X-ray Spectroscopic and Quantum-Chemical Characterization of Hydrofullerene $C_{60}H_{36}$

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X-ray emission and X-ray photoelectron investigation of hydrofullerene $C_{60}H_{36}$ prepared by hydrogen transfer from 9,10-dihydroanthracene to fullerene was performed. Experimental spectra were interpreted by the results of quantum-chemical calculations of three isomers using PM3 semiempirical method. Cls and C Kα spectra of hydrofullerene $C_{60}H_{36}$ are in the closest agreement with the theoretical spectra of *T* symmetry isomer in which the benzenoid rings occupy tetrahedral positions. Comparison between X-ray emission spectra of C_{60}, $C_{60}H_{36}$ and C_6H_6 shows that benzenoid fragments are really involved in hydrofullerene structure.

Introduction

After it had become possible to produce fullerenes in gram quantities,[1] these compounds turned out to be the subject of intensive research. One of the first reactions with fullerenes was the Birch reduction[2] that gave hydrofullerene $C_{60}H_{36}$. Since only conjugated double bonds are involved in the reactions of such kind, it was assumed all double bonds in the molecule $C_{60}H_{36}$ were isolated from each other. The most symmetric isomer having a double bond on each pentagon belongs to the T_h point-group symmetry. The composition of the hydrofullerene of $C_{60}H_{36}$ was obtained by other methods (for a survey, see ref 3).

Studies of $C_{60}H_{36}$ by various spectral techniques[3,4] showed the molecules to have a rather high symmetry, though lower than T_h. If a molecule contains a 3-fold axis, the number of possible isomers of $C_{60}H_{36}$ is equal to 63; the calculations of them were carried out using the AM1 method.[5] Of these isomers, the *T* and D_{3d} symmetric structures are most thermodynamically stable. In the *T* isomer all double bonds distribute among four six-membered rings located at tetrahedral positions on the C_{60} cage. The structure of D_{3d} symmetry is intermediate between T_h and *T* isomers. It contains benzenoid rings at the poles; other six double bonds are isolated and located along parallels of C_{60} sphere. Calculations of $C_{60}H_{36}$ isomers by different quantum-chemical methods have shown that the *T* symmetry isomer is most stable as compared to other possible structures.[6−10]

So far the comparison of experimental evidence for $C_{60}H_{36}$ and quantum-chemical calculation results has not led to unambiguous description of its molecular structure. Spectral characteristics of $C_{60}H_{36}$ produced by hydrogen radical induced hydrogenation of fullerite show better agreement with calculation results for D_{3d} or C_{3i} structures.[11] Electron diffraction data for hydrofullerene prepared by high-pressure hydrogenation of fullerite demonstrate that the $C_{60}H_{36}$ is best described by a structure having D_{3d} symmetry.[12] FTIR, NMR, and UV spectra of $C_{60}H_{36}$ obtained by Birch reduction showed the bands characteristic of benzenoid rings.[13] Comparison of the ^{3}He NMR spectra for $^3He@C_{60}H_{36}$ samples prepared by two different synthetic methods[14] with the calculated ^{3}He chemical shifts[9] points to the formation of $D_{3d'}$ isomer (all double bonds are located along the molecule's equator). It has also been shown that IR, ^{1}H, and ^{13}C NMR spectra of solid hydrofullerene synthesized from transfer hydrogenation using 9,10-dihydroanthracene as the source of hydrogen are better described by the *T* symmetric structure.[15,16]

The different geometries of the $C_{60}H_{36}$ molecule lead to the electronic structure distinctions among its isomers. One of the experimental methods that allow the study of the electron density distribution in valence band of the compound is X-ray emission spectroscopy. According to dipole selection rules, in the Koopmans' theorem approximation, C Kα spectrum of fullerene compound corresponds to C2p electron density distribution.[17,18] Therefore, the $C_{60}H_{36}$ structure can be determined from the best agreement between experimental C Kα spectrum and electron density distribution of hydrofullerene isomers found from quantum-chemical calculations. We have used such an approach to determine molecular structure of $C_{60}F_{24}$.[19]

The goal of the present contribution is to determine a molecular structure of hydrofullerene $C_{60}H_{36}$ on the basis of quantum-chemical modeling of X-ray emission and X-ray photoelectron spectra.

