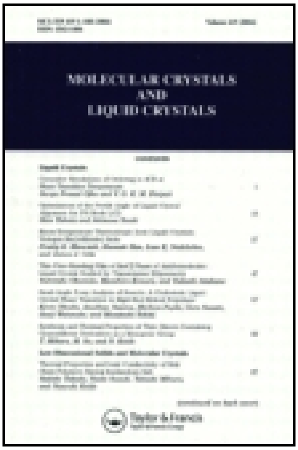

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Functional Organic Structures with Neutral and Charge Electronic Excitations Transfer for Molecular Electronics

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Compounds possessing the predicted unidirectional excitation conductivity and metal-organic nanostructures based on them are fabricated and investigated. The unidirectional excitation transfer in these compounds is confirmed. Computer simulations of electronic excitations passing through a functional macromolecule are carried out. Spectral investigations confirm that adenosine-thymidine sequences are electronic excitation traps in the nucleotide-containing molecular systems [1]. The formation of a chain of progressively lower energy levels in chromophores along the molecular system predicts not only the unidirectional neutral excitation transfer, but the unidirectional charge carrier current as well. Diode-like VAC-characteristics for the metal-organic systems of gold islands connected by π-electron-containing molecules are observed experimentally.

Keywords: electronic excitations transfer; π-electron-containing molecules; nanoelectronics

1. INTODUCTION

One of the main problems of modern nanoelectronics (including molecular electronics) is the development of basic elements. Such

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elements can be created, by using the specially designed and synthesized molecules or nanostructures that can realize some functions in the information processing and storage. The basic elements joined in a certain way can serve as nanodevices. In particular, such elements can be created using π-electron-containing macromolecules (including biomacromolecules) that possess the predetermined energy structure and, as a result, the predicted functionality.

In general, the π-electron containing macromolecules can be divided into two types: in type (1), π-electrons are spread along a macromolecule (for example, in polyacethylene); in type (2), π-electrons are localized in individual polymer cells (polystyrene, polyvinylcarbazole, polyvinylnaphthalene, RNA, DNA, some proteins, etc.). Optical absorption studies of polymer macromolecules of type (2) proved that the electronic energy sites of these polymers are determined mainly by peculiarities of the energy structure of the π-electron systems of individual macromolecular cells [1–4]. Therefore, it appears possible to modify or to change individual chromophores in a polymer macromolecule without significantly affecting the rest of them. Such modifications, however, are complicated by the migration of electronic excitations (singlet and triplet excitons) resulting from the weak interaction between neighboring π-electron systems in a macromolecule [2–25]. The main characteristics of singlet and triplet excitons in many macromolecules (the spreading length, the number of jumps, the critical jump length) were evaluated earlier [1,3,4,7,13,19,20,22–25,29,31–33].

The possibility of a modification of macromolecules opens the ways to design the functional (smart) macromolecules (or molecular systems) for nanoelectronics and nanophotonics. In addition, by using such modifications, new unique experiments can be realized. In one of such experiments, by varying the distances between the π-electron-containing cells in a macromolecule gave us the possibility to evaluate the critical hope distances for singlet and triplet excitons in carbazole and benzocarbazole macromolecules [23,24,31]. These experiments allow also the identification of the centers generating charge carriers in aromatic macromolecules [30]. By varying the length of macromolecules and by creating exciton traps, the total exciton spreading lengths were evaluated [3,13,19,20–22,24,25,29].

