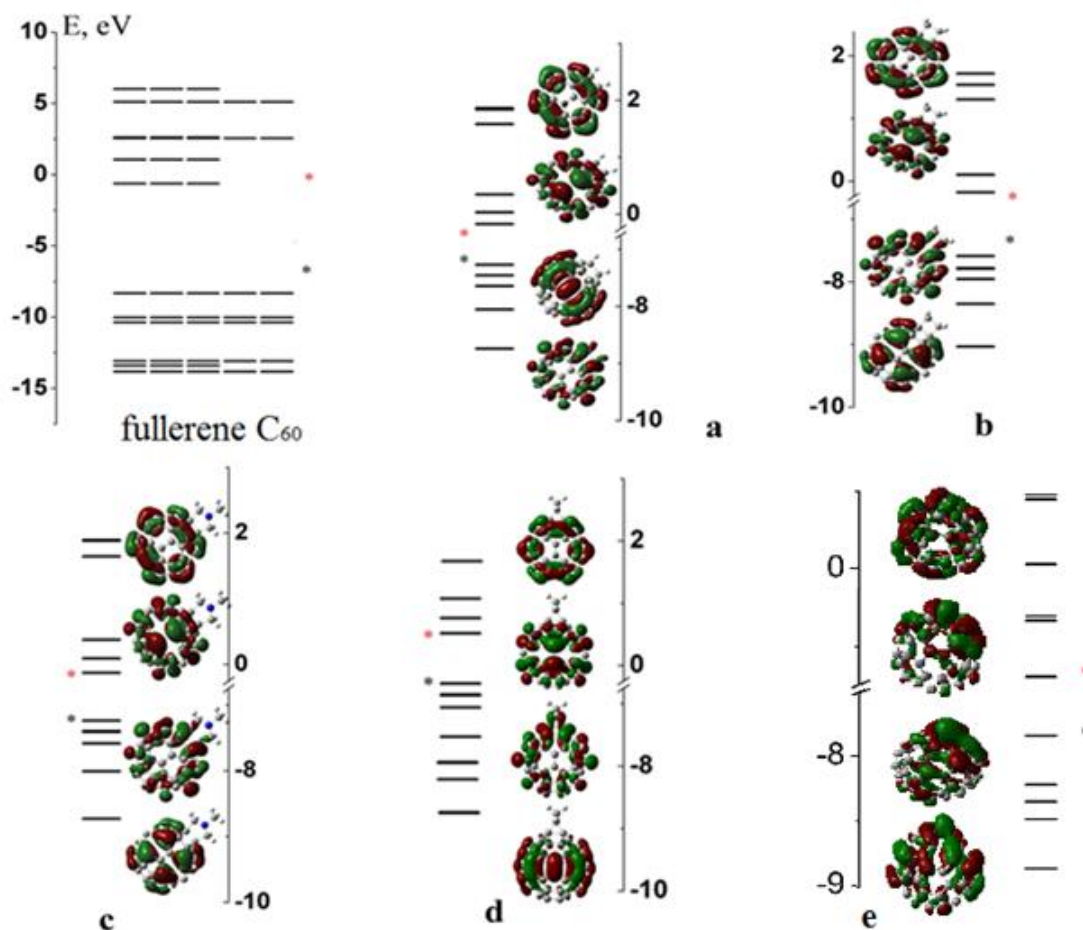


Fig. 3. Forms of molecular orbitals for compounds C_{60} , $C_{60}H_2$ (a); $C_{60}-C_2H_4$ (b); $C_{60}-C_5H_7N$ (c); $C_{60}-C-(CH_3)_2$ (d), and C_{59} (e). Stars show HOMO(*), LUMO(*) levels

Table 2

Characteristics of electron transitions in model molecular systems
 C_{60} , $C_{60}H_2$, $C_{60}-C_2H_4$, $C_{60}-C_5H_7N$, $C_{60}-C-(CH_3)_2$, and C_{59}