Experimental Section

Fullerene C_{60} (99.5%) was produced by the Kratschmer−Huffman method as described in ref 20. Dihydroanthracene (99%) was supplied by Lancaster Synthesis Ltd., and purified by double sublimation. Transfer hydrogenation of C_{60} with dihydroanthracene was conducted in glass tube in argon atmosphere; the synthetic details are given in refs 15 and 16. The final product of $C_{60}H_{36}$ composition was light yellow. Characterization of hydrofullerene was carried out by mass spectrometric, IR, UV, and NMR spectroscopic methods.[15,16]

X-ray fluorescence spectra of $C_{60,}$ $C_{60}H_{36}$ and benzene were obtained using a spectrometer, "Stearat". The samples of fullerite and hydrofullerene were deposited on copper supports and cooled to liquid nitrogen temperature in a vacuum chamber of the X-ray tube. Solid benzene specimen was obtained by precipitating benzene vapors on the cooled substrate by the

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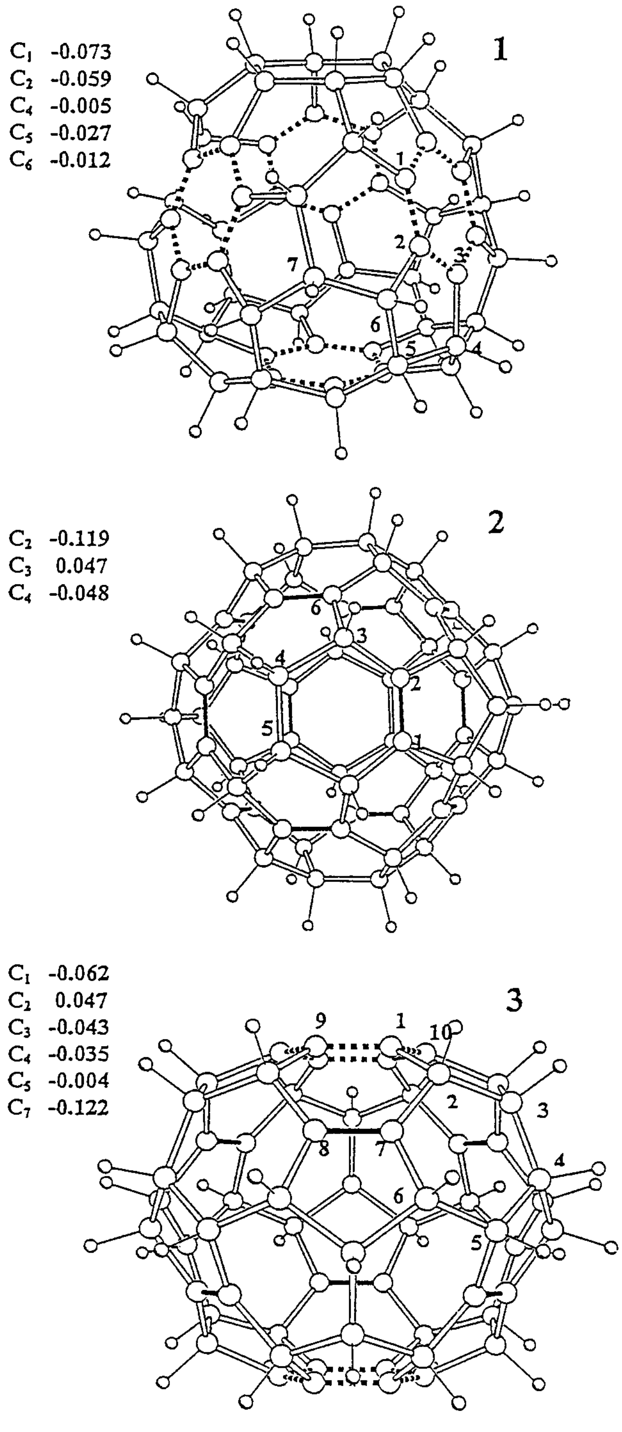

Figure 1. Calculated structures of isomers **1**−**3** for $C_{60}H_{36}$ and charges on the symmetrically inequivalent carbon atoms. Formally double bonds are indicated by bold lines, dashed lines connect the atoms in benzenoid fragments.

method given in ref 21. Operating conditions of X-ray tube with a copper anode was $U = 6$ kV $I = 0.5$ A. Spectra resolution was 0.4 eV. NAP single crystal was used as a crystal-analyzer. The technique of applying this crystal-analyzer to obtain C Kα spectra is described in ref 22. Determination accuracy of X-ray band energy was ±0.15 eV.

