UDC 539.19;544.15

MOLECULAR STRUCTURES AND THERMOCHEMISTRY OF THE DERIVATIVES OF C24 FULLERENE BY ATTACHING A VARIETY OF CHEMICAL GROUPS

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A series of exohedrally functionalized derivatives of the D_6-symmetrical C_{24} fullerene, with attached —CH_2OH, —$CONH_2$, —COOH, and —COH chemical groups, have been investigated by using density-functional theory approach at the UB3LYP/6-31G(d) level. According to the calculated results, the C_{24}(COOH) is the most stable structure, with –73.58 kcal mol^{-1} value for the functionalization reaction energy and 3.16 eV for the dissociation energy, while C_{24}($CONH_2$) displays the largest dipole moment (3.09 D). It was also found that the HOMO— LUMO energy gaps, the vertical ionization potentials (VIP), and vertical electron affinities (VEA) of these functionalized derivatives are similar to those of the more stable C_{24} fullerene. Moreover, their corresponding HOMO and LUMO orbitals are mainly associated with the surface of the cage. Also, the vibrational frequencies of these derivatives are discussed. It was concluded that it would be possible to produce novel species for bio-medical applications by attaching selected chemical groups.

K e y w o r d s: C_{24} fullerene, derivative, structure, thermochemistry, DFT.

INTRODUCTION

Since the fullerene C_{60} was prepared using laser vaporization methods in 1985 [1], the fullerenes have attracted great interest in that they have possessed a large number of physical and chemical properties which could facilitate the development of novel technologies. For instance, the previous findings have reported the formation of many organic derivatives, and have significantly expanded the scope of carbon clusters [2—8]. These derivatives have also enhanced the stability of the endohedral fullerenes [9—12], which might be very interesting for applications in medicinal chemistry, materials science, and nanotechnology [13]. In addition, several types of functionalized fullerenes have been recently synthesized for possible applications in electronic and optical devices as well as for developing possible applications in biology and medicine [14—17].

In a previous study, the derivatives of some fullerenes have been extensively studied. For instance. Seven possible isomers for both methano- and imino-[50]fullerenes have been investigated by *ab initio* calculations [18]. In the later year, Xu et al. [19] have also studied the 1,3-dipolar cycloaddition of methyl azide (N_3CH_3) to [50]fullerene using semiempirical AM1 method, and found that the closed [5,6] isomer of $C_{50}NCH_3$ is more stable than its closed [5,5] isomer. Hu et al. [20] have calculated the structures and energies of glyccie-C_{60} complexes at the B3LYP/6-31G(d) level DFT, and it was indicated that fullerene cages might be unable to form stable bindings to proteins via their amino nitrogen, hydroxyl oxygen and carbonyl oxygen active sites. Additionally, the thermodynamic

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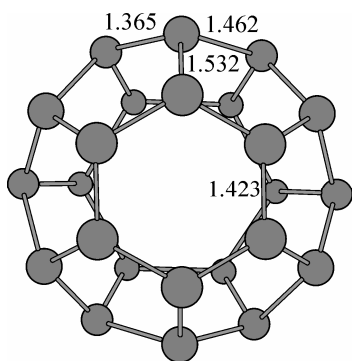
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Fig. 1. Optimized ground-state structure of the C_{24} molecule as viewed along the direction perpendicular to one of its hexagonal faces. All bond distances are in Angstroms

stability of $C_{60}(Glycine)_n$ (where $n = 1$—4) has also been studied by means of AM1 calculations to determine the positions where glycine molecules are preferentially added onto [60]fullerene molecule [21]. Currently many *ab initio* and density functional theory (DFT) computational studies are devoted to the structure and stability of C_{24} isomers: ring, bowl, and fullerene [22—25]. The ground-state structure of D_6-symmetrical C_{24} has also been predicted [26—29]. However to our knowledge, no theoretical investigation on the derivatives of C_{24} fullerene by attaching a various chemical groups has been conducted.