ZINDO	$S_0 \rightarrow S_1$	λ , nm	Energy, eV	f_{osc}	$N_k \rightarrow N_m$	Type
1	2	3	4	5	6	7
C_{60}	$S_0 \rightarrow S_1$	553	2.24	0.0000	HOMO \rightarrow LUMO	$\pi \rightarrow \pi$
	$S_0 \rightarrow S_2$	553	2.24	0.0000	HOMO(-2) \rightarrow LUMO	$\pi \rightarrow \pi$
	$S_0 \rightarrow S_3$	553	2.24	0.0000	HOMO(-4) \rightarrow LUMO(+2)	$\pi \rightarrow \pi$
$C_{60}-H_2$	$S_0 \rightarrow S_1$	576	2.15	0.0078	HOMO \rightarrow LUMO	$\pi \rightarrow \pi$
	$S_0 \rightarrow S_2$	566	2.18	0	HOMO \rightarrow LUMO(+1)	$\pi \rightarrow \pi$
	$S_0 \rightarrow S_3$	557	2.22	0.0003	HOMO(-2) \rightarrow LUMO	$\pi \rightarrow \pi$
$C_{62}-H_4$	$S_0 \rightarrow S_1$	572	2.16	0.007	HOMO \rightarrow LUMO	$\pi \rightarrow \pi$
	$S_0 \rightarrow S_2$	564	2.19	0	HOMO \rightarrow LUMO(+1)	$\pi \rightarrow \pi$
	$S_0 \rightarrow S_3$	558	2.22	0.0002	HOMO(-2) \rightarrow LUMO	$\pi \rightarrow \pi$
$C_{60}C_5H_7N$	$S_0 \rightarrow S_1$	577	2.15	0.0082	HOMO \rightarrow LUMO	$\pi \rightarrow \pi$
	$S_0 \rightarrow S_2$	565	2.19	0.0000	HOMO \rightarrow LUMO(+1)	$\pi \rightarrow \pi$
	$S_0 \rightarrow S_3$	558	2.22	0.0003	HOMO(-2) \rightarrow LUMO	$\pi \rightarrow \pi$
$C_{60}-C-(CH_3)_2$	$S_0 \rightarrow S_1$	566	2.19	0.0054	HOMO \rightarrow LUMO	$\pi \rightarrow \pi$
	$S_0 \rightarrow S_2$	560	2.19	0	HOMO \rightarrow LUMO(+1)	$\pi \rightarrow \pi$
	$S_0 \rightarrow S_3$	557	2.23	0.0002	HOMO(-2) \rightarrow LUMO	$\pi \rightarrow \pi$
C_{59}	$S_0 \rightarrow S_1$	879	1.41	0.0267	HOMO \rightarrow LUMO	$\pi \rightarrow \pi$
	$S_0 \rightarrow S_2$	697	1.78	0.0095	HOMO(-2) \rightarrow LUMO	$\pi \rightarrow \pi$
	$S_0 \rightarrow S_3$	693	1.79	0.0022	HOMO(-1) \rightarrow LUMO	$\pi \rightarrow \pi$

1	2	3	4	5	6	7
TD SCF	$S_0 \rightarrow S_i$	λ, nm	Energy, eV	F_{osc}	$N_k \rightarrow N_m$	Type
C ₆₀	$S_0 \rightarrow S_1$	561	2.21	0	HOMOLUMO(+1)	$\pi \rightarrow \pi$
	$S_0 \rightarrow S_2$	560	2.21	0	HOMO(-3) \rightarrow LUMO(+2)	$\pi \rightarrow \pi$
	$S_0 \rightarrow S_3$	560	2.21	0	HOMO(-3) \rightarrow LUMO(+1)	$\pi \rightarrow \pi$
C ₆₀ -H ₂	$S_0 \rightarrow S_1$	653	1.89	0.0023	HOMO \rightarrow LUMO	$\pi \rightarrow \pi$
	$S_0 \rightarrow S_2$	621	1.99	0.0000	HOMO \rightarrow LUMO(+1)	$\pi \rightarrow \pi$
	$S_0 \rightarrow S_3$	606	2.04	0	HOMO(-1) \rightarrow LUMO	$\pi \rightarrow \pi$
C ₆₂ -H ₄	$S_0 \rightarrow S_1$	615	2.02	0.0024	HOMO \rightarrow LUMO	$\pi \rightarrow \pi$
	$S_0 \rightarrow S_2$	585	2.12	0	HOMO \rightarrow LUMO(+1)	$\pi \rightarrow \pi$
	$S_0 \rightarrow S_3$	576	2.15	0	HOMO(-1) \rightarrow LUMO	$\pi \rightarrow \pi$
C ₆₀ C ₅ H ₇ N	$S_0 \rightarrow S_1$	616	2.01	0.0024	HOMO \rightarrow LUMO	$\pi \rightarrow \pi$
	$S_0 \rightarrow S_2$	584	2.12	0	HOMO \rightarrow LUMO(+1)	$\pi \rightarrow \pi$
	$S_0 \rightarrow S_3$	577	2.15	0	HOMO(-1) \rightarrow LUMO	$\pi \rightarrow \pi$
C ₆₀ -C-(CH ₃) ₂	$S_0 \rightarrow S_1$	607	2.04	0.0016	HOMO \rightarrow LUMO	$\pi \rightarrow \pi$
	$S_0 \rightarrow S_2$	587	2.11	0	HOMO \rightarrow LUMO(+1)	$\pi \rightarrow \pi$
	$S_0 \rightarrow S_3$	570	2.18	0	HOMO(-2) \rightarrow LUMO	$\pi \rightarrow \pi$
C ₅₉	$S_0 \rightarrow S_1$	1037	1.19	0.0031	HOMO(-1) \rightarrow LUMO	$\pi \rightarrow \pi$
	$S_0 \rightarrow S_2$	827	1.41	0.0093	HOMO \rightarrow LUMO	$\pi \rightarrow \pi$
	$S_0 \rightarrow S_3$	832	1.49	0.0002	HOMO(-2) \rightarrow LUMO	$\pi \rightarrow \pi$

