Molecular and electronic structure of several heterofullerene BNC_{58} and $B_2N_2C_{56}$ oligomers and $[B_2N_2C_{56}]_n$ macromolecule

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Molecular and electronic structure of heterofullerene BNC_{58} (C_s) and $B_2N_2C_{56}$ (C_{2h}) monomers, $B_2N_2C_{116}$ and $B_4N_4C_{112}$ dimers, and $B_6N_6C_{168}$ trimer (the last three molecules with C_{2h} symmetry) was simulated by the MNDO method. Clusters BNC_{58} and $B_2N_2C_{56}$ are formed by replacement of carbon atoms participating in one or two of the most distant oppositely lying (6,6)-type C—C bonds in fullerene C_{60} by B and N atoms. In one of the two studied isomers of the $B_2N_2C_{116}$ dimer, the monomers are linked by the four-membered carbon cycle, while the heteroatoms form the most distant oppositely lying bonds of the dimer. In the other isomer of the $B_2N_2C_{116}$ dimer, as well as in the $B_4N_4C_{112}$ dimer and $B_6N_6C_{168}$ trimer, the monomers are linked by four-membered B_2N_2 cycles with alternation of the atoms. For all the systems studied, the optimum geometric parameters, heats of formation, ionization potentials, and atomic charges were calculated. Dimerization energies of heterofullerenes BNC_{58} and $B_2N_2C_{56}$ lie in the range from 33 to 49 kcal mol^{-1}. It was found that the $B_2N_2C_{116}$ dimer, in which the monomers are linked by the four-membered carbon cycle, is the most stable system. In the case of $B_2N_2C_{56}$ trimerization, the energy gain (compared to the triple monomer energy) is about twice as large as the dimerization energy. Molecular structure of the quasi-linear $[B_2N_2C_{56}]_n$ macromolecule was simulated, and extended Hückel calculations of its energy band structure by the crystal orbital method were performed. It was found that the electron energy spectrum is of semiconducting type (the band gap is equal to 1.27 eV).

Key words: fullerenes, heterofullerenes, dimers, trimers; quantum-chemical calculations, MNDO method.

Fullerene-like structures in which a portion of C atoms is replaced by atoms of other elements are usually considered as heterofullerenes. The possibility for such systems to exist was first theoretically substantiated taking a B_2C_{18} dodecahedral cluster as an example.[1,2]

First experimental data which confirmed the existence of heterofullerenes were obtained in the early 1990's taking BC_{59} and NC_{59} clusters as an example.[3–5] Recently, syntheses of stable $(NC_{59})_2$ dimers[6] and NC_{59} crystals doped with potassium[7] were reported. Heterofullerenes $B_nN_mC_{60-n+m}$ obtained by carbon arc-discharge technique using electrodes coated with boron nitride particles were characterized by ESR, IR, and Raman spectroscopy.[8]

According to theoretical studies,[9–12] fullerene-like structures of the $B_nN_mC_{60-n-m}$ type containing no N—N or B—B bonds must exhibit a pronouncedly high stability.

The problem of stability of polyhedral boron nitrides $[BN]_k$ built of four- and six-membered cycles is also discussed. In these systems, the only neighbors of boron atoms are N atoms and *v.v.*, which should lead to stabilization of this type of heterofullerenes. These qualitative conclusions were confirmed by the results of quantum-chemical calculations of fullerene-like $B_{12+3n}N_{12+3n}$ systems.[13–15]

The syntheses of BN- and BNC-tubes (tubular forms of boron nitride and boron carbonitride) were reported[16,17] and electronic structure of these systems built of only six-membered cycles was studied.[18–20] It was shown that, depending on the composition and type of the atomic arrangement, BNC-tubes can possess either metallic or dielectric properties.