In this paper, based on the D_6-symmetrical C_{24} (Fig. 1) and the previous report for the derivatives of $C_{24}H_{24}$ fullerene [8], we have investigated the chemical derivatives of C_{24} fullerene using the hybrid DFT-UB3LYP functional in conjunction with 6-31G(d) basis sets. Four neutral chemical groups have been introduced as substituents in the C_{24} fullerene, namely (i) —CH_2OH, (ii) —$CONH_2$, (iii) —COOH, and (iv) —COH. The choice was due to the observation that these chemical groups are commonly present in both natural and synthetic molecules that have ability to interact non-covalently with the side-chain residues of biological receptors [30]. Moreover, computer-aided drug design has greatly contributed to the development of molecules that can selectively bind the active site of their putative receptors through the interactions [8]. Hence, for understanding these interactions, we needed to assess how the electronic structure of C_{24} fullerene is affected by the chemical groups.

COMPUTATIONAL METHODS

Becke′s three-parameter hybrid exchange functional [31] with the Lee, Yang, and Parr′s correlation functional [32], hereafter referred to as B3LYP, has been employed in all DFT calculations. Considering reasonable computational costs with accuracy sufficient for describing this system, the 6-31G(d) basis set [33] containing one polarization function has been utilized here. Based on the D_6-symmetrical C_{24} fullerene, its derivatives, which have been exohedrally functionalized by attaching —CH_2OH, —$CONH_2$, —COOH, and —COH chemical groups, have been calculated at the UB3LYP/6-31G(d) level of theory. Some properties have been investigated for the stable structures, including the optimized structures, vibrational frequencies, dipole moments, reaction energies, dissociation energies, HOMO—LUMO energy gaps, vertical ionization potentials (VIP), and vertical electron affinities (VEA). All the stationary point geometries have been analyzed by the evaluation of their harmonic vibrational frequencies at the same theoretical level. All calculations were performed using Gaussian 03 [34] program package. The default numerical integration grid (75,302) of Gaussian 03 was applied.

RESULTS AND DISCUSSION

1. The structures of C_{24} and its derivatives. According to previous studies [26—29], the ground-state structure of C_{24} fullerene has D_6 symmetry. We have also found that the structure corresponds to an $^1A_1$ electronic state at UB3LYP/6-31G(d) level of theory. The structure is shown in Fig. 1; the C—C bond lengths calculated by B3LYP are 1.423 and 1.532 Å for the two groups of twelve equivalent C—C bonds, bonds belonging to two hexagons and bonds adjacent to the haxagons,
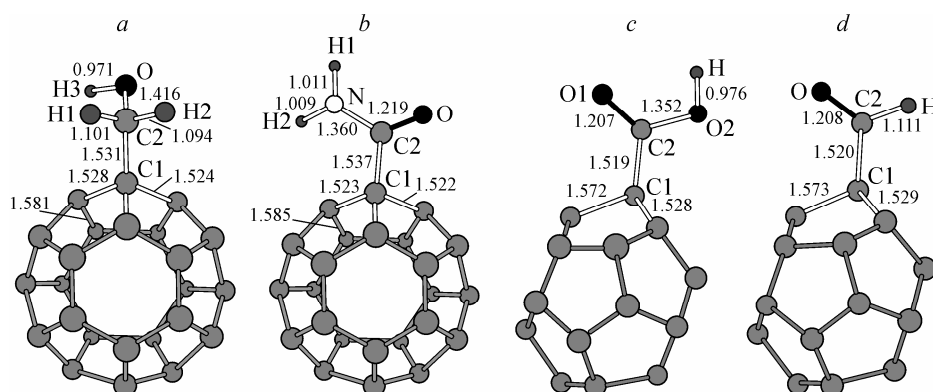
Fig. 2. Optimized ground-state structures of (*a*) C$_{24}$(CH$_2$OH), (*b*) C$_{24}$(CONH$_2$), (*c*) C$_{24}$(COOH), and (*d*) C$_{24}$(COH). All bond distances are in Å

respectively. Other C—C bond distances predicted by B3LYP are 1.365 and 1.462 Å for the two groups of six equivalent C—C bonds in the equatorial region of the structure (Fig. 1).

The optimized ground-state structures of functionalized derivatives are shown in Fig. 2. Let us first assess in what extent the symmetric D_6 structures of C$_{24}$ become distorted by attaching the chemical groups mentioned above. When attaching the —CH$_2$OH group (Fig. 2, *a*), the three C—C distances adjacent to C1 atom are lengthened because of the decrease of bond energies, becoming 1.528, 1.524, and 1.581 Å. The optimized bond length are 1.531 Å for C1—C2 bond, 1.416 Å for C2—O bond, 0.971 Å for O—H3 bond, and 1.101 and 1.094 Å for the C2—H1 and C2—H2 bonds in the —CH$_2$OH group. It can be seen that the O—H3 bond becomes twisted, and it does not lie in the C1—C2—O plane. Thus, it has a C_1 symmetry with ^{2}A state. The C1—C2—O bond angle is 112.3°, the C2—O—H3 bond angle is 107.7°, and the H1—C2—H2 bond angle is 107.8°. Additionally, the corresponding C1—C2—O—H dihedral angle is 66.2°.

