Simulation of molecular and electronic structure of polyhydrogenated (*n*,0)-tubulenes and their analogs intercalated with lithium

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Molecular and electronic structure of four polyhydrogenated (*n*,0)-tubulenes, namely, $[-C_{24}H_4-]_m$ (**1**), two isomers of composition $[-C_{28}H_4-]_m$ (**2** and **3**), and $[-C_{32}H_4-]_m$ (**4**) with *n* benzene rings in the cross section ($n = 6, 7, 7$, and 8, respectively), was simulated at $m \gg 1$ (*m* is the number of repeating fragments). It was assumed that hydrogen atoms are attached to all carbon atoms lying on the two most distant elements of the cylinders of the corresponding tubulenes. The energy band structures of macromolecules **1**—**4** and their Li-intercalated analogs $[-C_{24}H_4Li-]_m$ (**5**), $[-C_{28}H_4Li-]_m$ (two isomers, **6** and **7**), and $[-C_{32}H_4Li-]_m$ (**8**), containing one Li atom per repeating unit at each center, were obtained in the EHT approximation by the crystal orbital method. Geometric parameters of repeating units of structures **1**—**8** were found after MNDO/PM3 optimization of the energies of hydrocarbon molecules $C_{72}H_{24}$, $C_{84}H_{26}$ (two geometric isomers), and $C_{96}H_{28}$, containing three repeating units of corresponding tubulenes **1**—**4** each. The conductivity types of polyhydrogenated tubulenes **1**—**4** are the same as those of their precursors, (6,0)-, (7,0)-, and (8,0)-tubulenes. Dispersion curves of systems **5**—**8** are much the same as those of macromolecules **1**—**4**; however, electron energy spectra of **5**—**8** possess metallic conductivity type and the positions of Fermi levels for these systems are higher than for compounds **1**—**4**.

Key words: tubulenes (carbon nanotubes), polyhydrogenated tubulenes, polyhydrogenated tubulenes intercalated with Li, molecular mechanics method, quantum-chemical calculations, EHT approximation, crystal orbital method, MNDO/PM3 method.

The discovery of tubulenes (carbon nanotubes) is usually associated with the study[1] reported in 1991, though tubular forms of carbon were described as early as 1959 (see, *e.g.*, monograph[2] and references cited therein). According to modern classification, tubulenes are divided into single-layered and multilayered ones. Ideal single-layered nanotubes are translationally invariant, have a cylindrical shape (Fig. 1), and depending on the arrangement of hexagons with respect to the axis of the cylinder, are characterized by two indices (*n*,*m*), where *n* and *m* are nonnegative integers. If $m = 0$, the *n* value is equal to the order of the principal symmetry axis of a tubulene and coincides with the number of hexagons in its elementary fragment (EF). For instance, at $n = 6$ the corresponding (6,0)-tubulene is built of hexagons, each having two sides parallel to the sixth-fold symmetry axis (see Fig. 1, *a*). (*n*,*n*)-Tubulenes, built of hexagons each having two sides perpendicular to the symmetry axis of the cylinder, correspond to the case $m = n$. At $0 < m < n$, hexagons are helically arranged on the lateral surface of the cylinder.

Carbon nanotubes and, especially, composites based on fullerenes and nanotubulenes have attracted the attention of researchers because of their unusual electronic and mechanical properties.[3] Depending on the *m* value, carbon nanotubes can possess properties of either metals or semiconductors with narrow or wide band gaps.[4] Strong diamagnetism of tubulenes was reported.[5] Recently,[6] preparation of specimens characterized by substantially increased hardness using high-temperature and -pressure treatment of a mixture of single-layered carbon nanotubes and fullerenes was reported. Properties of tubulenes were described in more detail in several reviews.[4,7—9]

