

# Topological Coding: Towards New Materials for Molecular Electronics\*\*

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In order to develop a new theoretical basis for autonomous devices of molecular electronics, a model of topological coding of chain polymers is proposed. The model is based on the property of the main chain of polymers to form a helix due to conjugated ionic-hydrogen-bond systems (connectivity). It includes the topological code, the algorithm of coding, and the system of physical operators for reconstruction of the encoded structure. The basic principle of the approach consists of the analogy between a 4-link fragment of a polymer and 4-arc graph. It was found that 64 connectivity states (conformations) of the graph can be described in the binary system by matrices of 6 variables that form a supermatrix containing 4 blocks. Using the 4-letter alphabet, matrices and the supermatrix are converted into triplets and the topological code. An algorithm suitable for computer programming is proposed for coding the  $n$ -arc graph and polymer chain. Physical operators were shown either to enhance or suppress the spontaneous capacity of polymers to form helices. Physical operators are assigned to the triplets of the topological code. From the viewpoint of the model, only proteins, nucleic acids, and their close analogs are recognized as prospective materials of future devices for molecular electronics.

## 1. Introduction

There are two major trends in molecular electronics,<sup>[1–4]</sup> one of which is concerned with the search for materials for use in molecular wires and construction elements of molecular electronics devices.<sup>[2,3]</sup> Within this approach molecules are assumed to function as molecular wires.<sup>[5]</sup> Nearly all the materials considered in this connection belong to polyconjugated systems, and significant results have been achieved in this area. New materials include polyacetylene (PA),<sup>[6]</sup> poly(*p*-phenylenevinylene) (PPV) and its derivatives,<sup>[7,8]</sup> phthalocyanines,<sup>[9]</sup> oligoporphyrins,<sup>[10]</sup> polycyclic hydrocarbons,<sup>[11]</sup> and others.<sup>[12]</sup> Many of these materials, e.g., doped PA and PPV derivatives, are used for the fabrication of organic wires,<sup>[6]</sup> transistors,<sup>[13]</sup> photodiodes,<sup>[14]</sup> and light-emitting diodes.<sup>[7]</sup> Although these organic polymers can effectively replace metallic and silicic materials, they cannot be used for the creation of functional devices of molecular size.

The alternative (bionic) approach suggests elaboration of principles and methods of constructing autonomous molecular devices.<sup>[4]</sup> This implies analysis of those properties of biostructures that can be applied to a new technology focusing on various artificial molecular devices. Thus, we proposed a model of molecular electronics using the concept of conjugated ionic-hydrogen bond systems (CIHBSs).<sup>[4]</sup> Unlike other models pre-

suming intramolecular paths for charge and energy transfer,<sup>[1–3]</sup> the one we have developed assumes that such paths emerge when molecules assemble into supramolecular structures, which resolves the problem of contacts in molecular devices.<sup>[15]</sup> CIHBSs arise from the interaction of polar groups of polymers, which, unlike polymers with polyconjugated systems, are readily soluble in polar solvents including water.<sup>[12]</sup>

Two basic principles of the above concept<sup>[4]</sup> are continuity of CIHBSs and conjugation via hydrogen bonds for energy transfer through CIHBSs in macro- and supramolecular structures. Different classes of biomolecules (amino acids, phospholipids) were analyzed as modules of an electronic network with molecules of nucleotide triphosphates functioning as charge sources.<sup>[4]</sup> The principles were also applied<sup>[4]</sup> to develop the zone-block model of biomembranes, the trigger model of enzymatic function, in the analysis of artificial crystals containing CIHBSs (systems of HO-P=O-groups),<sup>[16]</sup> and in the reconstruction of a fragment of the biomembrane structure.<sup>[17]</sup>

Further progress in this field depends on the availability of approaches to designing devices on the basis of CIHBSs. At present, Langmuir–Blodgett films are most commonly used in the fabrication of molecular devices.<sup>[18]</sup> However, only a few (2–3) types of molecules can be used to make the films. Development of a system of molecular modules connected into chains capable of self-assembly into an integral structure could be an alternative. Such an approach was proposed for the operator-free assembly of integrated circuits.<sup>[19]</sup> This process has much in common with the synthesis and self-assembly of proteins. Therefore, one can presume that polymers may prove suitable construction material. In this connection, development of principles of molecular design, topological coding, and self-assembly of the appropriate polymers becomes very important.<sup>[20]</sup>

The present work aims at the development of a model of topological coding of the structure of polymers for the pur-

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[\*\*] The work was financially supported in part by research grants from the Russian Foundation for Basic Research (RFFI) code 99-04-49836.

poses of molecular electronics on the basis of the previously obtained results.<sup>[21–24]</sup> It mainly focuses on the elucidation of conditions of self-organization of the polymers during their synthesis and their assessment as feasible construction materials for molecular electronics.

## 2. Principles of Topological Coding of Chain Polymers

Analysis of polymers as putative materials for molecular electronics is based on a model that includes a topological code, an algorithm for structure coding–decoding, and a mechanism of reconstruction of encoded structures.<sup>[21–24]</sup> We used *n*-arc graphs for model representation of unbranched chain polymers,<sup>[21]</sup> with the 4-arc graph as a minimal unit. In such a graph, (Fig. 1b), vertices (*i*, *i*–1, ..., *i*–4) correspond to the atoms of the periodically repeated link of the polymer (Fig. 1a). Structural edges (solid lines, Fig. 1b), which connect vicinal vertices, correspond to groups of bonds uniting modules into a

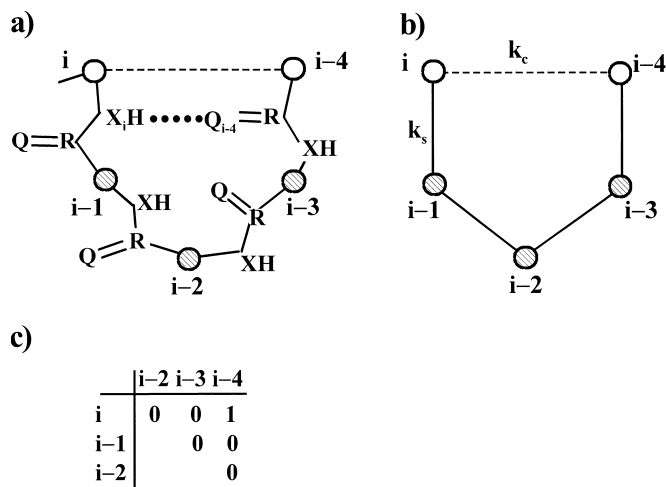


Fig. 1. Fragment of the linear chain polymer (a), its graph (b), and matrix (c). ) HQ–R=X are groups of atoms connecting *i*–*i*–1, ..., *i*–3–*i*–4 atoms into the chain; atoms *X<sub>i</sub>* and *Q<sub>i–4</sub>* are connected by a hydrogen bond and provide fixation of the *i*th and *i*–4th atoms. b) Structural edges bind vertices *i*–*i*–1, ..., *i*–3–*i*–4; the connectivity edge connects vertices *i*–*i*–4; in the matrix (c) the connectivity edge corresponds to 1.