The optimized ground-state structure of the derivative functionalized with a —CONH$_2$ group is shown in Fig. 2, *b*. The molecule has a C_1 symmetry with ^{2}A state because —NH$_2$ group is slightly istorted relative to the other part of the cluster. The C1—C2—O bond angle is 121.0°, the C1—C2—N bond angle is 114.9°, the C2—N—H1 bond angle is 118.4°, and the C2—N—H2 bond angle is 122.0°. The dihedral angles are 2.6° and 177.2° for O—C2—N—H1 and O—C2—N—H2, respectively. The three C—C distances for the bonds adjacent to C1 atom are 1.523, 1.522, and 1.585 Å. The optimized distances are 1.537 Å for C1—C2 bond, 1.219 Å for C2—O bond, 1.360 Å for C2—N bond, and 1.011 and 1.009 Å for N—H1 and N—H2 bonds. The remaining C—C bonds are almost unchanged as compared with the C$_{24}$ fullerene.

The geometry of ground state of the derivative functionalized with a —COOH group is displayed in Fig. 2, *c*. The molecule has a C_s symmetry with ^{2}A″ state. For C$_{24}$(COOH), the lengths of the three C—C bonds adjacent to C1 atom are 1.528, 1.528, and 1.572 Å. The optimized distances are 1.519 Å for C1—C2 bond, 1.207 Å for C2—O1 bond, 1.352 Å for C2—O2 bond, and 0.976 Å for O2—H bond in the COOH group. While the C1—C2—O1 bond angle is 125.3°, the C1—C2—O2 bond angle is 110.8°, and the C2—O2—H bond angle is 106.6°. The dihedral angles are 180.0° and 0.0° for C1—C2—O2—H and O1—C2—O2—H, respectively.

Attaching to C$_{24}$ fullerene —COH group yields the functionalized derivative displayed in Fig. 2, *d*. Our B3LYP results show C_s symmetry with ^{2}A″ state for the ground state of C$_{24}$(COH). The three C—C distances for the bonds adjacent to C1 atom are 1.529, 1.529, and 1.573 Å. The C1—C2 bond distance is 1.520 Å, and the C2—O and C2—H bond distances are 1.208 and 1.111 Å, respectively. The C1—C2—O—H dihedral angle is 180°, the C1—C2—O bond angle is 123.7°, and the C1—C2—H bond angle is 114.5°. There are no experimental or theoretical values for comparison.