X-ray photoelectron Cls spectra of C_{60} and $C_{60}H_{36}$ were recorded using a VG Microtech spectrometer. Electron excitation was performed by characteristic Mg Kα -radiation, analyzer transmission energy − 20 eV. Full width at half-maximum (fwhm) of Ag $3d_{5/2}$ line is 0.9 eV.

TABLE 1: Calculated Heats of Formation (ΔH_f) and HOMO Ionization Potentials (IP) for Isomers 1−3 of $C_{60}H_{36}$

isomer	point group	ΔH_f (kcal/mol)	IP (eV)
1	T	254.81	8.70
2	T_h	263.06	8.99
3	D_{3d}	288.46	8.80

TABLE 2: Bond Lengths and Bond Orders for Isomer 1

bond	bond length (Å)	bond order
C_1-C_2	1.370	1.47
C_2-C_3	1.401	1.31
C_2-C_6	1.482	0.98
C_3-C_4	1.476	0.98
C_4-C_5	1.608	0.94
C_5-C_6	1.563	0.96
C_6-C_7	1.529	0.96

Calculations

Three isomers of $C_{60}H_{36}$ (Figure 1), one or more of which should correspond to the synthetically available, were calculated. These isomers are considerably differed by the character distribution of non-hydrogenated bonds on the C_{60} cage. The T_h symmetric structure possesses only the isolated doubly bonds, D_{3d} isomer has isolated double bonds as benzenoid rings, and, finally, in the structure of the T isomer, there are only benzenoid rings. Calculations were carried out using the PM3 semiempirical method[23] included into GAMESS package.[24] The geometries of isomers were fully optimized to the gradient value 10^{-4} Ha/bohr. The calculated charges of symmetrically inequivalent carbon atoms are given in Figure 1. In the PM3 method, the charge q_μ on the atom μ is calculated as follows:

$$q_\mu = N_\mu - \sum_i C_{\mu i}{}^2$$

where N_μ is the number of valence electrons of the atom and $C_{\mu i}$ is a coefficient describing the amount of atomic orbital (AO) to be found in the ith occupied molecular orbital (MO).

The intensity of a spectral line in the theoretical X-ray spectrum is obtained using the projection on the appropriate AOs in the ground state. It is calculated by summing up the squared coefficients of the 2p(C) AOs participating in the construction of a particular MO. The position of the line on the energy scale indicates the value of one-electron energy of MO, obtained by calculation. The lines were normalized and convoluted with a Lorentzian curve with a fwhm of 0.4 eV.

Experimental X-ray spectra are to be related to one-electron energy scale by the energy of 1s level for C_{60} (285 eV) with an allowance for the work function (5 eV). In Koopmans' theorem approximation, the one-electron energies of molecule correspond to its ionization potentials taken with the opposite sign. PM3 ionization potentials of fullerene molecules are higher than experimental values by 2 eV.[25] This discrepancy was taken into account in setting up correspondence between experimental and theoretical scales.

Results and Discussion

The heats of formation of the isomers are listed in Table 1, arranged in order of increasing of ΔH_f. By the PM3 calculation results, isomer **1** with T symmetry is the most stable isomer in considered series. The lengths of nonequivalent bonds and their orders for each isomer are listed in Tables 2−4. It should be noted that hydrogenated bonds on the pentagon−hexagon edge are elongated compared to characteristic carbon−carbon σ bonds of carbon containing compounds. Such are, for example, the

TABLE 3: Bond Lengths and Bond Orders for Isomer 2

bond	bond length (Å)	bond order
C_1-C_2	1.333	1.88
C_2-C_3	1.477	0.98
C_3-C_4	1.562	0.96
C_3-C_6	1.506	0.97
C_4-C_5	1.544	0.96