chain (Fig. 1a). To model the polymer conformation we close the graph structure by means of a virtual connectivity edge. The connectivity edge (Fig. 1b, dashed line) connects those atoms that are fixed by hydrogen bonds (in Fig. 1a, atoms *X<sub>i</sub>* and *Q<sub>i–4</sub>* are connected by hydrogen bonds, and atoms *i*–*i*–4 are fixed). The length of the structural edge is assumed to be constant, *k<sub>s</sub>*. The connectivity edge is ascribed the value of *k<sub>c</sub>*, which can vary in the range 0–2*k<sub>s</sub>*. We use “1” or “0”, respectively, to denote the occurrence or absence of the connectivity edge.

Matrix representation of the connectivity states is given by “upper triangular matrices” (Fig. 1c). In Figure 1b a connectivity edge connects vertices *i* and *i*–4. In the matrix, this pair is represented by “1”. Disconnected pairs of vertices *i*–*i*–2, *i*–

*i*–3, *i*–1–*i*–3, *i*–1–*i*–4 and *i*–2–*i*–4 are represented by “0”. The general form of the matrix is:

	<i>i</i> –2	<i>i</i> –3	<i>i</i> –4
<i>i</i>	<i>x</i> <sub>1</sub>	<i>x</i> <sub>2</sub>	<i>x</i> <sub>3</sub>
<i>i</i> –1		<i>x</i> <sub>4</sub>	<i>x</i> <sub>5</sub>
<i>i</i> –2			<i>x</i> <sub>6</sub>

where *i*, *i*–1, ..., *i*–4 are vertices of the graph, *x*<sub>1</sub>, *x*<sub>2</sub>, ..., *x*<sub>6</sub> are variables assuming values 0 or 1. We shall also use a notation: *x*<sub>1</sub>*x*<sub>2</sub>*x*<sub>3</sub>*x*<sub>4</sub>*x*<sub>5</sub>*x*<sub>6</sub>.

The most typical conformations of the 4-link fragments of chain polymers as well as the corresponding graphs and 6-digits matrices are shown in Figure 2. The completely extended conformation is represented by a graph that has no connectivity edges; the corresponding matrix contains only zeros (Fig. 2a). A folded structure is modeled by a graph with the connectivity edges *i*–*i*–2, *i*–1–*i*–3, *i*–2–*i*–4; each represented by “1” in the matrix. In the completely connected conformation (helical) (Fig. 2c) five vertices are connected by six connectivity edges, all represented by “1” in the matrix.

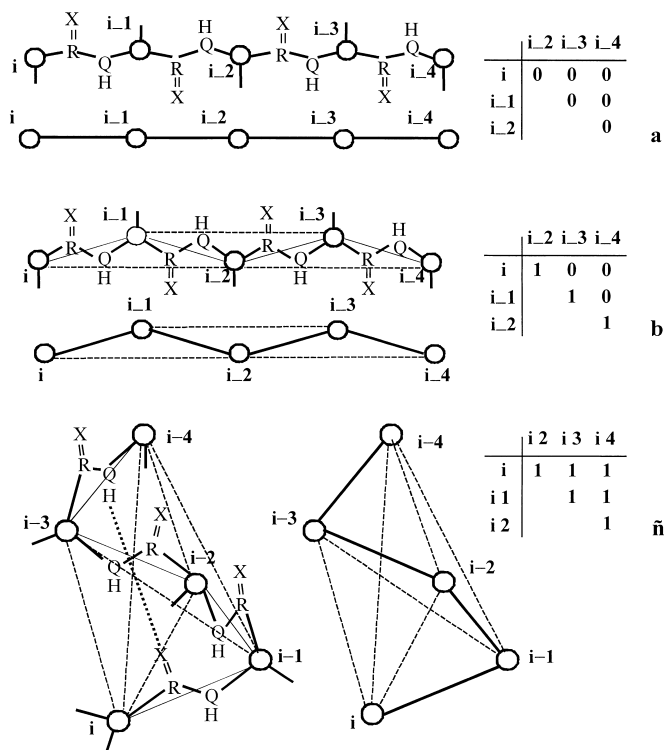


Fig. 2. 4-link fragments of typical polymer structures, their graphs and matrix description. a) unfolded conformation, b) β-folded structure, c) α-helix.

## 3. Model of the Topological Code and Algorithm of Coding

### 3.1 Matrix of the Connectivity States for the 4-Arc Graph

There are 64 matrices describing connectivity states of the 4-arc graph, from completely extended (matrix containing only

0-elements) to completely connected (matrix containing six elements equal to 1).<sup>[21-24]</sup> They can be converged to a supermatrix of connectivity states (SCS) (Fig. 3). The rows of SCS are generated by the first pair of variables ( $x_1x_2$ ) in the sequence 00, 10, 01, 11, and columns by the third pair of vari-

Each pair of variables  $x_i x_{i+1}$  can assume values 00, 01, 10, 11, which can be encoded by means of the 4-letter alphabet (K, L, N, P):

$$K = 00, L = 01, N = 10, P = 11 \quad (3)$$

Using this assignment, we transform the SCS (matrices) into the triplet topological code (Fig. 3). The information on the structure of the 4-arc graph in terms of the 4-letter code assumes the form of a linear chain.