2. Vibrational frequencies. The calculated vibrational frequencies of C_{24} fullerene are shown in Fig. 3. According to the group representation theory in chemistry, we can easily deduce that there are
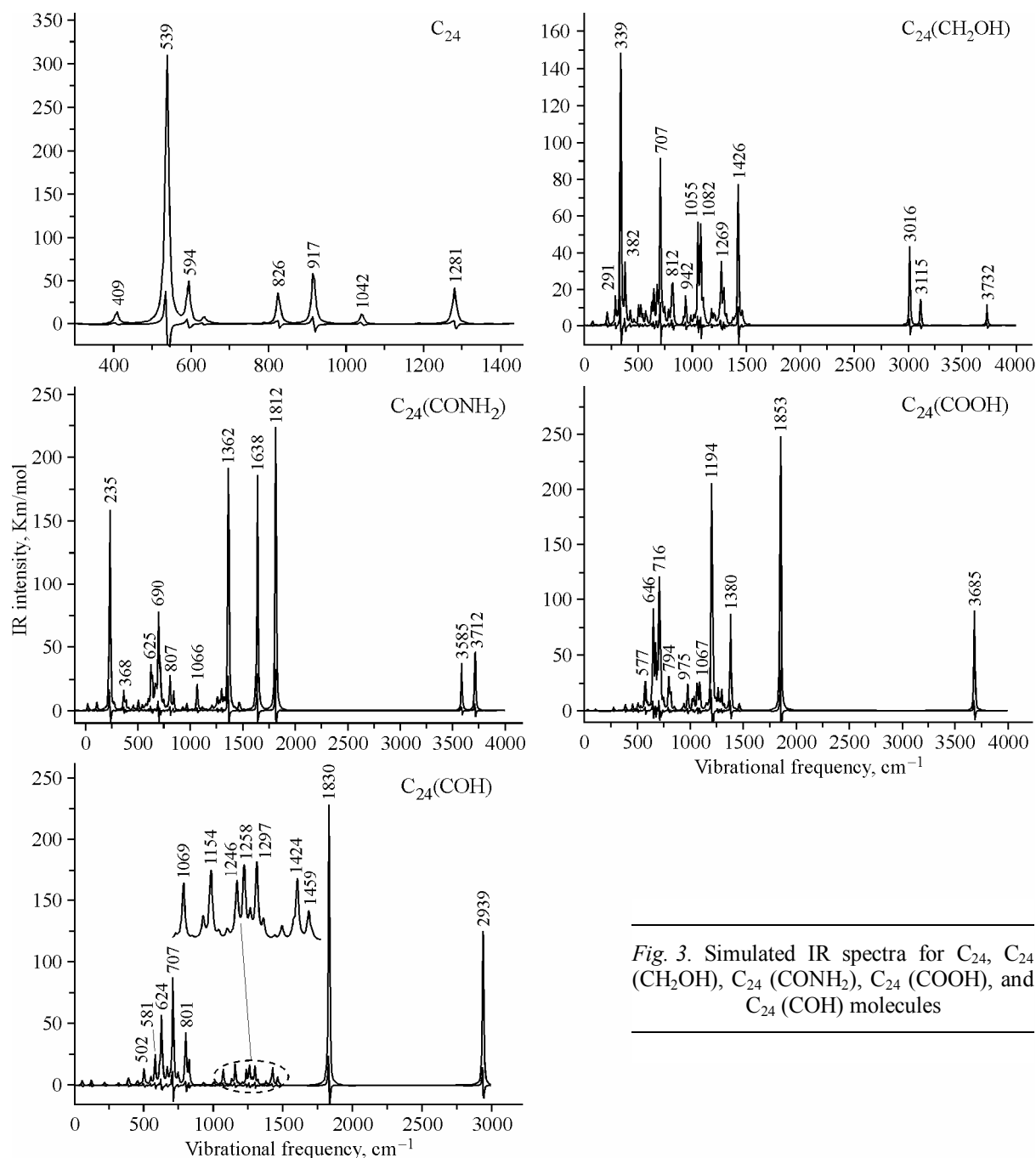

Fig. 3. Simulated IR spectra for C_{24}, C_{24} (CH_2OH), C_{24} ($CONH_2$), C_{24} ($COOH$), and C_{24} (COH) molecules

66 kinds of vibrational modes for C_{24} with D_6 symmetry, which are $20e_1 + 24e_2 + 6a_1 + 6b_1 + 4a_2 + 6b_2$. Among these normal modes, the strongest IR absorption peak is a_2 mode, which located at 539 cm^{-1}. The simulated IR spectra of derivatives functionalized by attaching —CH_2OH, —$CONH_2$, —COOH, and —COH groups are also shown in Fig. 3. For the C_{24}(CH_2OH) molecule, its the strongest absorption peaks is located at 339 cm^{-1}, which is lower than that of C_{24} fullerene. The reason is that the strongest absorption peaks of C_{24}(CH_2OH) molecule arise from the twisting vibration of H—O in the CH_2OH group, while the strongest peaks of C_{24} are caused by the C—C stretching vibration of the twelve-member-ring. The characteristic peaks are 339, 1426, 3016, 3115 and 3732 cm^{-1} for CH_2OH group, 235, 1362, 1638, 1812, 3585 and 3712 cm^{-1} for $CONH_2$ group, 1380, 1853 and 3685 cm^{-1} for

COOH group, and 1424, 1830 and 2939 cm^{-1} for COH group. Additionally, the strongest absorption peaks of C$_{24}$(CONH$_2$), C$_{24}$(COOH), and C$_{24}$(COH), located 1812, 1853 and 1830 cm^{-1}, appear to be