TABLE 4: Bond Lengths and Bond Orders for Isomer 3

bond	bond length (Å)	bond order
C_1-C_2	1.500	0.97
C_1-C_9	1.386	1.41
C_1-C_{10}	1.396	1.36
C_2-C_3	1.555	0.96
C_2-C_7	1.482	0.98
C_3-C_4	1.531	0.97
C_4-C_5	1.573	0.96
C_5-C_6	1.522	0.96
C_6-C_7	1.484	0.98
C_7-C_8	1.346	1.88

bonds C_4-C_5 and C_5-C_6 in isomer **1** (Table 2). In Figure 1 bold lines indicate the bonds with the order exceeding 1.70. Formally, they may be classed as double bonds. The bonds with the order ranging from 1.30 to 1.50 are similar to aromatic bonds in benzene. By PM3 calculation results, the bond order in C_6H_6 is 1.42. In Figure 1 bonds of aromatic type are denoted by dashed lines.

For isomer **1**, in non-hydrogenated hexagons, the delocalization of π electron density is observed. Six-membered cycles located at the poles of isomer **3** are also aromatic. Lengths and orders of non-hydrogenated bonds positioned along parallels of the sphere C_{60} are close to the corresponding values for isomer **2**, e.g., formally double bonds.

Characterization of $C_{60}H_{36}$ Based on X-ray Photoelectron Spectra. Fullerene C_{60} and hydrofullerene $C_{60}H_{36}$ are dielectrics with low thermal conductivity.[26,27] Exposure of such materials to X-rays accompanied by electron emission can result in charging and heating of a specimen. As is known from the literature, the binding energy of C1s electrons in fullerene C_{60} is equal to 285.0 eV.[28,29] For $C_{60}H_{36}$ such data are not determined. We established that for $C_{60}H_{36}$ films applied on aluminum or titanium surface the position of Cls peak was shifted relative to that for C_{60} by 0.2−0.4 eV toward lower binding energies. Thus the energy position of Cls peak of $C_{60}H_{36}$ spectrum was found to be 284.7 ± 0.1 eV. Besides, the hydrofullerene spectrum has a larger fwhm (by 0.6 eV) than that of the fullerene one (Figure 2). Displacement of C1s line toward low binding energies and its asymmetry point to the presence of negative charges on carbon atoms of the hydrofullerene $C_{60}H_{36}$. The values of charges given by quantum-chemical calculations may be associated with binding energies of inner electrons.[30] According to Figure 1, only in isomer **1** the charges on carbon atoms are negative or close to zero, and positive charges are absent.

To model theoretical X-ray photoelectron spectra, it is necessary to determine the proportionality coefficient (C) between the calculated charge $q(e)$ and energy shift Δ (eV) of the inner Cls level, as well as experimental fwhm δ of lines. In fullerene C_{60} all atoms are equivalent, and Cls spectrum width for this compound is primarily determined by the instrument broadening. The best agreement between experimental and theoretical X-ray photoelectron spectra of C_{60} (Figure 2) is achieved by approximating the theoretical spectrum by the line of the Gaussian shape with $\delta = 1.35$ eV. Proportionality coefficient C found by comparing binding energies of Cls electrons in C_6H_6[31] and the charges on carbon atoms of benzene molecule calculated by PM3 method is equal to $C = 13.9$ eV/e.