As is known,[10] under specific conditions the molecules of fullerene C_{60} undergo dimerization and even polymerization. In these cases, fullerene fragments are, as a rule, linked by four-membered cycles. This is usually interpreted as a result of [2+2]-cycloaddition reaction. Analogous processes can also occur in the case of (*n*,*m*)-tubulenes. In (*n*,0)-tubulenes, one third of the C—C bonds is on elements of the lateral surface of the

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cylinder, which makes possible joining of two and more tubulenes involving carbon atoms of all such bonds. In principle, such a procedure makes it possible to use (*n*,0)-tubulenes for preparation of quasi-1D supertubulenes, quasi-2D (layered), or three-dimensional covalently bonded structures (*e.g.*, of zeolite type[11]) with increased hardness and unusual electronic properties. Naturally, the formation of covalent bonds between an (*n*,0)-tubulene and the atoms lying on the elements of lateral surfaces of other (*n*,0)-tubulenes causes changes

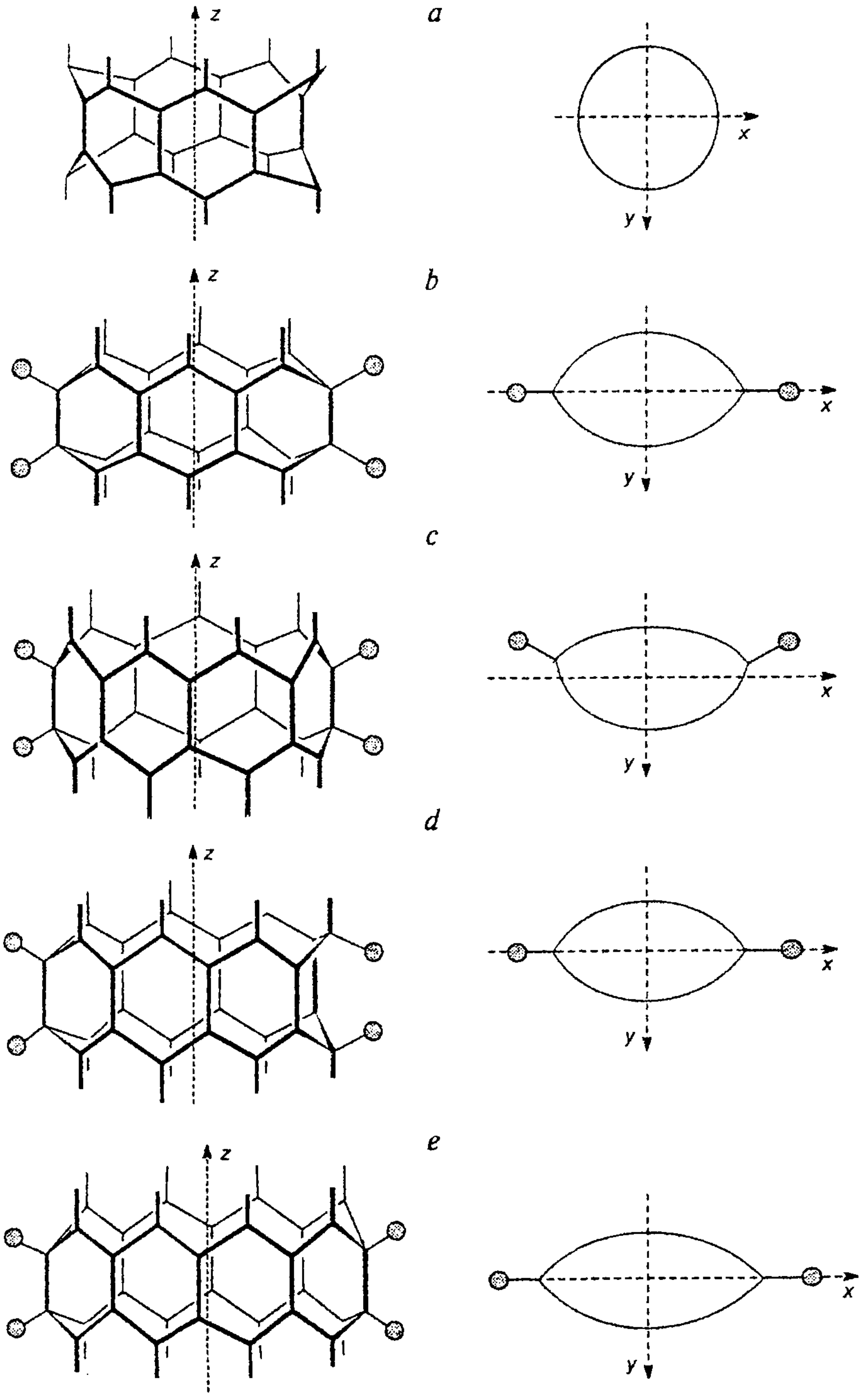
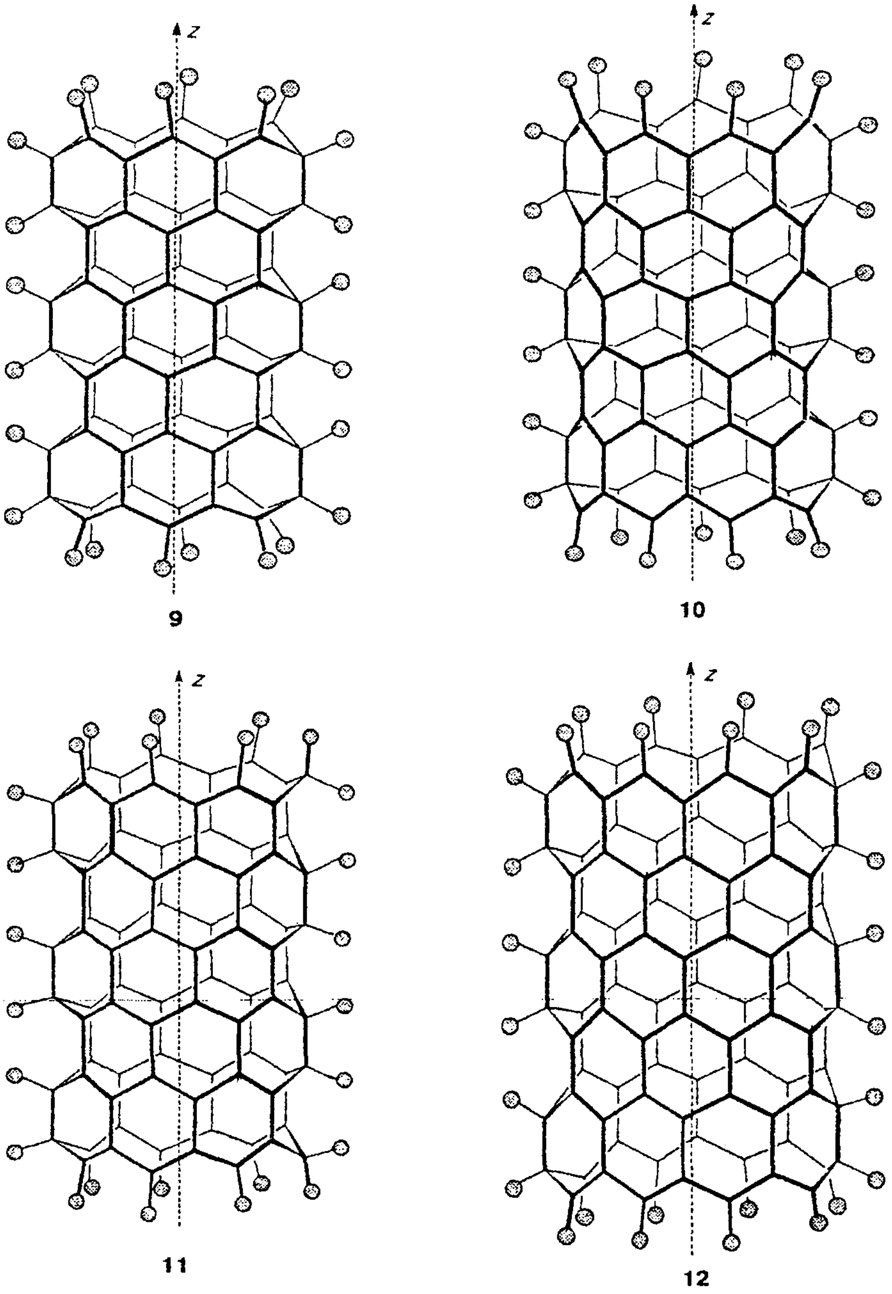