Dipole moments (Dipole), Reaction energies (ΔH), Dissociation energies (D$_e$), HOMO—LUMO energy gaps (E_{gap}), vertical ionization potentials (VIP), and vertical electron affinities (VEA) of C$_{24}$ and studied derivatives [a]

Molecules	State (symmetry)	Dipole, D	ΔH, kcal·mol^{-1}	D$_e$, eV	E_{gap}, eV	VIP, eV	VEA, eV
C$_{24}$	$^1A_1(D_6)$	0.00	—	—	1.82 [b]	7.34	2.17
C$_{24}$(CH$_2$OH)	$^2A(C_1)$	1.13	−70.95	3.04	1.75	7.39	2.17
C$_{24}$(CONH$_2$)	$^2A(C_1)$	3.09	−68.58	2.95	1.74	7.44	2.24
C$_{24}$(COOH)	$^2A''(C_s)$	1.46	−73.58	3.16	1.74	7.51	2.27
C$_{24}$(COH)	$^2A''(C_s)$	2.02	−65.82	2.81	1.73	7.62	2.37

[a] All the calculations were performed at the UB3LYP/6-31G(d) level of theory.

[b] The HOMO—LUMO energy gap of C$_{24}$ is 0.0290 Hartree with the SCC-DFTB calculations [in Ref. 29].

quite similar in general shapes. All are providing clear theoretical evidences to characterize the stable complexes in future spectroscopic investigations. There are no experimental or other theoretical values for comparison.

3. Thermochemistry and relative stabilities. The reaction energies (ΔH), dissociation energies (D$_e$), HOMO—LUMO energy gaps (E_{gap}), vertical ionization potentials (VIP), and vertical electron affinities (VEA) of the functionalized derivatives evaluated by B3LYP method are listed in Table.

The reaction energies and dissociation energies are as follows: $\Delta H = H(C_{24}(X)) - H(C_{24}) - H(X)$ and D$_e$ = $E(C_{24}) + E(X) - E(C_{24}(X))$. Here X = CH$_2$OH, CONH$_2$, COOH, and COH, H and E represent the enthalpies and zero-point corrected total energies, respectively. Thermodynamic stability is expected when ΔH is negative, and the more negative the values of ΔH, the more stable the C$_{24}$(X) molecules are. With D$_e$, the situation is the opposite, that is the more positive the values of D$_e$, the more stable the C$_{24}$(X) molecules are. As it can be seen from Table, the most negative ΔH and positive D$_e$ are −73.58 kcal/mol and 3.16 eV, respectively. So it is implied that C$_{24}$(COOH) is the most stable structure which is similar to the previous report for COOH chemical group [8]. Meanwhile, the stability order for the other functionalized derivatives is C$_{24}$(CH$_2$OH) > C$_{24}$(CONH$_2$) > C$_{24}$(COH).

The electronic structures of C$_{24}$ and its functionalized derivatives are shown in Fig. 4, with the vibrational modes and orbital energies (eV) in parentheses. The HOMO and LUMO orbitals of C$_{24}$ and the studied derivatives are associated with the cage, and the HOMO and LUMO orbitals have their main weight on the surface of the cage, but not around the center of the cage. Meanwhile, our calculated HOMO—LUMO energy gaps for the functionalized derivatives are nearly the same as in the case of not functionalized C$_{24}$ fullerene, being 1.75, 1.74, 1.74, and 1.73 eV. Interestingly, the C$_{24}$ derivatives possess a net dipole moment, and the dipole moment of C$_{24}$(CONH$_2$) is the largest, 3.09 D, which is also in agreement with the previous study for CONH$_2$ chemical group [8] (listed in Table 1).

The calculated vertical ionization potentials (VIP) and vertical electron affinities (VEA) of the C$_{24}$ fullerene are reported in Table. We can see that the VIP of C$_{24}$ is 7.34 eV while its VEA is computed to be only 2.17 eV. In comparison, the experimental VIP of C$_{60}$ fullerene corresponds to 7.58 eV [35] while its VEA is 2.666 eV [36]. These results show that C$_{24}$ fullerene is very stable, and it should be possible to develop a variety of new derivatives. The VIP and VEA of the functionalized derivatives with —CH$_2$OH, —CONH$_2$, —COOH, and —COH groups are also similar to those calculated for C$_{24}$ fullerene. Thus, they are predicted to be very stable species, too.

To our knowledge, there are no experimental or theoretical data regarding these properties for the studied functionalized derivatives. Our results may thus provide a reference for future studies.