The character of exciton motions in polymer macromolecules (with non-conjugated cells) has been well studied now, and they are believed to be random walks [4,5,21,22,25]. The resulting exciton dislocation length (l) is defined as the distance between the points of exciton creation and deactivation. As was shown [22,25], this length is considerably shorter than the total distance traveled by excitons (L) during their lifetime, $L > l$. For example, in polyvinyl-7-benzocarbazole

(PV7BCa) macromolecules, the total number of singlet exciton jumps is, on the average, $n = 4000$ [22], which gives $L = n \cdot a = 10000$ Å (a – the distance between neighboring cells), whereas $l = a \cdot \sqrt{n} = 150$ Å. Direct evaluations of l for singlet excitons in PV7BCa give $l \approx 300 \div 400$ Å [3,25]. The corresponding values for triplet excitons in PV7BCa are still larger: $L \approx 2.5 \cdot 10^5$ Å [24] and $l = 2000$ Å. The question arises whether it is possible to create a macromolecule with unidirectional exciton motion that realizes the energy transfer by the following steps: 1) photon absorption by the first cell *only*; 2) one-way direct excitation energy transfer; 3) excitation localization in the end cell *only*. Such macromolecules could act as one-way exciton conductors in nanoelectronics.

The knowledge of the positions of energy sites of a molecular system separated by links is important for the design of basic elements. These positions can be obtained by spectral methods. On the other hand, the measurement of the volt-ampere characteristics (VACs) of separated molecular systems is necessary for the design of nanodevices. There are a few approaches to measure VACs of single molecular systems. In this paper, two approaches were used: (1) the use of mesostructures, in which separated molecular systems circuit gold nanoislets; (2) the measurement of VACs of single molecules in oriented monomolecular layers.

2. SOME PREVIOUS RESULTS ON THE DESIGN, SYNTHESIS, AND TESTING OF FUNCTIONAL MOLECULAR SYSTEMS

The first steps in the design, synthesis, and spectral testing of the functionality of molecular structures with the predicted unidirectional electronic excitation transfer were described in [26–28]. Two molecular systems of this type have been selected as the best performers.

The corresponding energy levels and the predicted spectral processes for the basic units of the first system, aminophenol (APH) and phtalimide (PHTI), and their mutual system, oxyphenylphthalimide, are presented in Figure 1.

The possible use of the unidirectional electronic excitation energy transfer to initiate or stop the photochemical reactions was studied by us earlier [27].

The second system is the block-copolymer oligonucleotide d(CCCGGGTTTAAA) – with its basic units (dCMP, dGMP, dTMP, and dAMP), polymer poly$(dAdT)_2$ – whose energy levels and phosphorescence spectra are presented in Figure 2. Nucleosides in the oligonucleotide d(CCCGGGTTTAAA) are linked by PO_4H-groups; trimer

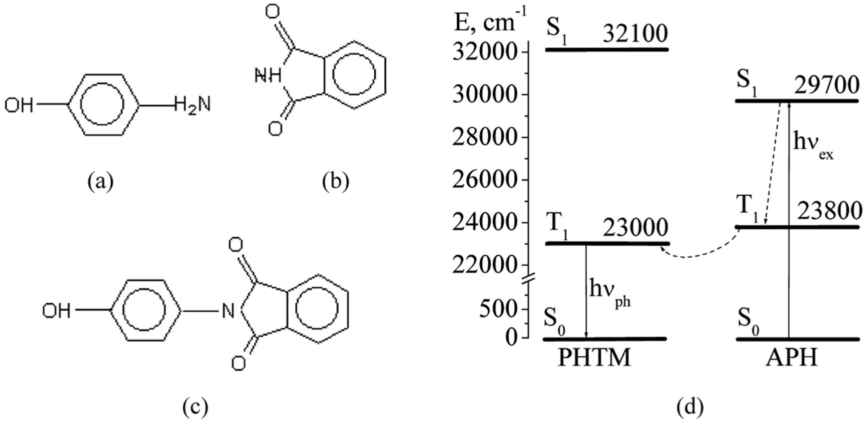

FIGURE 1 Structure of aminophenol (APH) (a), phtalimide (PHTI) (b), and their mutual system – oxyphenylphthalimide (c); energy levels of the cells in oxyphenylphtalimide (d).

d(ATC), dimer d(AT), and polymer poly(dAdT)$_2$ were investigated with the aim to study the nature of the d(CCCGGGTTTAAA) phosphorescence.