Fig. 1. Elementary fragments and schematic view of projections of (6,0)-tubulene (*a*) and polyhydrogenated tubulenes **1**—**4** (*b*—*e*, respectively) on the (x,y) plane. Hereafter hydrogen atoms are shown by shaded circles.

in the molecular and electronic structure of the former. This can lead to changes in physicochemical properties of such systems as compared to isolated (n,0)-tubulenes (see Refs. 4, 12—19).

The aim of this work is to study the effect of covalent bonding between (n,0)-tubulenes on their geometry and electronic structure. To solve this problem, we first consider isolated (n,0)-tubulenes with n values from 6 to 8. Then, hydrogen atoms are attached to all carbon atoms lying on the two most distant elements of the lateral surfaces. Such polyhydrogenated (n,0)-tubulenes are described by the general formula $[-C_{4n}H_4-]_m$ ($m \gg 1$) and can be considered as model tubulenes cut from a quasi-2D layer of (n,0)-tubulenes linked by covalent bonds between carbon atoms lying on corresponding elements of lateral surfaces of adjacent (n,0)-tubulenes; in this case, "free" valences are saturated with hydrogen atoms.

We studied four polyhydrogenated (n,0)-tubulenes, namely, $[-C_{24}H_4-]_m$ (**1**), $[-C_{28}H_4-]_m$ (two isomers, **2** and **3**), and $[-C_{32}H_4-]_m$ (**4**) with n = 6, 7, 7, and 8, respectively. The structures of EFs of systems **1**—**4** are



9

10

11

12

Fig. 2. Structures of hydrocarbon molecules **9**—**12**.

shown in Fig. 1, *b—e*. In addition, we studied four polyhydrogenated tubulenes intercalated with lithium, namely, $[-C_{24}H_4Li-]_m$ (**5**), $[-C_{28}H_4Li-]_m$ (two isomers, **6** and **7**), and $[-C_{32}H_4Li-]_m$ (**8**). These macromolecules are obtained from tubulene molecules **1—4** by placing one lithium atom at the center of each EF. Small lithium atoms occupy a small space inside macromolecules **1—4**, so the geometric parameters of the latter remain virtually unchanged.

Calculation procedure

To simulate the EF structures of polyhydrogenated (*n*,0)-tubulenes, we calculated cylindrical hydrocarbon molecules $C_{72}H_{24}$ (**9**), $C_{84}H_{26}$ (two isomers, **10** and **11**), and $C_{96}H_{28}$ (**12**) (Fig. 2). Carbon cages of these molecules comprise three EF of the corresponding polyhydrogenated tubulenes, with hydrogen atoms attached to the terminal carbon atoms. Systems **9—12**, respectively, have D_{2h}, C_{2v} (C_2 axis coincides with the *y* axis), C_{2v} (C_2 axis coincides with the *x* axis), and D_{2h} symmetry. Atomic coordinates obtained by the molecular mechanics (MM) method were used as an initial approximation when optimizing the geometries of molecules **9—12**, which then were refined by the MNDO/PM3 method with retention of the symmetry using the GAMESS program package[20] on a DEC 3000 Alpha-AXP 400X workstation. Electron energy spectra of tubulenes were obtained in the EHT approximation[21] by the crystal orbital method using the LATTIC program.[22]

Results and Discussion

Molecular and electronic structure of model molecules 9—12 (see Fig. 2). For all systems **9—12**, MNDO/PM3 calculations revealed local minima on the potential energy surfaces (PES). It was established that molecules **9—12** have closed electron shells, positive heats of formation (ΔH_f), and energy differences between the LUMO and HOMO exceeding 4.5 eV (Table 1). Charges on all atoms are virtually equal to zero. All these data indicate the possibility for such unusual (cylindrical) hydrocarbon molecules and corresponding tubulenes **1—4** to exist. We will point out that the energy of isomer **10** is 31.6 kcal mol^{-1} higher than that of isomer **11**.