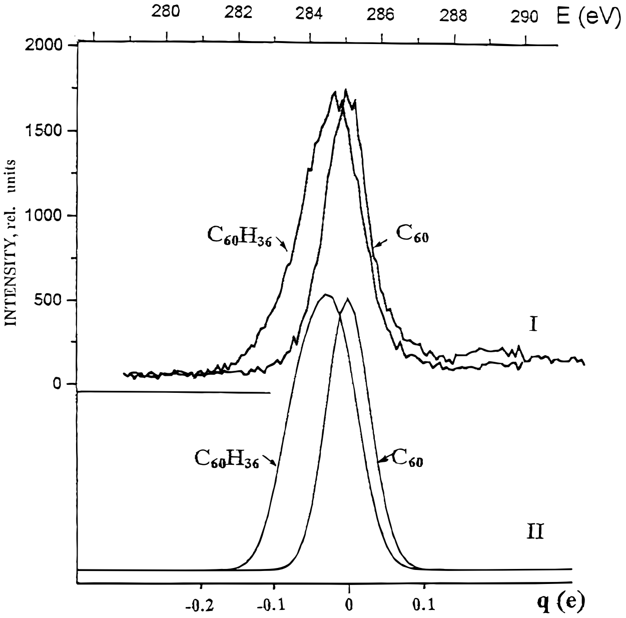

Figure 2. X-ray photoelectron spectra of C_{60} and $C_{60}H_{36}$. (I) experimental spectra, (II) theoretical spectra, which are plotted in the scale of charges calculated for molecule C_{60} and the *T* symmetry isomer of $C_{60}H_{36}$.

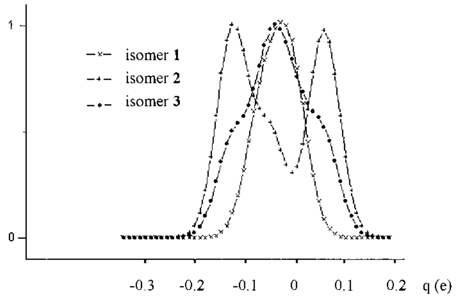

Figure 3. Calculated X-ray photoelectron spectra for isomers **1**−**3** of $C_{60}H_{36}$.

X-ray photoelectron spectra of isomers **1**−**3** modeled with allowance for the parameters C and δ are shown in Figure 3. The spectra are normalized on maximal line. Isomer **1** shows the closest agreement with experiment. Cls spectrum of isomers **3** is essentially broadened, and the spectrum of isomer **2** is evenly split. This is due to positive charges on carbon atoms.

Characterization of the $C_{60}H_{36}$ Based on C Kα Spectra. C Kα fluorescence spectrum of hydrofullerene is given in Figure 4. To interpret the spectrum and to determine the molecular structure of $C_{60}H_{36}$, the theoretical X-ray spectra of isomers **1**−**3** were constructed with allowance for Cls levels energy shift in accordance with the theoretical X-ray photoelectron spectra (Figure 3).

The shape of X-ray emission spectrum of $C_{60}H_{36}$ depends essentially on the isomer structure. In the experimental spectrum of $C_{60}H_{36}$ three basic features labeled by letters A, B, and C may be distinguished. Maximum A corresponds to the X-ray transitions from MOs of π type. Hydrogenation of fullerene disrupts the π system of C_{60} molecule, and the distribution of π electron density in valence band of the $C_{60}H_{36}$ will depend on the manner in which its π system is organized. Two basic types of π system organization may be distinguished in considered isomers: the isolated double bonds and the double

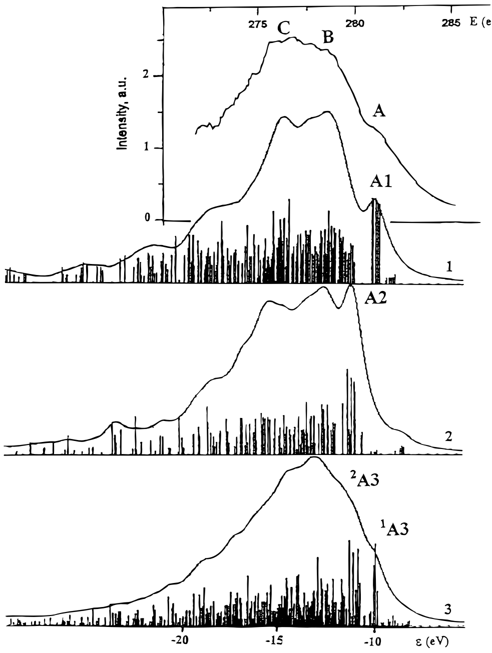

Figure 4. Experimental C Kα spectrum of hydrofullerene (top) and theoretical X-ray spectra for isomers **1**−**3** of $C_{60}H_{36}$.

bonds incorporating in aromatic hexagons. Depending on the type and relative position of different structural units of π system, the X-ray spectrum of $C_{60}H_{36}$ will considerably vary in the short-wave region.