It was shown by us in [1,33,34] that the phosphorescence spectra of the functional oligomer d(CCCGGGTTTAAA) practically coincides with the DNA, d(ATC), d(AT) and poly(dAdT)$_2$ phosphorescence spectra (Fig. 2b). This means that the main triplet traps in d(CCCGGGTTTAAA), as well as in DNA, are the AT-sequences that form a complex as exciplex.

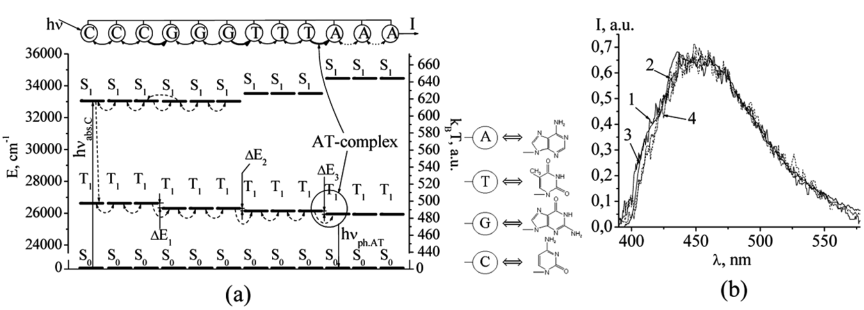

FIGURE 2 Scheme of energy levels and transitions between the cells in d(CCCGGGTTTAAA) (a); phosphorescence spectra (b) of poly(dAdT)$_2$ (1), d(CCCGGGTTTAA) (2), d(AT) (3) and d(ATC) (4) ($\lambda_{ex} = 300\,nm$) at $T = 77\,K$, water solutions.

3. CALCULATION OF THE TRIPLET EXCITON CURRENT ALONG A MODEL 12-CELL OLIGOMER MACROMOLECULE

The theoretical calculations of electronic excitation transfer along a 12-cell oligomer macromolecule (as d(CCCGGGTTTAAA)) are carried out under assumption of random walks of electronic excitations in triads taking the reverse exciton currents that can be significant at higher temperatures into account (Fig. 3).

The energy structure of such a model system allows the first (initial) cell to be excited (by photons of a certain wavelength) without exciting the other cells. The excited cell can either be deactivated by spontaneous radiative or irradiative transitions to the ground state with a general probability α or can transfer its excitation to the neighboring right-hand cell with the probability $(1-\alpha)$. This second excited cell again can either be deactivated with the same probability α or can transfer its energy to the first and the third cells with the probability $(1-\alpha)/2$. The same considerations are applied to the cells with positions 3,5,6,8,9,11,12. The 4, 7, and 10 cells differ in that they can transfer their excitations to the neighboring right-hand cells with the probability $(1-\alpha)/2$ and to the neighboring left-hand cells with the probability $\frac{1-\alpha}{1+e^{-d}}$, where $d = \frac{\Delta E}{kT}$.

These considerations allow estimates of the number of excitations (C) localized to the last (12th) cell if the number of excitations generated in the first cell is known. Using the MAPLE7 software, the C values under the assumption that only one excitation was generated in the first cell are calculated. The results of these calculations are presented in Figure 4. The calculations are described in more details in Appendix 1.

For the cases with $d = 17.353$ at $T = 4.2$ K, $d = 7.843$ at $T = 77$ K and $d = 2.057$ at $T = 293$ K and $\alpha \leq 0.001$, $C = I_0/I > 0.9$. The value

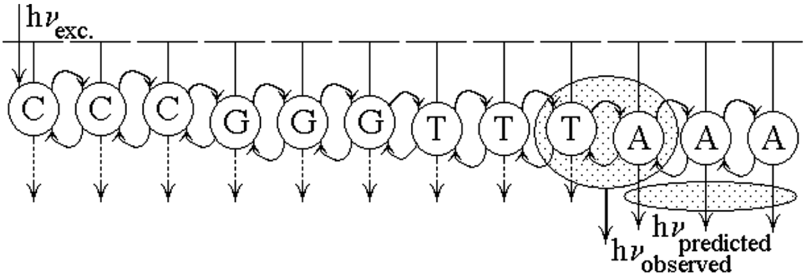

FIGURE 3 Model of the electronic excitation transfer along a 12-cell macromolecule.