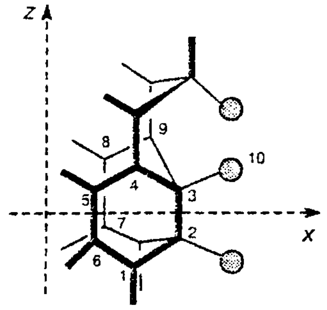


Fig. 3. Fragment of repeating units of tubulenes **1—4** and the numbering of atoms necessary for discussing the geometric parameters of systems **9—12**.

Selected geometric parameters of molecules **9—12** are listed in Table 1 and the numbering of atoms is shown in Fig. 3. The l_x and l_y values characterize deviation of the tubulene shape from a circular cylinder. In Fig. 1, *b—e* the direction of the *y* axis is such that the diameter of tubulene, drawn along this direction in the (*x*,*y*) cross section, is the smallest. From these schemes it can be seen that, unlike hydrogenated (*n*,0)-tubulenes, molecules **9—12** can be represented as cylinders for which the cross sections in the (*x*,*y*) plane are extended along the *x* axis. This is explained by the fact that the energies of angular deformations for sp^3-AOs are lower than for sp^2-AOs. As should be expected, cross-sectional dimensions of tubulenes increase as the number of benzene rings *n* in the EF increases. The parameter l_x increases much faster than l_y. Because of this, at sufficiently large *n* values the polyhydrogenated tubulene becomes similar to two extended fragments of graphitic sheets linked along the edges by sp^3-hybridized carbon atoms with attached hydrogen atoms. The length of the translation vector determining the translation period (Tr_z) is virtually independent of tubulene diameter.

It should be noted that linear dimensions of terminal fragments of systems **9—12** become somewhat increased because of the repulsion between attached hydrogen atoms. This leads to slight distortions of the structure of the central fragment; therefore averaged geometric parameters are listed in Table 1. However, the deviations of bond lengths from average values do not exceed ±0.02 Å. This makes it possible to use the obtained

Table 1. Geometric and energy characteristics of $C_{72}H_{24}$ (**9**), $C_{84}H_{26}$ (two isomers, **10** and **11**), and $C_{96}H_{28}$ (**12**) molecules calculated by the MNDO/PM3 method

Molecule	l_x	l_y	Tr_z	$l_{2,3}$	$l_{1,2}$	$\alpha_{2,3,4}$	$\alpha_{4,3,9}$	$\theta_{6,2,3,8}$	ΔH_f	δE
9	6.01	4.10	4.29	1.527	1.526	115.1	98.1	89.3	734.6	4.56
10	6.84	4.56	4.29	1.515	1.524	115.9	100.4	93.7	628.8	5.90
11	7.01	4.58	4.29	1.523	1.519	115.5	99.7	94.1	597.2	5.93
12	8.24	4.89	4.29	1.511	1.522	115.5	100.1	93.4	625.1	5.97

Note: l_x/Å and l_y/Å are linear dimensions of the cross sections of central fragments along the *x* and *y* coordinate axes, respectively; Tr_z/Å is the length of the vector of EF translation along the *z* axis; $l_{2,3}$/Å and $l_{1,2}$/Å are the bond lengths; $\alpha_{2,3,4}$/deg and $\alpha_{4,3,9}$/deg are the bond angles; $\theta_{6,2,3,8}$/deg is the torsion angle; ΔH_f/kcal mol^{-1} is the heat of formation; δE/eV = $E_{LUMO} - E_{HOMO}$ is the band gap (the numbering of atoms is given in Fig. 3).