2 1	K ↔ 00				L ↔ 01			
	K ↔ 00	L ↔ 01	N ↔ 10	P ↔ 11	K ↔ 00	L ↔ 01	N ↔ 10	P ↔ 11
00 ↑ K	0 0 0 0 0 0 0 0 0	0 0 0 0 0 1 0 1 0	0 0 0 0 1 0 0 0 1	0 0 0 0 1 0 0 0 1	0 0 0 1 0 0 0 1 0	0 0 0 1 0 0 0 1 0	0 0 0 1 1 0 0 1 0	0 0 0 1 1 0 0 1 0
10 ↑ N	1 0 0 0 0 0 0 0 0	1 0 0 0 0 0 0 0 0	1 0 0 0 0 1 0 0 1	1 0 0 0 0 1 0 0 1	1 0 0 1 0 0 0 1 0	1 0 0 1 0 0 0 1 0	1 0 0 1 1 0 0 1 0	1 0 0 1 1 0 0 1 0
01 ↑ L	0 1 0 0 0 0 0 0 0	0 1 0 0 0 1 0 1 0	0 1 0 0 1 0 0 1 0	0 1 0 0 1 0 0 1 0	0 1 0 1 0 0 0 1 0	0 1 0 1 0 0 0 1 0	0 1 0 1 1 0 0 1 0	0 1 0 1 1 0 0 1 0
11 ↑ P	1 1 0 0 0 0 0 0 0	1 1 0 0 0 0 0 0 0	1 1 0 0 0 1 0 0 1	1 1 0 0 0 1 0 0 1	1 1 0 1 0 0 0 1 0	1 1 0 1 0 0 0 1 0	1 1 0 1 1 0 0 1 0	1 1 0 1 1 0 0 1 0
00 ↑ K	0 0 1 0 0 0 0 0 0	0 0 1 0 0 0 0 0 0	0 0 1 0 0 1 0 0 1	0 0 1 0 0 1 0 0 1	0 0 1 1 0 0 0 1 0	0 0 1 1 0 0 0 1 0	0 0 1 1 1 0 0 1 0	0 0 1 1 1 0 0 1 0
10 ↑ N	1 0 1 0 0 0 0 0 0	1 0 1 0 0 0 0 0 0	1 0 1 0 0 1 0 0 1	1 0 1 0 0 1 0 0 1	1 0 1 1 0 0 0 1 0	1 0 1 1 0 0 0 1 0	1 0 1 1 1 0 0 1 0	1 0 1 1 1 0 0 1 0
01 ↑ L	0 1 1 0 0 0 0 0 0	0 1 1 0 0 0 0 0 0	0 1 1 0 0 1 0 0 1	0 1 1 0 0 1 0 0 1	0 1 1 1 0 0 0 1 0	0 1 1 1 0 0 0 1 0	0 1 1 1 1 0 0 1 0	0 1 1 1 1 0 0 1 0
11 ↑ P	1 1 1 0 0 0 0 0 0	1 1 1 0 0 0 0 0 0	1 1 1 0 0 1 0 0 1	1 1 1 0 0 1 0 0 1	1 1 1 1 0 0 0 1 0	1 1 1 1 0 0 0 1 0	1 1 1 1 1 0 0 1 0	1 1 1 1 1 0 0 1 0
2	N ↔ 10				P ↔ 11			

Fig. 3. Supermatrix of the connectivity states of the 4-arc graph and its transformation into the triplet topological code. Pairs of variables are indicated by figures in the matrix.

ables ( $x_5x_6$ ) in the sequence 00, 01, 10, 11. Thus, the SCS consists of four blocks, comprising 16 states each. Each block has common second pairs of variables ( $x_3x_4$  of 00, 01, 10, 11). In the obtained table, the 0-connectivity state corresponds to the upper left element and disconnected graph, and the completely connected state to the lower right element and helix conformation of the graph. The symmetry of the obtained structure as well as conformations of the 4-arc graphs from each of the four blocks have been analyzed previously.<sup>[23,24]</sup> The geometry representation of the supermatrix is Boolean hypercube.<sup>6 [22,23]</sup>

### 3.2 Coding of the SCS by Means of the 4-Letter Alphabet

To facilitate processes of transmission, reproduction, and copying, information about the graph structure should be transformed into a suitable form of unbranched chain. There are 6 variables in matrices of the 4-arc graph  $x_1x_2x_3x_4x_5x_6$ . We shall group them into 3 pairs:

$$x_1x_2 = X, x_3x_4 = Y, x_5x_6 = Z \quad (2)$$

Thus, the combination XYZ (triplet) can be related to the matrices.

### 3.3 Coding-Decoding Algorithm

Previously, to represent the short-range order of the  $n$ -arc graph we introduced a quasidiagonal (Q-) matrix), in which each row contains three variables (Fig. 4).<sup>[21-23]</sup> The number of a row is given by the first figure in the sub-index, e.g., in the 0th row there are elements  $y_{01}, y_{02}, y_{03}$ , in the 1st row  $y_{11}, y_{12}, y_{13}$ , etc. Variables  $y_{ij}$  as well as  $x_i$  can assume values 0 or 1. The coding procedure suggests that each variable is expanded, as illustrated with the arrows drawn from the Q-matrix, into the sum of two values: “1” and “0”, admitting the following formalism of «disjunction» ■ Do these chevrons have a mathematical meaning? <b> ■ summation:<sup>[25]</sup>

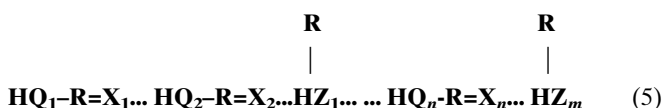
$$0 + 0 = 0, 1 + 0 = 1, 0 + 1 = 1, 1 + 1 = 1 \quad (4)$$

Pairs of variables in the marked matrices are encoded as triplets and written in the order indicated in Figure 4:  $X_0Y_0Z_0, X_1Y_1Z_1, X_2Y_2Z_2, \dots, X_iY_iZ_i$ . To reproduce the encoded structure, physical operators written down in the left column: such as Ini, Abc, and Uxy (amino acids in the case of protein) should correspond to each triplet. The coding-decoding of the chain polymer proceeds from the bottom to the top (Fig. 4). The algorithm yields many triplet sequences when used for coding. The decoding procedure is unambiguous. As shown in Figure 4, a reference 0-operator, Ini, encoded by the initiation triplet  $X_0Y_0Z_0$ , is needed for the correct reconstruction procedure.

## 4. Reconstruction of the Polymer Structure

### 4.1 Self-organization Principles of the Polymeric Structures

A polymeric chain is capable of fixing its conformation (called the property of connectivity), which implies that groups connecting units in the polymers, can form systems of hydrogen bonds. The groups, denoted as simple (R-Z) or resonance (Q-R=X), can be encountered in bioorganic compounds. Previously, we classified groups containing elements C, N, O, P, S.<sup>[4]</sup> Combinations C-O, C-N, C-S are examples of simple groups and N-C=N, N-C=O, O-C=O, O-P=O of the resonance ones. We showed that most of them are capable of forming CIHBSs:



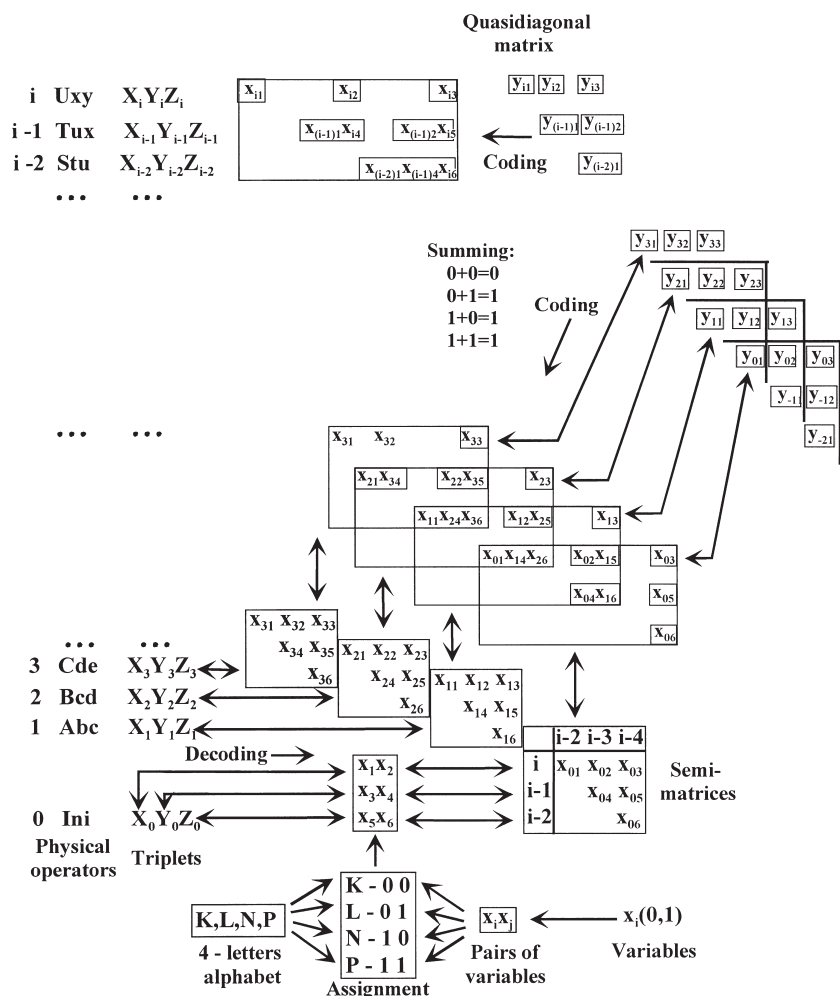


Fig. 4. Algorithm for coding-decoding of  $n$ -arc graph and  $n$ -link chain polymers.

If abstract units in Equation 5 are replaced by real biomolecular units bearing both simple and resonance groups, various biopolymeric structures based on CIHBS continuity may arise.<sup>[4]</sup> The arrangement of protons in CIHBSs is asymmetric. All the hydrogen atoms are localized on the same side as the corresponding groups, which makes a jump-wise mechanism of charge transfer along the CIHBS possible.<sup>[4,16]</sup>

To generate the encoded structures, the groups should possess rigidity and stability of bond lengths, combined with the capacity of rotating within a link. This increases the probability of CIHBS formation. In the absence of the side chains, the main chain tends to realize the CIHBS continuity, which is favored thermodynamically. Helical structures, involving groups of the HQ-R=X-type, emerge. Side chains may affect this process, either contributing to the formation of helices or obstructing it. In the latter case other types of structures may appear, e.g., pleated structures. Thus, the final structure results from the balance of forces that influence the spontaneous capacity of the main chain to form helical structures with the CIHBS. The key problem is to relate the above spontaneous process and reconstruction of the structure encoded by triplets.

## 4.2 Physical Operators and Triplets of the Topological Code

The 4-arc graph can assume open and closed conformations: respectively, pairs of blocks 00 and 01 are open, and 10 and 11 are closed in the SCS  $\blacksquare \langle b \rangle \text{OK} \langle b \rangle \blacksquare$ . The symmetry of pairs of conformation is respected.<sup>[23,24]</sup> The main prerequisite of the reconstruction procedure is adequacy of the combination of the properties of the main and side chains of the polymer in representing the physical structure and graph conformation.<sup>[23]</sup> The polymer chain, possessing connectivity, forms a 4-link cycle fixed by the hydrogen bond of the groups  $X_{i-1}=\text{R}-\text{Q}_i\text{H}\cdots X_{i-4}=\text{R}-\text{Q}_{i-3}\text{H}$  (arrow in Fig. 5a). Other groups (not shown) are not involved in this process. Physical operators in the units, which emerge as the synthesis of the structure proceeds, can act only on this bond. By the effect produced, two types of operators can be distinguished.

Connectivity operators are side polymer chains, which provide an additional fixation of a 4-link fragment, e.g., by hydrogen bonds, as encoded in the fragment of the 4-arc-graph. Thus, the  $i$ th side chain of the connectivity operator (Fig. 5b) has a terminal group  $\text{Q}=\text{R}-\text{XH}$  capable of forming a hydrogen bond with the group  $\text{Q}_{i-4}=\text{R}-\text{XH}$  (variable  $x_3=1$  in the matrix).

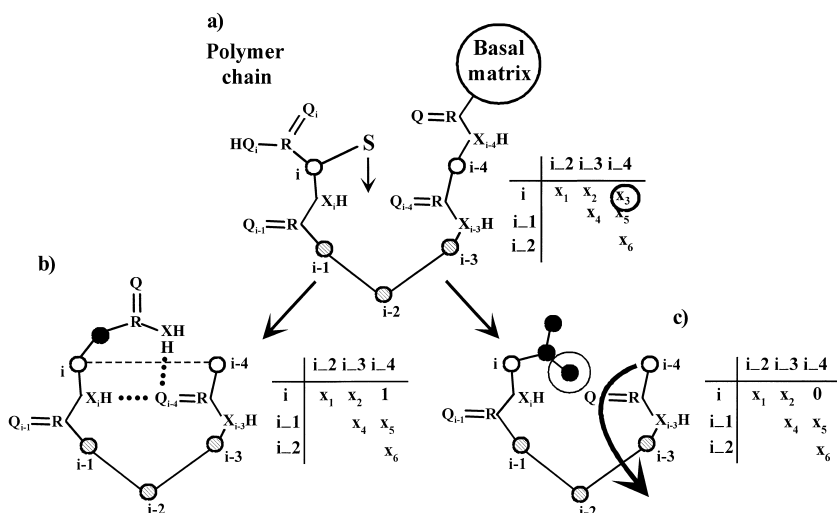


Fig. 5. Physical operators: a) 4-link polymer fragment, b) connectivity operator, c) anti-connectivity operator. Big circles represent the electron shell radius of the methyl group. Black circles represent carbon atoms.

Anti-connectivity operators are side polymer chains, which build into the zone of the hydrogen bond of the main chain (Fig. 5c), obstructing formation of the 4-link cycle (variable  $x_3=0$  in the matrix).