The π system of isomer **1** is represented by π MOs of four aromatic hexagons. Weak energy splitting (0.2 eV) of the three upper occupied levels 12e, 34t, and 33t indicates that π systems of the hexagons almost do not interact with each other. Aromatic hexagons have two symmetrically inequivalent carbon atoms that differ little in charge value. As a result, maximum A1 in the theoretical spectrum located in energy region about −10 eV corresponds to the X-ray transitions from three upper π type levels of isomer **1**.

In isomer **2** all double bonds are isolated, and 12 π type levels occupy a narrow energy interval (0.4 eV). The symmetrically equivalence of atoms of the double bonds brings about the formation of intensive maximum A2 in X-ray spectrum of the isomer. Energy position of this maximum is shifted into long-wave region with respect to that of maximum A1 of isomer **1** and corresponds to −11 eV.

X-ray transition energies from π molecular orbitals of $C_{60}H_{36}$ isomers are determined by the type of structural units composing π system of an isomer. It can be assumed that in isomers involving isolated double bonds and aromatic hexagons total π system will manifest itself in theoretical X-ray spectrum as two maxima with energies −10 and −11 eV. The example of such a structure is isomer **3**; its π system involves the π systems of six isolated double bonds and two aromatic hexagons. The upper occupied π MOs of isomer **3** are formed by the AOs of these two structural units. Due to different charges on carbon atoms nonbonded with hydrogen atoms, X-ray transitions from π levels form two short-wave shoulders ^{1}A3 and ^{2}A3 corresponding by the energetic position to the A1 and A2 maxima of isomers **1** and **2**.

The specific feature of experimental spectrum of hydrofullerene $C_{60}H_{36}$ is well-marked short-wave maximum A. Its intensity and energy relative to maxima B and C may be used as a measure of correspondence between theoretical and experimental X-ray spectra. The comparison given in Figure 4 shows that the best agreement is observed for the isomer **1**.

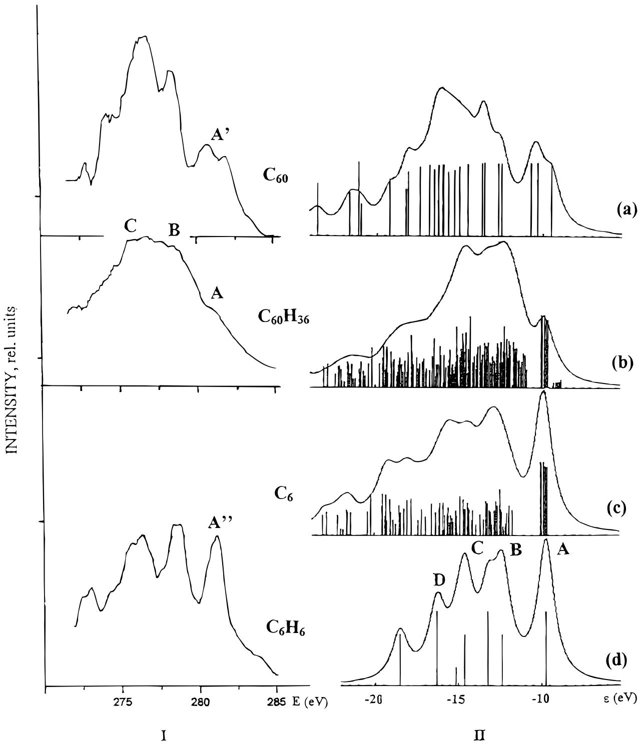

Figure 5. Experimental C Kα spectra (I) of (a) C_{60}, (b), hydrofullerene $C_{60}H_{36}$, and (d) benzene. Theoretical X-ray spectra (II) for (a) fullerene, (b) isomer **1** of $C_{60}H_{36}$, (c) carbon atoms, which are involved in the benzenoid fragments of isomer **1**, and (d) C_6H_6.

Peculiarities of $C_{60}H_{36}$ Electronic Structure. X-ray emission, X-ray photoelectron and quantum-chemical studies of hydrofullerene $C_{60}H_{36}$ have demonstrated that molecular structure of the synthesized compound corresponds to isomer **1** that belongs to the *T* point group. The short-wave maximum A in the experimental X-ray spectrum corresponds to the upper occupied π MOs of aromatic six-membered rings of the molecule. It can be assumed that these orbitals are similar to the highest occupied MO (HOMO) of benzene molecule. Comparing X-ray spectra of $C_{60}H_{36}$, benzene and fullerene (Figure 5) makes it possible to study experimentally the variation of their electronic structure.