Table 2. Energy characteristics (E/eV) of hydrogenated tubulenes **1**—**8** calculated in the EHT approximation by the crystal orbital method

Tubulene	$-E_{\text{aver}}$	δE	$-E_F$ (E'_F)
1 (**5**)	1765.49 (1787.25)	0.0 (0.0)	10.52 (10.18)
2 (**6**)	2051.74 (2065.88)	0.50 (0.0)	10.67 (10.04)
3 (**7**)	2053.05 (2065.69)	0.76 (0.0)	10.87 (9.38)
4 (**8**)	2334.82 (2349.75)	0.31 (0.0)	10.61 (10.23)

Note: E_{aver} is the energy per elementary fragment of tubulene; $\delta E = E_{\text{LUMO}} - E_{\text{HOMO}}$ is the band gap; E_F is the position of the Fermi level for systems **1**—**4**; E'_F is the position of the Fermi level for Li-intercalated systems **5**—**8** (data for systems **5**—**8** are given in parentheses).

coordinates of the atoms of central units of molecules **9**—**12** in calculations of the band structure of electron energy spectra for infinite hydrogenated tubulenes **1**—**8**.

Electron energy spectra of tubulenes 1—8. The energy band structures for macromolecules **1**—**8** are shown in Fig. 4 and the results of calculations are listed in Table 2. From these data it follows that the conductivity type of polyhydrogenated tubulenes does not qualitatively differ from that of their carbon precursors, (n,0)-tubulenes (n = 6—8). For instance, as in the case of (6,0)-tubulene, the band gap (δE) for system **1** is equal to zero (see Fig. 4, *a*, *b*). The energy band structures for systems **2**—**4** are analogous to those of (7,0)- and (8,0)-tubulenes and are characterized by nonzero band gaps (*cf.* with 1.0 and 0.84 eV for (7,0)- and (8,0)-tubulenes, respectively[18]). Thus, at a qualitative level, the patterns of changes in δE values for structures **1**—**4** and (6,0)—(8,0)-tubulenes are identical. Because of this, tubulenes **2**—**4**, as well as (7,0)- and (8,0)-tubulenes, belong to the semiconducting type. However, the electron energy spectrum of hydrogenated tubulene **1** has a metallic type, whereas that of (6,0)-tubulene has a semimetallic type. This can be seen in Fig. 4, *a* in which the spectrum of (6,0)-tubulene is shown for comparison. This spectrum was obtained using the same procedure as that used for calculating the spectra of polyhydrogenated systems. From the data in Table 2 it follows that isomer **3** is more stable than **2** (the energy difference between these isomers is 1.31 eV). This conclusion is in agreement with the results of MNDO/PM3 calculations of hydrocarbon molecules **10** and **11**, which indicate that molecule **11** is 31.6 kcal mol^{-1} more stable than its isomer **10**.

It was also found that the patterns of dispersion curves for systems **1**—**4** and corresponding Li-intercalated tubulenes **5**—**8** are virtually identical. Only positions of the Fermi levels (E_F and E'_F) change in the spectra of tubulenes **5**—**8** (see Table 2 and Fig. 4, *b*—*e*), which is due to the presence of extra electrons supplied by Li atoms. As a result, the electron energy spectra of polyhydrogenated tubulenes **5**—**8** intercalated with Li acquire a metallic type as in the case of K- and Li-intercalated carbon (6,0)-tubulenes[15] (see also Ref. 28).