Along with tubular forms of boron carbonitride, oligomeric or polymeric systems formed by linked heterofullerenes can also exist, which can be illustrated taking a $(C_{59}N)_2$ dimer as an example. Electronic structure of this cluster and heterofullerenes NC_{59} and NHC_{59} has been discussed.[21]

Replacement of carbon atoms in carbofullerenes or their oligomers by B and N heteroatoms can lead to the

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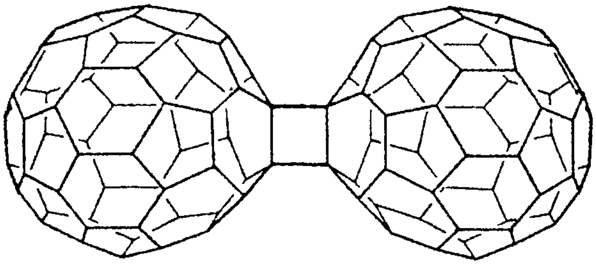
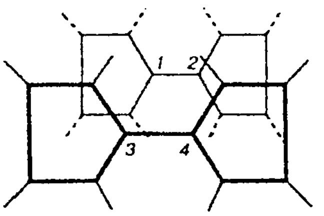


Fig. 1. Cluster C_{120}, a dimer of fullerene C_{60}.

appearance of unusual properties of the compounds formed. In this connection it is of interest to study properties of the simplest heterofullerenes and their oligomers with donor-acceptor B—N bonds and to compare them with the properties of carbon analogs. To this end, we simulated molecular and electronic structure of oligomers of clusters BNC_{58} and $B_2N_2C_{56}$ and performed analogous calculations for a quasi-linear macromolecule $[B_2N_2C_{56}]_n$ ($n = \infty$).

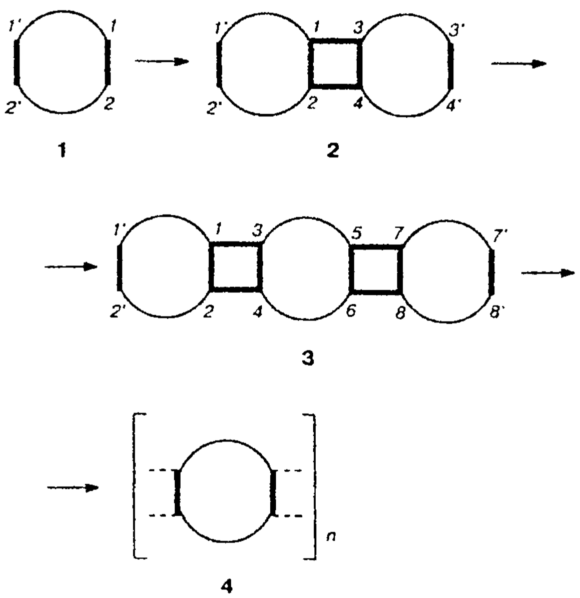
The structure of oligomers considered below can be illustrated by Scheme 1, in which the fragments of two C_{60} monomers participating in the formation of bonds between the molecules are shown.

Scheme 1



Replacement of two sp^2-hybridized carbon atoms (*1* and *2*) of one C_{60} molecule, arranged at the vertices of neighboring five-membered cycles, and two corresponding carbon atoms (*3* and *4*) of the other C_{60} molecule by sp^3-hybridized atoms can lead to the formation of new bonds, *1*—*3* and *2*—*4*, between these two clusters. In this case a C_{120} dimer is formed in which the monomers are linked by the four-membered carbon cycle (Fig. 1). The process of successive addition of monomers resulting in the formation of an infinite quasi-linear macromolecule is illustrated by Scheme 2, in which the bonds participating in the oligomerization reaction are shown by bold lines.

Scheme 2



Cluster **1** corresponds to fullerene C_{60}, cluster **2** corresponds to the C_{120} dimer (see Fig. 1), cluster **3** corresponds to the C_{180} trimer (Fig. 2), and cluster **4** corresponds to a $[C_{60}]_n$ macromolecule. In these systems, all numbered atoms lie in the picture plane coinciding with the symmetry plane. Oligomers **2** and **3** have a D_{2h} symmetry. Earlier,[26–28] molecular and electronic structure of clusters **2** and **3** has been studied in detail by the AM1 and MNDO/PM3 methods.