The introduced operators function as retro-operators, acting on the preceding structure (backwards). They belong to one stereoconfiguration (chirality). The size of the operator is determined by the zone (Fig. 5a), where it acts on the bond  $X_iH \cdots Q_{i-4}$ . That is why the side chains, in which the terminal polar groups  $Q=R-XH$  are situated closer or further than the length of the hydrogen bond  $X_iH \cdots Q_{i-4}$ , do not function as connectivity operators. This also applies to anti-connectivity operators. They cannot be shorter or longer than the length specified by the zone of the bond  $X_iH \cdots Q_{i-4}$ . Systems of physical operators with different parameters of the side chains can be created depending on the type of  $Q=R-XH$ . Connectivity operators (polar side chains, variable  $x_3 = 1$ ) are assigned to blocks 10 and 11, whereas anti-connectivity operators (non-polar side chains, variable  $x_3 = 0$ ) are assigned to blocks 00 and 01 (Fig. 5b,c). Hence, in topological code (Fig. 3), connectivity operators become assigned to the low two blocks of triplets ( $N \leftrightarrow 10$  and  $P \leftrightarrow 11$ ) and the anti-connectivity ones to the upper two ( $K \leftrightarrow 00$  and  $L \leftrightarrow 01$ ).

During chain formation new units may attach to the basal matrix in the same position, whereas the side chains (operators) may vary. In Figure 6 these are connectivity operators with similar properties but of different size. Functional groups situated at the end of the chains are denoted as  $Q_1=R-X_1$  and  $Q_2=R-X_2$ . Hydrogen bonds of two side chains having different lengths have different slopes and, hence, differently directed field lines. Connectivity of  $i$ th  $-(i-4)$ th  $\alpha$ -carbon atoms in the two cycles is the same (dotted line), whereas the connectivity of other atoms is different. For the left operator the traction force is directed to the left (dashed lines) so that  $i$ th  $-(i-2)$ th atoms are connected. For the right operator atoms  $(i-2)$ th  $-(i-4)$ th are connected. This is also true for anti-connectivity operators. In the topological code obtained from the SCS (Fig. 3), symmetrical triplets must occupy symmetrical positions with respect to the main diagonals of the blocks. Both physical operators assigned to such triplets differ and corresponding elements in the matrix must differ. Thus, the operator assigned to the triplet PPK must differ from that assigned to the symmetrical triplet KPP, and the operator assigned to the triplet LPL from that assigned to the triplet NPN, etc. Degeneration of the third letter in the triplet renders reconstruction of symmetrical conformations, situated on the main diagonals, a trivial task.

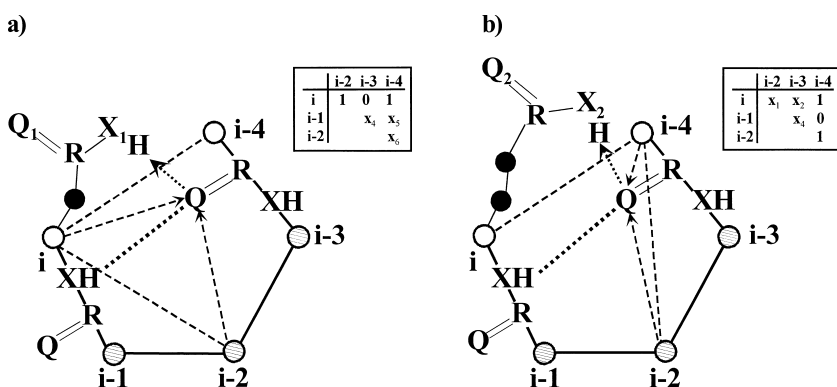


Fig. 6. Realization of symmetrical conformations of a 4-link fragment of protein by means physical operators: a) and b) are symmetrical connectivity operators.

### 4.3 Application of the Coding Algorithm: Analysis of the Results

The coding–decoding procedure for the  $i$ th triplet (Fig. 4), corresponding to the  $i$ th stage of protein synthesis is shown in Table 1.

It is implied that variables  $x_{i1}$ ,  $x_{i2}$ , and  $x_{i3}$  are the most important in the specific activity of the physical operator. Variable  $x_{i3}$  is common for the whole block, while  $x_{i1}x_{i2}$  correspond to the first letter of the triplet ( $X_i$ ). This letter accounts for the difference between the side chains of operators from neighboring rows (Fig. 3). Thus, operators (LKK, LKL, LKN, LKP), which belong to the row beginning with the letter L, must differ in their structure from the operators (PKK, PKL, PKN, PKP) of the next row. The part of the graph conformation encoded in the second letter, can be completely realized only for variable  $x_{i3}$  corresponding to the true value  $y_{i3}$ . The conformation pattern (open or closed) therewith is reproduced by the physical operator. At the  $i$ th stage, variable  $x_{i4}$  is added to  $x_{(i-1)1}$  and  $x_{i5}$  to  $x_{(i-1)2}$ , the performance of which depends on the values (either 0 or 1) of  $x_{i4}$  and  $x_{i5}$ , and on the letter that may appear in the first position of the  $(i-1)$ th triplet ( $X_{i-1} = x_{(i-1)1}x_{(i-1)2}$ ).

Variable  $x_{i6}$ , from the group ( $x_{(i-2)1}x_{(i-1)4}x_{i6}$ ) is peculiar. Eight combinations are possible 000, 001, 010, 011, 100, 101, 110, 111. Seven of them contain “1”. In those cases addition according to disjunction logic leads to “1”. The probability of “0” is negligible (1:8). Thus, the value of  $x_{i6}$  (0 or 1) is of no importance. That means that the part of the 4-arc fragment of the protein structure described by variable  $x_{i6}$  ( $i-2-i-4$ ) is completely formed and cannot be influenced by the  $i$ th physical operator. Therefore, operators corresponding to triplets with the third letter K = 00 and L = 01, as well as N = 10 and P = 11, coincide. In the structure of the topological code (Fig. 3) these operators are assigned to the triplets, which form pairs, e.g., LPK and LPL, LPN and LPP; PPK and PPL, PPN and PPP, etc. Similar principles were discovered in the structure of the genetic code, which can be considered as a special case of the topological code for polypeptide chains.<sup>[24]</sup>

## 5. Discussion

Two aspects of the problem studied in our paper are particularly important. One is concerned with the mechanism of self-organization of supramolecular structures. The other deals with the requirements that polymers must meet in order to comply with the developed model. From the viewpoint of these criteria, different classes of polymers will be assessed as plausible materials for the technology implied by the model.

### 5.1 Self-Organization Mechanism of Polymers

The role of different types of interaction in the stabilization of supramolecular structures of polymers, including proteins, has been substantially reassessed several times. In the beginning, ionic and hydrogen bonds were considered as major factors.<sup>[26]</sup> Later,<sup>[27,28]</sup> a leading role of hydrophobic and van der Waals interactions was recognized, and attempts were made to realize self-assembly of polymers.<sup>[20]</sup> At present, a more balanced approach recognizing the role of all the above-mentioned factors is accepted.<sup>[29]</sup> In our model, a key role of polar interactions is presumed. Although hydrophobic forces can be rather powerful, they are not specific, and hence do not contribute to the formation of any system of bonds. The principle of continuity of CIHBSs is realized in supramolecular structures if groups with opposite properties (proton donors and proton acceptors) contribute to the formation of a continuous system of bonds.<sup>[4]</sup> Spontaneous formation of helices in polymers is facilitated by the occurrence in their structure of the groups of general formula HQ–R=X. Proteins contain groups of this type (HN–C=O groups) in their construction units (peptide bonds).