The above-mentioned similarity of the electron energy spectra of (n,0)-tubulenes and their hydrogenated analogs is determined in each case by different reasons. In this connection it will be recalled that the type of spectra of (n,0)-tubulenes changes with a periodicity of 3 as n increases[4] and that only for $n = 3k$ (k is an integer) does the spectrum has a metallic type. All carbon atoms of (n,0)-tubulenes are nearly sp^2-hybridized; therefore they have a common conjugated π-electron system. However, the presence of two groups of sp^3-hybridized carbon atoms in polyhydrogenated tubulenes **1**—**4** leads to the formation of two quasi-independent conjugated π-electron systems localized on the oppositely lying (most flattened) areas of the surfaces of corresponding oval cylinders. Each of the two conjugated systems of tubulenes **1**, **2**, and **4** is topologically equivalent to a conjugated system of one of the macromolecules belonging to the family of planar poly(*peri*-acenes) (PPA,

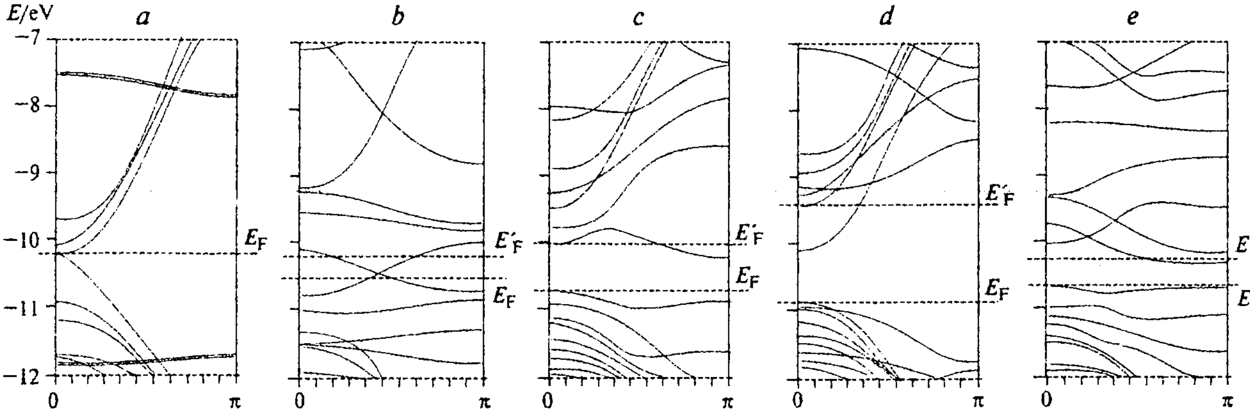


Fig. 4. Dispersion curves for (6,0)-tubulene (*a*) and polyhydrogenated tubulenes **1**, **5** (*b*); **2**, **6** (*c*); **3**, **7** (*d*); and **4**, **8** (*e*); E_F and E'_F are the Fermi levels for polyhydrogenated tubulene and its analog intercalated with Li atoms, respectively.

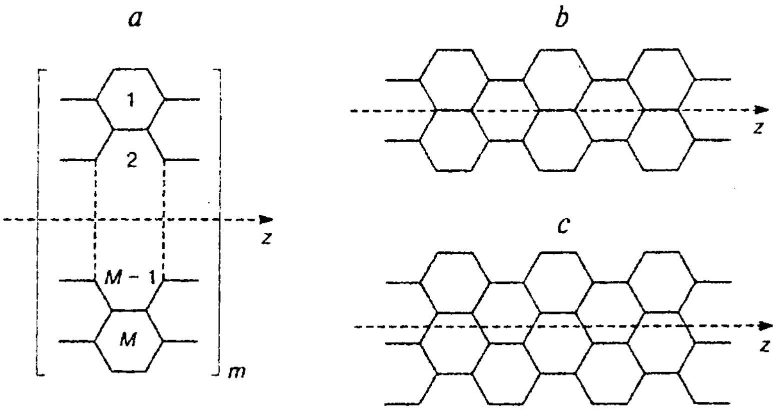


Fig. 5. General view of elementary fragment of a PPA macromolecule consisting of *M* six-membered cycles (*a*), where *m* is an integer, $m \gg 1$; a model PPA structure of type 2, corresponding to $k = 0$ and $M = 2$ (*b*); a model PPh structure (*c*).