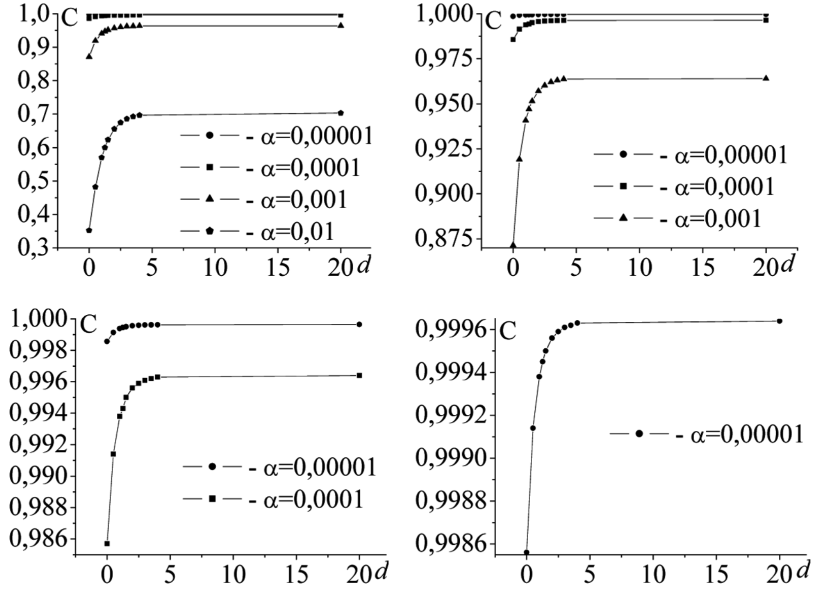

FIGURE 4 Dependence of the exit value of C on $d = \frac{\Delta E}{kT}$.

of $\alpha \leq 0.00001$ is typical of the triplet states of π-electron-containing molecular systems.

Thus, for these models of the block-copolymer compound, the losses of triplet excitons during their travel along the macromolecule are negligible.

4. SOME ELECTRICAL PROPERTIES OF FUNCTIONAL COMPOUNDS

We attempted to evaluated electrical properties of the functional compounds synthesized, by using a macromolecule model with the direct one-way exciton motion. The basic units, naphthalimide (NAPHMA) and aminophenole (APH), their mutual system (the dimer oxyphenylnaphthalimide) as well as the corresponding energy levels and the optical spectra are presented in Figure 5 (the phosphorescence spectra of dimer (1), NAPHMA (2), and APH (3) under the excitation at $\lambda_{ex} = 337$ nm).

The data shown in Figure 5 prove the existence of the unidirectional neutral electronic excitation transfer in the oxyphenylnaphthalimide dimer. Furthermore, the progressively lower energy levels along the chromophore chain in the molecular system forecast not only the