In this work, we simulated molecular and electronic structure of heteroatomic clusters BNC_{58} (**5**), $B_2N_2C_{56}$ (**6**), two $B_2N_2C_{116}$ isomers (**7**, **8**), $B_4N_4C_{112}$ (**9**),

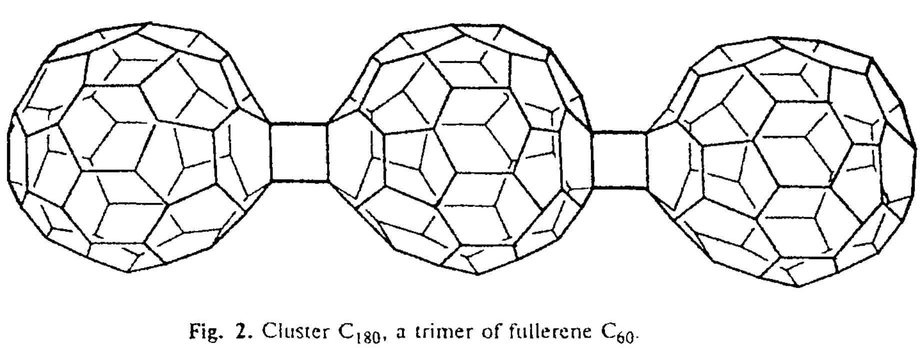
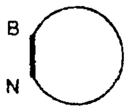


Fig. 2. Cluster C_{180}, a trimer of fullerene C_{60}.

$B_6N_6C_{168}$ (**10**), and of a quasi-linear $[B_2N_2C_{56}]_n$ macromolecule (**11**).



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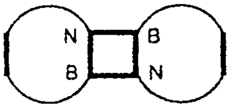

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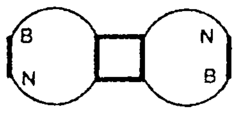

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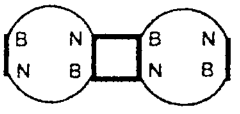

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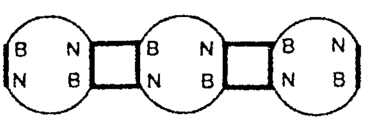

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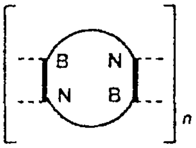

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Clusters **5** and **6** are formed by respective replacement of the atoms forming one or two most distant oppositely lying (6,6)-type C—C bonds in the fullerene molecule **1** by B and N atoms. In dimer **8**, the monomers are linked by the four-membered carbon cycle. In systems **7** and **9**—**10**, the monomers **5** or **6** are linked by the four-membered B_2N_2 cycles with alternation of the atoms. Clusters **7**—**10** have C_{2h} symmetry.

Calculation procedure

Electronic structure and geometric parameters of the above monomers, oligomers, and corresponding carbon systems were calculated by the MNDO method[22] with geometry optimization using the GAMESS program package.[23] The geometry obtained by the method of molecular mechanics using the ALCHEMY program was used as initial approximation. The energy band structure of the $[B_2N_2C_{56}]_n$ macromolecule and corresponding $[C_{60}]_n$ carbon system was obtained from extended Hückel calculations[24] by the crystal orbital method using the LATTIC program.[25] MNDO and extended Hückel calculations were carried out on a DEC 3000 Alpha-AXP 400X workstation.

Results and Discussion

According to our MNDO calculations, there are local minima on the potential energy surfaces of clusters **1**—**3** and **5**—**10**. All these systems have closed electron shells, fairly high ionization potentials (~9 eV), and band gaps ($\delta E = E_{HOMO} - E_{LUMO}$) exceeding 6 eV (Table 1), which is indicative of their stability.

From the data in Table 1 it follows that the heats of formation (ΔH_f) of clusters **1**—**3** and **5**—**10** are positive. The heats of formation of dimers **7** and **8** are less than the double heat of formation of monomer **5**, while corresponding dimerization energies are equal to 33.8 and 49.1 kcal mol^{-1}, respectively. It should be noted that the molecule **8**, in which B—N bonds are the most distant oppositely lying (6,6)-type bonds, is more stable than its isomer **7**, in which they form the central four-membered cycle.