A short-wave structure A′ in X-ray spectrum of fullerene C_{60} consists of two maxima and corresponds to the π type MOs of C_{60} molecule.[32] For $C_{60}H_{36}$ only one maximum A is observed in the same energy region. The energy position of this maximum corresponds to that of maximum A″ in the benzene spectrum which appears as the result of X-ray transitions from HOMO of the molecule. A relative integral intensity of maximum A in the $C_{60}H_{36}$ spectrum decreases noticeably as compared to that in benzene spectrum. This points to the presence of several benzenoid fragments in the structure of $C_{60}H_{36}$.

Comparison of the calculated electron density distribution in the valence band of C_{60} molecule, isomer **1** of $C_{60}H_{36}$ and C_6H_6 is given in Figure 5.II. Variations observed in theoretical spectra correspond to those in experimental ones. We constructed X-ray spectrum for carbon atoms constituting the aromatic six-membered rings of isomer **1** (Figure 5.II (c)). The basic features A, B, C, and D of benzene theoretical spectrum (Figure 5.II (d)) are also preserved in this simulated spectrum. Furthermore, the position of these maxima and their relative integral intensity remain almost unchanged. However, the spectrum constructed for carbon atoms of four benzenoid fragments is broadened as the result of the levels splitting which is caused by the local symmetry lowering of the aromatic hexagons in isomer **1**. The

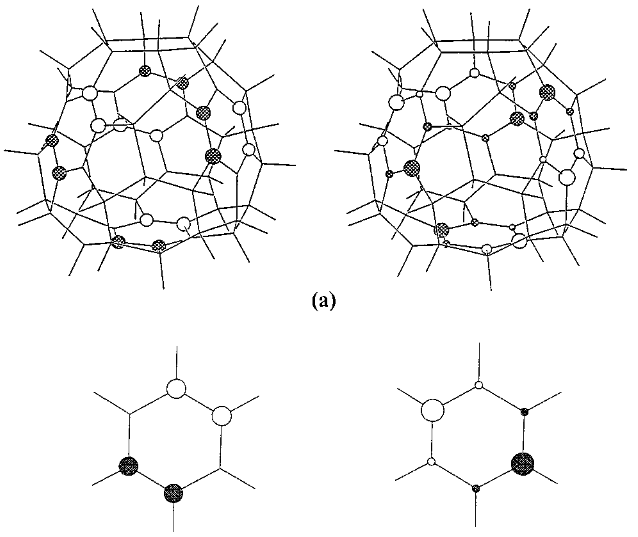

Figure 6. Schematic representation of double degenerated HOMO in (a) isomer **1** of $C_{60}H_{36}$ and in (b) benzene molecule.

greatest difference between the spectra is observed about maxima C and D, which is due to the change in the character of the σ system.

The HOMO structure of isomer **1** also favors the view that the π systems of hydrofullerene and benzene are similar. Both components of doubly degenerate orbital are shown for isomer **1** and benzene molecule (Figure 6). The size of the circle is proportional to the sum of the squares of coefficients with which 2p AOs of the corresponding atom participate in the construction of MO. The change in the circle color corresponds to the change in the wave function phase. As is seen from the figure, the electron density from the HOMO of isomer **1** is localized on non-hydrogenated carbon hexagons. Electron density distribution for the separate hexagon is analogous to that from HOMO e_{1g} of benzene molecule.

Conclusion

Combined X-ray emission, X-ray photoelectron, and quantum-chemical investigations of hydrofullerene $C_{60}H_{36}$ prepared from the transfer hydrogenation of C_{60} with 9,10-dihydroantracene show that the most probable structure of the molecule belongs to the T symmetry. Comparison of C Kα spectra of C_{60}, $C_{60}H_{36}$; and C_6H_6 demonstrates the similarity of hydrofullerene and benzene π systems. Localization of the HOMO electron density of $C_{60}H_{36}$ on non-hydrogenated hexagons suggests to the possibility of synthesizing η^6 complexes.

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