However, spontaneous helix formation is only a prerequisite for self-organization of complex structures. Our model suggests an important role of the side chains in this process. A set of such chains (physical operators of connectivity and anti-connectivity) regulating the behavior of the chain polymer during helix formation is necessary for reconstruction of the designed final structure. It is well known<sup>[30]</sup> that polar side chains are localized in helical fragments, while non-polar chains, e.g., proline, are normally found in randomly arranged zones of proteins. Our model does not contradict these observations. In our work we lay the emphasis on the interaction of the side chains within polymer molecules capable of spontaneous helix formation. This approach can be considered complementary to that recognizing the effect of the medium as a major factor of self-organization of polymeric molecules.<sup>[3]</sup> As stated earlier,<sup>[24]</sup> we stick to the co-translation mechanism of self-organization of proteins, i.e., we hold to the idea that basically the structure must be formed during biosynthesis. This is clearly implied by our model. It suggests that physical operators should function in the course of the polymer synthesis. In organic chemistry a step-by-step synthesis of chained polymers is a well-elaborated process, particularly for the protein synthesis, e.g., solid-phase synthesis according to Merryfield<sup>■</sup>Ref. 31 is not Merryfield<sup>■</sup>.<sup>[31]</sup> We believe that the approach developed in our work can be applied to describe syntheses of other classes of polymer molecules. One can expect that, in the future, ribosome-like molecular devices capable of template-directed synthesis of chain polymers will be created.

Table 1. The coding–decoding procedure for the  $i$ th triplet (Fig. 4), corresponding to the  $i$ th stage of protein synthesis. ■OK?■

AA	Triplets	Matrices			Q-matrix			
I	Uxy	$X_iY_iZ_i$	$x_{i1}$	$x_{i2}$	$x_{i3}$	$y_{i1}$	$y_{i2}$	$y_{i3}$
$i-1$	Tux	$X_{i-1}Y_{i-1}Z_{i-1}$	$x_{(i-1)1}x_{i4}$	$x_{(i-1)2}x_{i5}$		$y_{(i-1)1}$		$y_{(i-1)2}$
$i-2$	Stu	$X_{i-2}Y_{i-2}Z_{i-2}$		$x_{(i-2)1}x_{(i-1)4}x_{i6}$				$y_{(i-2)1}$

## 6. Feasible Materials for Molecular Electronics

### 6.1 Selection Criteria

The following selection criteria can be employed in order to assess compatibility of different polymer substances with our model: 1) the polymer should not be branched; 2) the polymer chain should be quasi one-dimensional with two degrees of freedom (neither ribbon-like chains with one degree of freedom nor voluminous chains are suitable); 3) topological links in the polymer should contain groups capable of forming continuous CIHBSs and helices; 4) the number of atoms in links should be minimal, so that their conformation could be controlled by the physical operators (side chains).

On the basis of these criteria such substances as dendrimers, polycyclic aromatic hydrocarbons, poly(*para*-phenylene)-type ladder compounds, tetrathiafulvalene, perilene derivatives, and PPV<sup>[20]</sup> must be rejected. In Table 2 simple chain polymers that do not meet the last two criteria are listed. Topological links of polymers that cannot be regarded as suitable candidates, have groups that are either not capable of forming structures involving hydrogen bonds, e.g., polyethylene oxide, polyethylene sulfide, polyesters, polyethylene sulfone, or the hydrogen bonds

that they do form do not lead to CIHBSs, e.g., polyethylene imine.<sup>[32]</sup> PA was considered as a feasible material for molecular electronics<sup>[6]</sup> due to its property of being a good conductor in the presence of ions. However, it also belongs to the group of polymers hardly interesting from the viewpoint of the model. These polymers are not capable of self-organizing owing to rigidity of their conformation caused by delocalization of the  $\pi$ -conjugation along the whole chain.<sup>[32]</sup> The remaining polymers from Table 2 (polyamide and polyethylene phosphate) are considered as poor candidates because, apart from groups capable of forming CIHBS, they include  $_2$ -groups that impart difficult-to-control conformational lability to the polymer links.

### 6.2 Suitable Materials for the Developed Model

Quite expectedly, biopolymers (proteins and nucleic acids) are among feasible candidates for the model (Table 3). Thus, the rigid and planar peptide group of proteins can rotate within the link.<sup>[28,30]</sup> The most stable conformation of the polypeptide chain that can form spontaneously is the  $\alpha$ -helix. In the  $\alpha$ -helix a hydrogen bond emerges between  $O=C-N_iH$  and  $O_{i-4}=C-$

Table 2. Polymers with no prospect for topological coding of structures.

Polymer	Chemical	Link		Brief characterization
		Chemical	Topological	
Polyethylene	$[-\overset{\text{R}}{\text{C}}\text{H}-\text{CH}_2-]_n$	$-\overset{\text{R}_1}{\text{C}}\text{H}-\text{CH}_2-\overset{\text{R}_2}{\text{C}}\text{H}-$		Forms neither H-bonds nor helices
Polyethylene imine	$[-\overset{\text{R}}{\text{C}}\text{H}-\text{CH}_2-\text{NH}-]_n$	$-\overset{\text{R}_1}{\text{C}}\text{H}-\text{CH}_2-\text{NH}-\overset{\text{R}_2}{\text{C}}\text{H}-$		Forms double helices and H-bonds but does not form CIHBS
Poly(ethylene oxide)	$[-\overset{\text{R}}{\text{C}}\text{H}-\text{CH}_2-\text{O}-]_n$	$-\overset{\text{R}_1}{\text{C}}\text{H}-\text{CH}_2-\text{O}-\overset{\text{R}_2}{\text{C}}\text{H}-$		Forms neither H-bonds nor helices
Poly(ethylene sulfide)	$[-\overset{\text{R}}{\text{C}}\text{H}-\text{CH}_2-\text{S}-]_n$	$-\overset{\text{R}_1}{\text{C}}\text{H}-\text{CH}_2-\text{S}-\overset{\text{R}_2}{\text{C}}\text{H}-$		Forms neither H-bonds nor helices
Polyacetylene	$[-\overset{\text{R}}{\text{C}}\text{H}=\text{CH}_2-]_n$	$-\overset{\text{R}_1}{\text{C}}\text{H}=\text{CH}_2-\overset{\text{R}_2}{\text{C}}\text{H}=\text{CH}_2-$		Forms neither H-bonds nor helices
Polyesters	$[-\overset{\text{R}}{\text{O}}-\overset{\text{R}}{\text{C}}\text{H}-\overset{\text{R}}{\text{C}}-]_n$	$-\overset{\text{R}_1}{\text{C}}\text{H}-\overset{\text{R}_2}{\text{O}}-\overset{\text{R}_1}{\text{C}}\text{H}-\overset{\text{R}_2}{\text{C}}\text{H}-$		Forms neither H-bonds nor helices
Polyethylene sulfone	$[-\overset{\text{R}}{\text{C}}\text{H}-\text{CH}_2-\overset{\text{O}}{\parallel}\text{S}-]_n$	$-\overset{\text{R}_1}{\text{C}}\text{H}-\text{CH}_2-\overset{\text{O}}{\parallel}\text{S}-\overset{\text{R}_2}{\text{C}}\text{H}-$		Forms neither H-bonds nor helices
Polyamide	$[-\overset{\text{R}}{\text{NH}}\overset{\text{O}}{\parallel}\text{C}(\text{CH}_2)_m\text{C}-]_n$	$-\overset{\text{R}_1}{\text{C}}\text{H}(\text{CH}_2)_m\text{NH}\overset{\text{O}}{\parallel}\text{C}\overset{\text{R}_2}{\text{C}}\text{H}-$		Forms CIHBS, conformation of plane zigzag
Polyethylene phosphate	$[-\overset{\text{R}}{\text{C}}\text{H}\overset{\text{O}}{\parallel}\text{CH}_2\text{O}-\overset{\text{O}}{\parallel}\text{P}-]_n$	$[-\overset{\text{R}_1}{\text{C}}\text{H}\overset{\text{O}}{\parallel}\text{CH}_2\text{O}\overset{\text{O}}{\parallel}\text{P}\overset{\text{R}_2}{\text{C}}\text{H}-]_n$		Forms CIHBS, but conformation is not regulated