Table 1. Energy characteristics of clusters **1**—**3** and **5**—**10** calculated by the MNDO method: heats of formation (ΔH_f/kcal mol^{-1}); dimerization or trimerization energies (ΔE/kcal mol^{-1}); and δE/eV = $E_{LUMO} - E_{HOMO}$

Cluster	Symmetry	ΔH_f	ΔE	$-E_{HOMO}$	HOMO symmetry	δE
C_{60} (**1**)	I_h	869.3	—	9.13	h_u	6.57
C_{120} (**2**)	D_{2h}	1689.5	49.1	8.97	b_{2u}	6.37
C_{180} (**3**)	D_{2h}	2509.8	98.1	8.92	b_u	6.28
BNC_{58} (**5**)	C_s	834.4	—	9.01	—	6.40
$B_2N_2C_{56}$ (**6**)	C_{2h}	799.3	—	8.90	—	6.23
$B_2N_2C_{116}$ (**7**)	C_{2h}	1635.0	33.8	8.97	b_u	6.34
$B_2N_2C_{116}$ (**8**)	C_{2h}	1619.7	49.1	8.92	b_u	6.26
$B_4N_4C_{112}$ (**9**)	C_{2h}	1565.0	33.6	8.92	b_u*	6.26
$B_6N_6C_{168}$ (**10**)	C_{2h}	2330.5	67.4	8.92	b_u**	6.25

* Doubly degenerate level (random degeneration).

** Triply degenerate level (random degeneration).

The heats of formation of dimer **9** and trimer **10** are less than the double and triple heats of formation of cluster **6**, respectively. Thus, an energy gain is obtained upon the formation of compounds **9** and **10**; in this case the dimerization and trimerization energy is equal to 33.6 and 67.4 kcal mol^{-1}, respectively. Trimerization energies of clusters **1** and **6** are about twice as large as the corresponding dimerization energies of the systems (see Table 1). This conclusion is analogous to that obtained recently for fullerene C_{60} dimers and trimers by the MNDO/PM3 method.[26] On the whole, replacement of C atoms in the C_{60} molecule and its dimer by B and N atoms leads to systems with lower heats of formation.

In all clusters **5**—**10**, the charges on carbon atoms (q_C) and those on sp^3-hybridized inner heteroatoms (q_B and q_N) are small: $q_C < 0.01$ au, $q_N = 0.01$ au, and $q_B = 0.04$ au. The charges on sp^2-hybridized outer heteroatoms are $q_N = -0.15$ au and $q_B = 0.05$ au. In the latter case, partial charge transfer occurs from neighboring C atoms ($q_C = 0.11$ au) to N atoms.

Linear dimensions (the longest distances between C atoms along the *z* axis coinciding with the longitudinal axis of the cluster and along the *x* and *y* axes perpendicular to the *z* axis) of clusters **2**, **3**, and **7**—**10** are listed in Table 2. It was assumed that the *x* axis corresponds to the smallest diameter of the cluster in the (*x*,*y*) cross section; in the dimers and trimers, the (*x*,*y*) cross sections were passed through the center of one of the monomers and through the center of the inner fragment, respectively. From the data in Table 2 it can be seen that replacement of pairs of carbon atoms by boron-nitrogen pairs leads to some increase in *z*-dimensions of

Table 2. Linear dimensions (l_x, l_y, l_z/Å) of clusters **2**, **3**, and **7**—**10** along the x, y, and z coordinate axes; bond lengths (r_1, r_2/Å) in the four-membered cycles linking two monomers (bonds of length r_2 are formed by atoms of neighboring monomers)

Cluster	l_x	l_y	l_z	r_1	r_2
2	6.98	7.03	16.25	1.56	1.62
3	6.96	7.05	25.47	1.56	1.62
7	6.99	7.04	16.29	1.59	1.66
8	6.99	7.04	16.38	1.56	1.62
9	6.99	7.04	16.43	1.59	1.66
10	6.95	7.06	25.69	1.59	1.66

both dimers and trimers, whereas their cross-sectional dimensions remain virtually unchanged.

Our calculations showed alternation of bond lengths in the four-membered cycles of clusters **2** and **3** (see Table 2). In each of the cycles, there are two bonds of length r_1 linking the monomers and two bonds of length r_2 pertaining to monomers. The lengths of these bonds are close to those of analogous bonds calculated earlier using other quantum-chemical methods, *viz.*, 1.546 and 1.603 Å (AM1)[27] and 1.549 and 1.598 Å (MNDO/PM3).[26] Appreciable lengthening of two bonds of length r_2 in each of the two four-membered cycles as compared to conventional ordinary bonds indicates that these fragments are strained. MNDO calculations of molecules **7**—**10** showed that the introduction of B and N heteroatoms into clusters **2** and **3** has virtually no effect on the bond lengths in the four-membered cycles linking the monomers.