The second and third transitions are realized with the participation of orbital HOMO (-2) \rightarrow LUMO, HOMO (-4) \rightarrow LUMO (+2). In the splitting of π -conjugation, the transition HOMO \rightarrow LUMO becomes the first allowed in all cases of joining of atoms and functional groups. The maximum strength of the oscillator for the transition HOMO \rightarrow LUMO is for the functional group - C₅H₇N, is 0.08. Go to HOMO \rightarrow LUMO (+1) and become second and it remains forbidden, and the transition HOMO (-2) \rightarrow LUMO becomes the third allowed transition. The electronic transitions responsible for the bands in the experimental absorption spectra are realized from deeper levels (Tabl. 2).

CONCLUSION

Calculations show that for fullerene molecule C₆₀, because of the high symmetry, all its electronic levels are degenerated. Covalent bonding of two hydrogen atoms, two methyl groups and the pentagon with the nitrogen atom leads to splitting of levels in the optical range. The energy gap decreases. Breaking of π -conjugation for fullerene C₆₀ by the addition of two atoms of hydrogen, CH₃-, C₅H₇N-groups lowers symmetry fullerene due to charge redistribution across the molecule (the largest deviations in the charges is observed in the case of H₂), removal of degeneracy of energy levels and as a result, changes to the energy gap. HOMO-LUMO becomes allowed.

REFERENCES

1. S. Wang, E.I. Mayo, M. Dolores Perez, L. Griffe, G. Wei, et al. High efficiency organic photovoltaic cells based on a vapor deposited squaraine donor // *Appl. Phys. Lett.* 2009, v. 94, p. 233304.
2. R. Yin et al. Photodynamic therapy with decationic C₆₀ monoadducts: effect of light absorbing electron-donor antenna and micellar formulation //

Nanomedicine: Nanotechnology, Biology and Medicine. 2014, v. 10, p. 795-808.

3. G. Chen, D. Yokoyama, H. Sasabe, et al. Optical and electrical properties of a squaraine dye in photovoltaic cells // *Appl. Phys. Lett.* 2012, v. 101, p. 083904.

4. G. Orlandi, F. Negri. Electronic states and transitions in C₆₀ and C₇₀ fullerenes // *Photochem. Photobiol. Sci.* 2002, v. 1, p. 289-308.

5. M.E. Milanese, M.B. Spesia, M.P. Cormick, E.N. Durantini. Mechanistic studies on the photodynamic effect induced by a dicationic fullerene C₆₀ derivative on Escherichia coli and Candida albicans cells // *Photodiagn. Photodyn. Ther.* 2013, v. 3, p. 320-327.

6. O.P. Dmytrenko, N.P. Kulish, N.M. Belyi, et al. Dose dependences of the optical properties of fullerene films subjected to the electron irradiation // *Thin Sol. Films.* 2006, v. 495, p. 365-367.

7. O.P. Dmytrenko, N.P. Kulish, Y.I. Prylutsky, et al. Radiation damages of C₆₀ films under high energetic electron irradiation exposure // *Problems of Atomic Science and Technology.* 2008, N 2, p. 48-52.