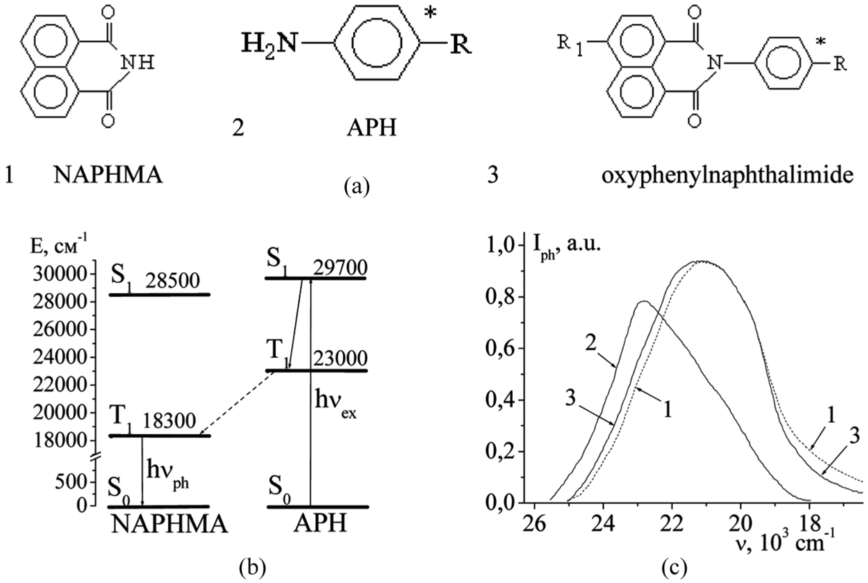

FIGURE 5 Structure of oxyphenylnaphthalimide and its cells; (a) the scheme of energy levels and transitions between the cells; (b) phosphorescence at $T = 77$ K (c), solutions in dioxane, 10 mole/l.

unidirectional neutral electronic excitation transfer but also the unidirectional charge carrier current. Indeed, the diode-like VACs (Fig. 6a,c) for metal-organic systems of gold islands connected by oxyphenylnaphthalimide molecules (Fig. 6b) deposited on the gold substrate were measured by a scanning tunneling microscope (STM) under ambient conditions (Fig. 6c).

The experiments were performed, by using a commercial STM (NT MDT) equipped with a home-built scanning head. The reconstructed Au(111) surfaces were prepared from gold films (~150 nm in thickness) deposited in vacuum on mica. The flamed Au-substrates revealed atomically flat terraces with typical reconstruction lines. The STM tips were mechanically cut from a Pt/Ir wire and tested on cleaved highly oriented pyrolytic graphite surfaces. First, the range of tunneling voltages which allows obtaining reproducible STM-images was determined. Typical imaging conditions were in a range from 0.1–10 nA and from 0.1–2 V. Several STM images recorded in the constant current mode were obtained with different samples and tips to check for the reproducibility and to ensure that results are free from artifacts. The STS measurements were performed as follows. The

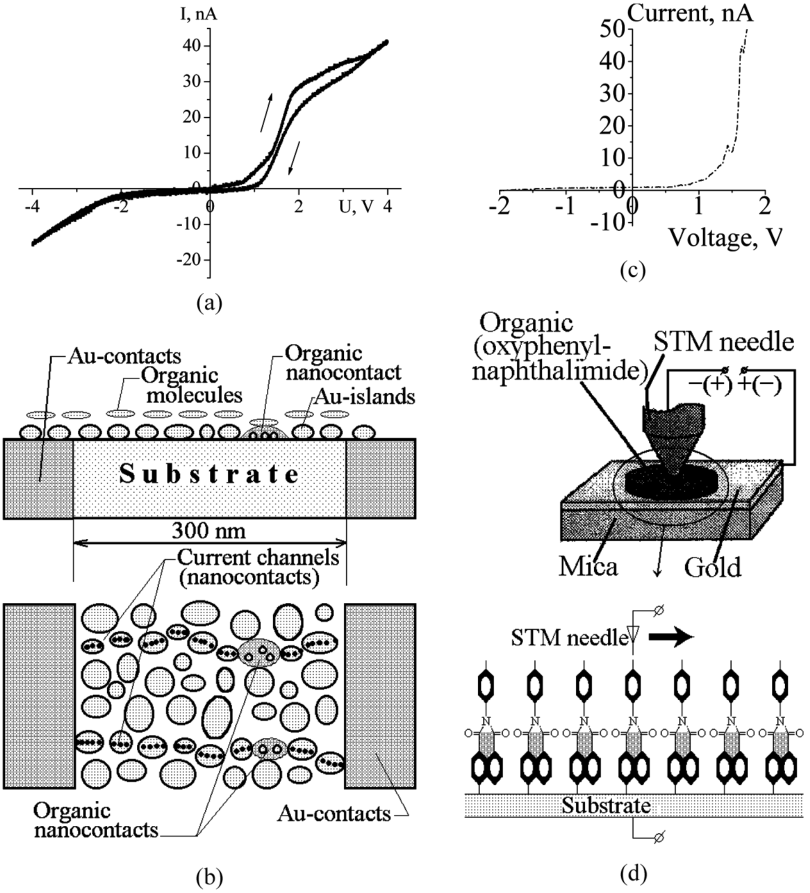

FIGURE 6 $I(U)$ characteristics (a, c); the structure of metal-organic composites (b); STM investigations (d).