Table 3. Plausible polymer candidates for topological coding [a].

Polymer	Chemical	Link		Brief characterization
		Chemical	Topological	
Polypeptides and proteins	$[-\overset{\text{R}}{\text{NH}}-\overset{\text{O}}{\parallel}\text{C}-]_n$	$-\overset{\text{R}_1}{\text{C}}\text{H}-\overset{\text{O}}{\parallel}\text{NH}-\overset{\text{R}_2}{\text{C}}\text{H}-$		Forms helices on the basis of CIHBS
Thiopolypeptides	$[-(\text{NH}-\overset{\text{R}}{\text{C}}\text{H}-\overset{\text{S}}{\parallel})-]_n$	$-\overset{\text{R}_1}{\text{C}}\text{H}-\overset{\text{S}}{\parallel}\text{NH}-\overset{\text{R}_2}{\text{C}}\text{H}-$		Forms helices on the basis of CIHBS
Poly (acetonitril methyl amine)	$[-\overset{\text{R}}{\text{C}}\text{H}-\overset{\text{H}}{\parallel}\text{N}-\overset{\text{R}}{\text{C}}-]_n$	$-\overset{\text{R}_1}{\text{C}}\text{H}-\overset{\text{H}}{\parallel}\text{N}-\overset{\text{R}_2}{\text{C}}\text{H}-$		Forms CIHBS, Poorly studied
Poly imidazoles	$[-\overset{\text{R}}{\text{C}}\text{H}-\overset{\text{H}}{\parallel}\text{N}-\overset{\text{H}}{\parallel}\text{C}-]_n$	$-\overset{\text{R}_1}{\text{C}}\text{H}-\overset{\text{H}}{\parallel}\text{N}-\overset{\text{R}_2}{\text{C}}\text{H}-$		Capable of forming helices on the basis of CIHBS, poorly studied
Nucleic acids	$[-\text{H}_2\text{C}-\overset{\text{R}}{\text{C}}\text{H}-\overset{\text{O}}{\parallel}\text{C}-\text{OH}]_n$	$-\overset{\text{H}_2\text{C}}{\text{C}}\text{H}-\overset{\text{O}}{\parallel}\text{C}-\text{O}-\overset{\text{R}_1}{\text{C}}\text{H}-\overset{\text{O}}{\parallel}\text{C}-\text{O}-\overset{\text{R}_2}{\text{C}}\text{H}-$		Capable of forming helices on the basis of CIHBS
Hypothetical analogs of nucleic acids				
Amino-phosphate analogue	$[-\overset{\text{R}}{\text{C}}\text{H}-\overset{\text{H}}{\parallel}\text{N}-\overset{\text{O}}{\parallel}\text{P}-\text{O}-]_n$	$-\overset{\text{R}_1}{\text{C}}\text{H}-\overset{\text{H}}{\parallel}\text{N}-\overset{\text{O}}{\parallel}\text{P}-\text{O}-\overset{\text{R}_2}{\text{C}}\text{H}-$		Capable of forming helices on the basis of CIHBS
Amino-sulfate analogue	$[-\overset{\text{R}}{\text{C}}\text{H}-\overset{\text{H}}{\parallel}\text{N}-\overset{\text{O}}{\parallel}\text{S}-\text{O}-]_n$	$-\overset{\text{R}_1}{\text{C}}\text{H}-\overset{\text{H}}{\parallel}\text{N}-\overset{\text{O}}{\parallel}\text{S}-\text{O}-\overset{\text{R}_2}{\text{C}}\text{H}-$		Capable of forming helices on the basis of CIHBS
Amino-silicate analogue	$[-\overset{\text{R}}{\text{C}}\text{H}-\overset{\text{H}}{\parallel}\text{N}-\overset{\text{O}}{\parallel}\text{Si}-\text{O}-]_n$	$-\overset{\text{R}_1}{\text{C}}\text{H}-\overset{\text{H}}{\parallel}\text{N}-\overset{\text{O}}{\parallel}\text{Si}-\text{O}-\overset{\text{R}_2}{\text{C}}\text{H}-$		Capable of forming helices on the basis of CIHBS

[a] The names of the main polymeric chains and conventional chemical links (R side chains or H atoms) are provided in the first and second columns; the third column contains topological links of polymers. Each link includes side chains regarded as plausible physical operators ( $R_1$  and  $R_2$ , which may differ or coincide) and groups placed between them.

NH-groups, i.e., a 4-link cycle is formed. This results in the formation of CIHBS on the basis of HN–C=O-groups with proton-donor and proton-acceptor properties (Table 4). These CIHBS were presumed to function as channels for charge transfer.<sup>[4]</sup> Side chains of amino acids were shown to meet the

Table 4. Types of CIHBSs in polymers that are capable of self-organizing.