The molecules of fullerene **1** and its hetero-analogs **5** and **6** are rather large; for this reason, each additional unit has virtually no effect on the structure of the central fragment. Therefore, structure simulation of repeating fragments of infinite quasi-linear systems **4** and **11** and estimates of lengths of corresponding translation vectors were performed using the geometric parameters of inner units of trimers **3** and **10**, respectively.

The results of calculations of the energy band structure for macromolecules **4** and **11** are shown in Fig. 3. For system **4**, the top of the valence band is at −11.14 eV (see Fig. 3, *a*). In the forbidden band, there is a level with an energy of −9.93 eV whose position is independent of the wave vector. The corresponding crystal orbital is composed of non-interacting MOs of the monomers. The bottom of the conduction band is at −9.83 eV. Therefore, the band gap for compound **4** is equal to 1.31 eV.

From Fig. 3, *b* it follows that the position of the top of the valence band for macromolecule **11** (at −11.21 eV) is lower than for system **4**. There is a narrow subband of width ~0.05 eV near the top of the valence band and a narrow subband of width ~0.07 eV near the bottom of the conduction band. The position of the latter corresponds to a local energy level in the spectrum of macromolecule **4**. Compound **11** has a band gap of 1.27 eV, which is somewhat smaller than for **4**. The small widths of the subbands near the bottom of the conduction band ($\delta E_c \approx 0.07$eV) and near the top of the valence band ($\delta E_v \approx 0.05$ eV) in the spectrum of macromolecule **11** indicate that in this case the effective masses of holes and electrons are larger than in the case of macromolecule **4**, which is characterized by $\delta E_c \approx 0.29$ eV and $\delta E_v \approx 0.18$ eV (see Fig. 3, *a*, *b*). For this reason, one should expect that systems **4** and **11** will possess strongly different photo- and electroconductivity.

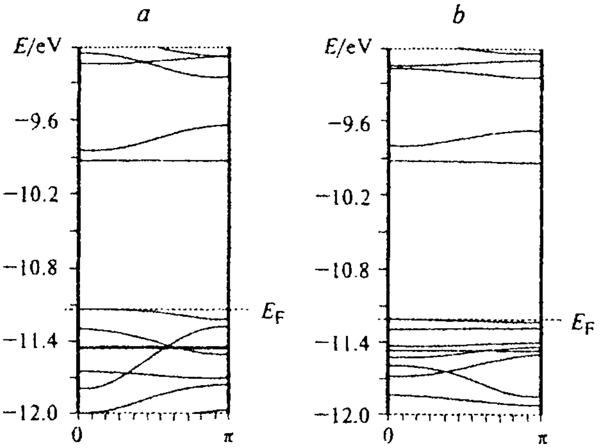

Fig. 3. Energy band structure of macromolecules **4** (*a*) and **11** (*b*).

It should be noted that the energy band structure of macromolecule **4** depends slightly on the procedure of calculation of the repeating unit geometry. At a qualitative level, the spectral pattern calculated for the quasi-linear system **4** using the geometry obtained by the MNDO/PM3 method[29] is retained and only small quantitative changes are observed: the position of the top of the valence band and the energy of the localized level increase to −11.09 and −9.86 eV, respectively, while the band gap increases to 1.34 eV.

Thus, replacement of several pairs of carbon atoms in the molecule of fullerene C_{60}, its dimer **2**, and trimer **3** by boron-nitrogen pairs leads to stable heteroatomic systems **5**—**10**. A considerable energy gain is obtained upon dimerization and trimerization of both fullerene C_{60} and its hetero-analogs BNC_{58} and $B_2N_2C_{56}$ as compared to the double and triple energies of the monomers. The local energy level of the $[C_{60}]_n$ macromolecule in the forbidden band is transformed into a narrow impurity conduction band on going to the heteroatomic system $[B_2N_2C_{56}]_n$.

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