tip was scanned over the surface to image the film at imaging conditions $I_t = 0.1\,\text{nA}$ and $U_t = 0.2\,\text{V}$. The recording of local I(V) curves was performed with an increased voltage by holding the tip-substrate distance defined by this imaging voltage and set tunneling current. As a reference, we registered $I(V)$ curves on bare Au(111). All $I(V)$ taken on the clean Au(111) substrate were symmetric and revealed a linear part between –0.5 and $+0.5\,\text{V}$ (are not shown here). On the top of the film, we registered the very reproducible $I(V)$ spectra for more than 20 images. An average value of ten of these curves is given by the solid graph in Figure 6c. The STM-measurements are carried out under ambient conditions. As compared to gold, the presented $I(V)$ curve reveals the rectifying behavior qualitatively similar to that measured between flat electrodes. The appearance of some peculiarities on the right part of the local $I(V)$ spectra (see two picks at 1.5 V and 1.7 V) can be attributed to the perturbation of molecular orbitals under the influence of a strong inhomogeneous electric field in the tunneling gap. The other peculiarities of this curve probably correspond to the tunneling levels of electrons generated by the mixing of the orbitals of gold and molecules.

5. CONCLUSIONS

The data presented above suggest the polymer macromolecules and oligomer compounds containing non-conjugated chromophores are promising templates for the design of molecular systems, whose functionality is determined by the specific energy level arrangements. Some of these systems (one-way excitonic and electronic conductors, diodes) based on organic molecules and biopolymer macromolecule fragments are demonstrated in this paper. Additional advantages of the proposed models for the description of excitonic and electronic processes as well as for a simple spectral testing of the system functionality take place.

The finding that the phosphorescence spectra of oligomer d(CCCGGGTTTAAA) practically coincide with the phosphorescence spectra of DNA suggests that the AT-sequences known to be the triplet traps in native DNAs are also the main triplet traps in the synthetic nucleotide-containing oligomer compound d(CCCGGGTTTAAA) and determine its phosphorescence.

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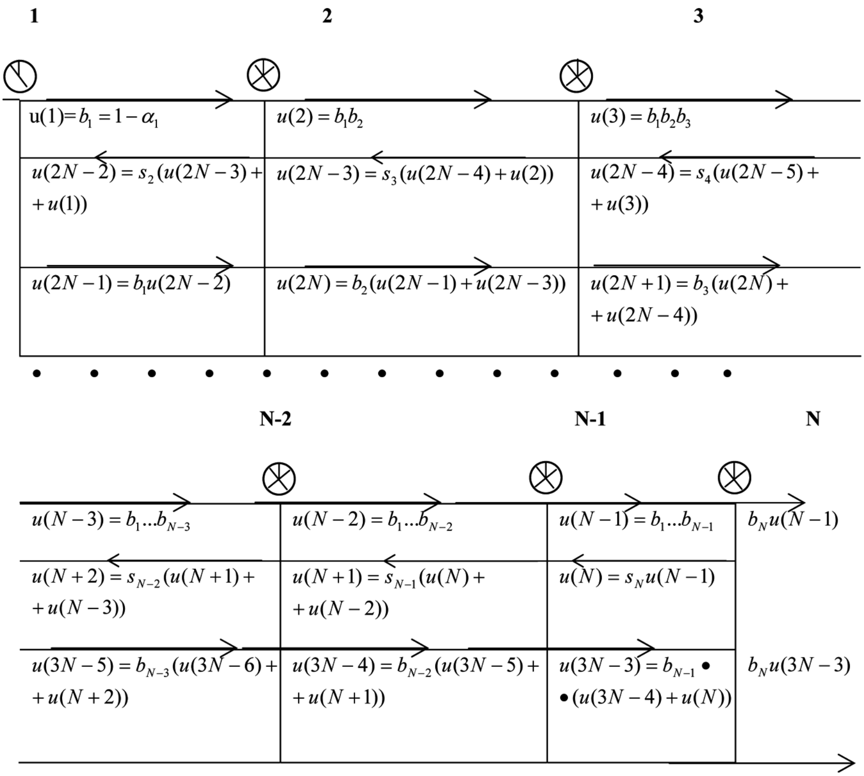
APPENDIX 1