Polymer	CIHBS
Polypeptides and proteins	... HN–C=O ... HN–C=O ... HN–C=O ...
Thiopoly-peptides	... HN–C=S ... HN–C=S ... HN–C=S ...
Poly(acetonitril-methylamine)	... HN–C=N ... HN–C=N ... HN–C=N ...                                         CH <sub>3</sub> CH <sub>3</sub> CH <sub>3</sub>
Polyimidazoles	... HN–C=N ... HN–C=N ... HN–C=N ...
Nucleic acids (NA)	... HO–P=O ... HO–P=O ... HO–P=O ...
Aminophosphate analogue of NA	... HN–P=O ... HN–P=O ... HN–P=O ...
Aminosulphate analogue of NA	... HN–S=O ... HN–S=O ... HN–S=O ...
Aminosilicate analogue of NA	... HN–Si=O ... HN–Si=O ... HN–Si=O ...

requirements of the model to physical operators.<sup>[24]</sup> Polymers containing thio-analogs of the peptide bond (HN–C=S-groups) can also be used in topological coding. Systems of thiopeptide groups are shown in Table 4. Oligothiopeptides with antibiotic activity were found in microorganisms.<sup>[33]</sup> It should be noted that, in this case, the structure of the side chains is different from that observed in proteins. Polymer material polyacetonitril methylamine can be considered as a feasible candidate for modeling. Its links contain HN–C=N-groups with donor–acceptor properties. This allows one to presume that this polymer contains helices that involve CIHBSs made up of HN–C=N-groups (Table 4). In such systems the nitrogen atom bound to the methyl group behaves as an analog of oxygen in the peptide bond.

Polymers containing links with planar ■ or plain?■ cyclic groups of the imidazole type,<sup>[32]</sup> shown in Table 3, also include HN–C=N-groups with donor–acceptor properties. They are capable of forming CIHBSs (Table 4). Helical structures are likely to appear as well. A weak side of such polymers is the slowing down of the charge transfer, which is accounted for by the time the charge takes to pass through the cyclic  $\pi$ -electron systems of imidazole groups. The system of operators in this case must be different from that based on amino acids.

Other feasible candidates are phosphorus-containing polymers. There can be no simple polyphosphates with only one H<sub>2</sub>-group in the link because bonds of O–CH<sub>2</sub>–O- type are not stable. Hence, the link should contain at least two CH<sub>2</sub>-groups. As follows from the polyethylene phosphate structure, a conformationally stable cycle involving such groups is favored, e.g., a five-element cycle (Table 3). This may explain why nucleic acids include

pentoses.<sup>[32]</sup> Helical structures similar to the  $\alpha$ -helix (Fig. 7) may form in this case. In such structures, CIHBSs, involving HO–P=O-groups, can emerge (Table 4). Previously we showed that crystals of isobutyl-2-aminoethyl phosphate hydrochloride and isobutyl-2-aminoethyl phosphate hydrobromide, which contain CIHBSs, manifest anomalous dielectric permittivity.<sup>[16]</sup> Their conductance is in good agreement with the requirements of the model of stepwise charge transfer. In addition, such materials have a relatively low activation energy (0.5–0.7 eV), which is about the energy of ATP hydrolysis.

Apparently, in the above “pseudo- $\alpha$ -helix”, side chains that are bigger than amino acid residues should function as physical operators. It is possible that nitrous bases including many minor ones, e.g., methylated bases, are natural physical operators in nucleic acids (Fig. 7). However, it cannot be excluded that other sets of connectivity and anti-connectivity operators would be found for the purposes of molecular electronics. Three hypothetical analogs of nucleic acids involving HN–P=O, HN–S=O, and HN–Si=O groups and their CIHBSs are shown in Tables 3 and 4, respectively. These analogs, especially those containing Si, may prove an alternative to biopolymers in future technical applications. Thus, preliminary screening of polymers from the standpoint of topological coding allowed us to choose mainly polymers containing peptide or phosphate groups and their derivatives as suitable material for modeling purposes.

## 7. Conclusion

In the present work, a theoretical approach to the design of autonomous devices of molecular electronics is proposed. According to this approach, devices of molecular electronics are built up of functional modules, which form a self-organizing linear polymer chain. Of key importance for the self-assembly process is the helix-forming capacity of the main chain. It is based on the continuity of CIHBSs, which contribute to the molecular architecture of the devices and function as channels of the charge transfer process.<sup>[4]</sup>

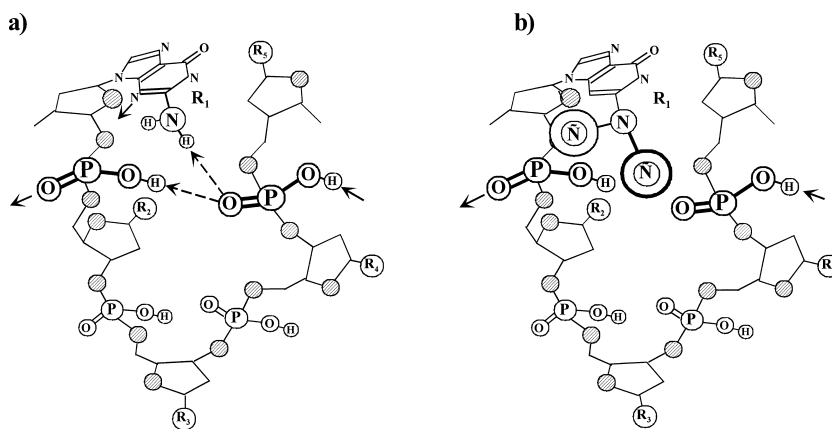


Fig. 7. Hypothetical “ $\alpha$ -helix” formed by polynucleotide chain with a) nitrous base (guanine) as connectivity operator, b) methylated nitrous base (N<sup>2</sup>-dimethyl guanine) as anti-connectivity operator. Oxygen atoms that do not contribute to the formation of hydrogen bonds are represented by cross-hatched circles; R<sub>2</sub>–R<sub>5</sub> are nitrous bases. Arrows indicate inputs and outputs of CIHBSs.



The above-stated principles are realized in the model we developed to describe the topology coding of chain polymers. The model is based on the capacity (connectivity property) of polymeric molecules to fix the conformation of fragments by means of hydrogen bonds. Apart from the topological code, we elaborated an algorithm of coding and a system of physical operators for reconstruction of the encoded structure. The operators determine the structure in accordance with the conformation of the 4-link fragments of the polymer molecule encoded by triplets. They either enhance (connectivity operators) or suppress (anti-connectivity operators) the spontaneous capacity of polymers to form a helix. Arrangement of the operators in the structure of the topological code is strictly determined.

The undertaken screening of polymers for their compatibility with the developed model showed that only a few polymer types meet the necessary requirements. These are proteins, nucleic acids, and their close analogs. The developed coding technique can be combined with the construction of logical electron circuits,<sup>[4]</sup> which may become an important step towards creating autonomous devices of molecular electronics.

Received: April 30, 2001  
Final Version: October 23, 2001

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