CONCLUSIONS

A series derivatives based on the D_6-symmetrical C_{24} fullerene functionalized by attached —CH_2OH, —$CONH_2$, —$COOH$, and —COH chemical groups have been investigated for the first time using the hybrid DFT-UB3LYP functional in conjunction with 6-31G(d) basis sets. Some proper-
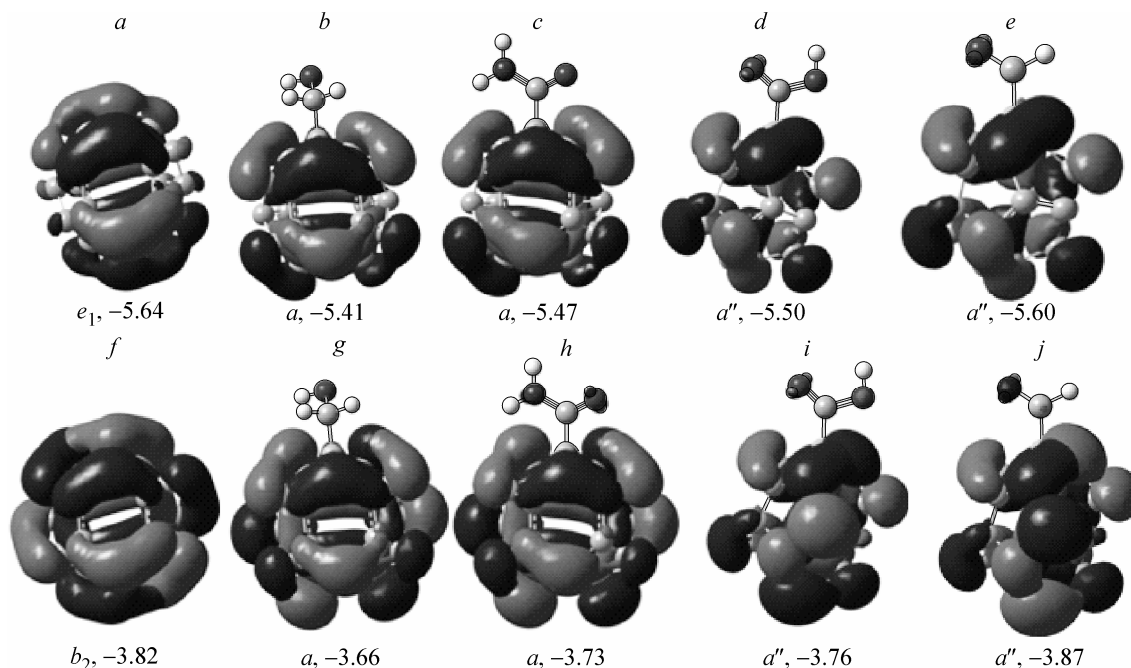

Fig. 4. (*a–e*) HOMO and (*f–j*) LUMO plots of (*a, f*) C_{24}, (*b, g*) $C_{24}(CH_2OH)$, (*c, h*) $C_{24}(CONH_2)$, (*d, i*) $C_{24}(COOH)$, and (*e, j*) $C_{24}(COH)$ molecules. The vibrational modes and orbital energies (eV) are given in parentheses

ties have been investigated for the stable structures, including the optimized structures, vibrational frequencies, dipole moments, reaction energies, dissociation energies, the HOMO—LUMO energy gaps, vertical ionization potentials (VIP), and vertical electron affinities (VEA). The calculations reported in this work show that the $C_{24}(COOH)$ derivative is the most stable structure from the values of ΔH and D_e, while the $C_{24}(CONH_2)$ derivative displays the largest dipole moment (3.09 D).The HOMO—LUMO energy gaps of all the derivatives are nearly the same as in the case of not functionalized C_{24} fullerene. Moreover, their corresponding HOMO and LUMO orbitals are associated with the surface of the cage. In addition, the vertical ionization potentials (VIP) and vertical electron affinities (VEA) of the studied functionalized derivatives are similar to those calculated for the more stable C_{24} fullerene. Therefore these derivatives are predicted to be very stable, too. Thus, it would be possible to produce novel species for bio-medical applications by attaching selected chemical groups. We hope that our results may provide a reference for further experimental and theoretical work as well as efforts directed toward the synthesis of these derivatives.

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