Evaluation of the Exciton Current Losses Along a Macromolecule

In the real systems, the values of ΔE, as a rule, are different for different molecules. In addition, there is an indication of the reverse currents that can be considerable if $\Delta E \sim kT$. It is essential also to take into account the multistage migration of electronic excitations (despite the energy asymmetry of the system). An approach to the calculation of the exciton current losses in a model system that is close to a real functional molecule is given below.

Let us assume that a macromolecule is composed of N chromophore cells. The arrangement of the energy levels of these chromophores and the probabilities of quantum transitions are such that a photon with definite wavelength can excite only the 1-st cell. During its lifetime, the excitation can be transferred to the 2-nd cell with the probability $\beta_1 = 1 - \alpha_1$ or spontaneously vanish (be deactivated) with the probability α_1 by means of a radiative or non-radiative transition. The excitation localized in the 2-nd cell can be either transferred to the 3-rd cell with the probability $\beta_2 = 1 - \alpha_2$ or returned back to the 1st cell with the probability α_2. In addition, the excitation can also be spontaneously deactivated with the probability α_2. The same processes happen on the other cells of a macromolecule when the excitation reaches them.

The task consists in finding the relative quantity of excitations (generated in the 1-st cell) that reach the last cell of a macromolecule.



Let us arrange the N cells of a macromolecule (in Fig. 11, they are marked by daggers) along a straight line with identical distances between them. The excitations are spreading from left to right in the first row. Let us place the portion of these excitations in the «windows» of our simulation «stand» and designate them as $U(k)$. The first part of the excitations that will exit the first row will be equal to $\beta_N U(N-1)$. The second part of the excitations that will exit the second row will be equal to $\beta_N U(3N-3)$, and so on. The process of excitation spreading taking into account all the possible processes in every cell of a macromolecule is presented in Table 3.

The quantity of excitations exiting a macromolecule can be calculated by the formula

$$C = \beta_N \sum_{p=0}^{\infty} U(N-1+2(N-1)p).$$

The common term of the series, as implied by the «stand», is determined by the difference equation

$$U(n) = q_1(n)U(n-1) + q_2(n)U(2N-1+2(N-1)K-n),$$

where n varies from $(N-1)K+N$ to $(N-1)K+2N-2$ $(K=\overline{0,\infty})$. The coefficients in the difference equation are related to values of α_q and d_q by the following expressions:

$$q_1(N+2(N-1)l) = s_N, \quad q_1(2N-1+(2N-2)l) = \beta_1$$

$$q_2(N+(N-1)j) = 0_{(j,l=\overline{0,\infty})},$$

$$q_1(N+1+2(N-1)m+i) = q_2(N+1+2(N-1)m+i) = s_{N-1-i},$$

$$\begin{aligned} q_1(2N+2(N-1)m+i) &= q_2(2N+2(N-1)m+i) \\ &= \beta_{2+i}, (i=\overline{0,N-3}, m=\overline{0,\infty}) \end{aligned}.$$

The initial conditions for the difference equation are

$$U(1) = \beta_1, U(r) = \beta_r U(r-1), r = \overline{2,N-1}$$

Hence, $U(2) = \beta_1\beta_2$, $U(3) = \beta_1\beta_2\beta_3$, $\ldots$, $U(N-1) = \beta_1 \ldots \beta_{N-1}$.