8. O.L. Pavlenko, O.P. Dmytrenko, M.P. Kulish, et al. Radiation damages and polymerization of fullerite C₆₀ films under irradiation with Ti ions // *Problems of Atomic Science and Technology.* 2011, N 2, p. 22-27.

9. O.P. Dmytrenko, V.A. Brusentsov, O.L. Pavlenko, et al. Irradiation-induced polymerization and damages of fullerite C₆₀ under irradiation with Fe ions // *Problems of Atomic Science and Technology.* 2015, N 99(5), p. 8-14.

10. N.E. Kornienko, N.P. Kulish, S.A. Alekseev, et al. Fine Band Structure of the Vibrational Spectra of Fullerite C₆₀ and Enhancement of Intermolecular Interaction in High-Temperature Phase // *Opt. Spectr.* 2010, v. 109, p. 742-752.

11. E. Alvarez-Zauco, H. Sobral, E.V. Basiuk, et al. Polymerization of C₆₀ fullerene films by UV-pulsed laser irradiation // *Appl. Surf. Sci.* 2005, v. 248, p. 243-247.

12. J.B. Foresman. *Exploring chemistry with electronic structure methods*. Pittsburgh: ARR, 1996, 297 p.

13. V.V. Kurdiukov, O.I. Tolmachev, O.D. Kachkovsky, et al. Electron structure and nature of electron transitions of squaraine and thiosquaraine as well as their 1.2-isomers // *J. Mol. Str.* 2014, v. 1076, p. 583-591.

Статья поступила в редакцию 20.03.2018 г.

ЭЛЕКТРОННАЯ СТРУКТУРА ПРОИЗВОДНЫХ C₆₀ ПРИ РАЗРЫВЕ π-СОПРЯЖЕНИЯ В МОДЕЛЯХ C₆₀H₂, C₆₀-C₂H₄, C₆₀-C₅H₇N, C₆₀-C-(CH₃)₂ И C₅₉

*Е.Л. Павленко, Н.П. Кулиш, О.П. Дмитренко, А.М. Зарицкая,
В.А. Сендюк, А.Д. Качковский*

С помощью квантово-химических расчетов исследована электронная структура в молекулах C₆₀-H₂, C₆₀-C₂H₄, C₆₀-C₅H₇N, C₆₀-C-(CH₃)₂ и C₅₉, которые являются удобными модельными объектами для изучения изменений, происходящих в фуллеренах при ковалентном подсоединении к ним лигандов разного типа, а также в фуллерене C₅₉, который образуется при радиационном облучении и сопровождается разрывом π-сопряжения в фуллеренах C₆₀. Показано, что происходит нарушение равномерного распределения зарядов атомов молекулы фуллерена, а в области подсоединения функциональных групп и радиационного повреждения наблюдается максимальное чередование знаков зарядов на атомах углерода. Расщепление вырожденных электронных уровней фуллерена приводит к уменьшению энергетической щели и снятия запрета на переход НОМО-LUMO в спектрах поглощения.

ЕЛЕКТРОННА СТРУКТУРА ПОХІДНИХ C₆₀ ПРИ РОЗРИВІ π-СПРЯЖЕННЯ У МОДЕЛЯХ C₆₀H₂, C₆₀-C₂H₄, C₆₀-C₅H₇N, C₆₀-C-(CH₃)₂ ТА C₅₉

*О.Л. Павленко, М.П. Куліш, О.П. Дмитренко, А.М. Зарицька,
В.А. Сендюк, О.Д. Качковський*

За допомогою квантово-хімічних розрахунків досліджено електронну структуру в молекулах C₆₀-H₂, C₆₀-C₂H₄, C₆₀-C₅H₇N, C₆₀-C-(CH₃)₂ та C₅₉, які є зручними модельними об'єктами для вивчення змін, що відбуваються у фуллеренах при ковалентному під'єднанні до них лігандів різного типу, а також у фуллерені C₅₉, що утворюється при радіаційному опроміненні і що супроводжується розривом π-спряження у фуллеренах C₆₀. Показано, що відбувається порушення рівномірного розподілу зарядів атомів молекули фуллерену, а в околі місця під'єднання функціональних груп та радіаційного пошкодження спостерігається максимальне чергування знаків зарядів на атомах вуглецю. Розщеплення вироджених електронних рівнів фуллерену приводить до зменшення енергетичної щілини та зняття заборони на перехід НОМО-LUMO у спектрах поглинання.