Fig. 5, *a*, *b*). Each conjugated subsystem of tubulene **3** corresponds to a conjugated system of the polyphenanthrene (PPh) macromolecule (Fig. 5, *c*). The PPA and PPh macromolecules differ in symmetry with respect to the *z* axis. It should be noted that their electric and optical properties are of considerable practical interest and are the subject of wide speculation (see Refs. 23—27 and references cited therein). Thus, tubulenes **1**—**4** contain two quasi-independent conjugated π-electron systems of PPA or PPh macromolecules each, which determine their conducting properties.

The results of quantum-chemical investigations of the electronic structure of PPA and PPh at different numbers of benzene rings (*M*) in the repeating units were reported (see Ref. 25 and references cited therein). In particular, analytical expressions for π-electron dispersion curves of PPA macromolecules were obtained[25] in the EHT approximation and it was shown that, in the topological approximation, electronic properties of PPA depend on the number of six-membered cycles *M* in EF and that they are changed with a periodicity of 3 as in the case of (*n*,0)-tubulenes. Taking into account this fact, PPA molecules are divided into three groups with (1) $M = 3k + 1$; (2) $M = 3k + 2$; and (3) $M = 3k + 3$ ($k = 0, 1, 2, \ldots$). Spectra of PPA molecules belonging to groups 1 and 3 are characterized by nonzero band gaps separating the valence and conducting bands. Only systems belonging to group 2 have zero-width band gaps.

It is noteworthy that these regularities are also valid for hydrocarbon tubulenes **1**, **2**, and **4** even in EHT calculations with consideration of their metric properties. For instance, tubulene **1** with two conjugated subsystems of type 2 (see Fig. 5, *b*) has a zero-width band gap. One of the conjugated π-electron subsystems of tubulene **2** belongs to type 2, whereas the other one belongs to type 3 and it is the latter that determines the presence of nonzero band gap. Tubulene **4** also has a nonzero band gap, since both its conjugated subsystems belong to type 3.

As was mentioned above, the conjugated π-electron systems of hydrogenated (7,0)-tubulene **3** are topologically equivalent to two identical conjugated systems of PPh, whose energy band structure was studied recently.[26,27] Analytical expressions for π-electron dispersion curves of PPh were obtained in the EHT approximation and the existence of nonzero band gaps in their π-electron energy spectra was established.[26] Calculations of tubulene **3** performed in the framework of EHT approximation also confirm the existence of nonzero band gaps in the spectra of these systems.

From the aforesaid it follows that the conductivity type of polyhydrogenated tubulenes **1**—**4** can be fairly well described already in the π-electron approximation.

Thus, similarity of basic characteristics of electron energy spectra of (*n*,0)-tubulenes and their polyhydrogenated analogs is revealed already when performing calculations in the topological approximation. Unlike initial carbon (*n*,0)-nanotubes with circular cross sections, polyhydrogenated (*n*,0)-tubulenes, in which hydrogen atoms are attached to carbon atoms lying on the two most distant elements of the cylindrical surface of tubulene, have oval cross sections. At the same time, this fact, as well as the presence of two essentially independent conjugated π-electron systems does not lead to significant changes in the electronic properties of polyhydrogenated (*n*,0)-nanotubes as compared to initial tubulenes.

In addition, our EHT calculations by the crystal orbital method showed that (1) like (7,0)- and (8,0)-tubulenes, polyhydrogenated tubulenes $[-C_{28}H_4-]_m$ (two isomers) and $[-C_{32}H_4-]_m$ belong to the semiconducting type and (2) the electron energy spectrum of polyhydrogenated tubulene $[-C_{24}H_4-]_m$ has a metallic type, whereas that of (6,0)-tubulene has a semimetallic type. Spectra of Li-intercalated analogs of polyhydrogenated tubulenes, $[-C_{24}H_4Li-]_m$, $[-C_{28}H_4Li-]_m$ (two isomers), and $[-C_{32}H_4Li-]_m$ have a metallic type.

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