

PHOSPHATE GROUPS AS ACTIVATING AND ENERGY SUPPLYING
MODULES FOR THE CONJUGATED IONIC-HYDROGEN BONDS SYSTEMS
IN NANOBIOSTRUCTURES

V.A.Karasev¹, V.V.Luchinin¹, V.E.Stefanov

¹*St.-Petersburg State Electrotechnical University, Prof. Popov str. 5, St.-Petersburg,
197376 Russia e-mail: cmid@eltech.ru*

²Department of Biochemistry, St.Petersburg State University, Universitetskaya nab. 7/9,
St.-Petersburg, 199034 Russia

The concept of Conjugated Ionic-Hydrogen Bonds Systems (CIHBS), developed by us [1], considers simple (R–Z) and resonance (Q–R=X) groups connected by hydrogen bonds as basis for construction of supramolecular nanobiostructures and channels for energy transfer in such structures. Earlier, HN–C=O-groups in proteins had been presumed to function as energy transfer channels in proteins. However, this prototype of the CIHBS-concept failed to receive general recognition, apparently, because not all elements, which can contribute to the CIHBS, were taken into account. Apart from HN–C=O-groups, these are C–N, C–O, C–S simple and N–C=N, O–C=O, N–C=S resonance groups, etc. that belong to the side chains of amino acids, nitrous bases and other biomolecules. We are going to focus on O–P=O-groups, which are invariably present in many biostructures, contributing to the formation of CIHBS. The following structures contain these groups:

- nucleoproteids;
- complexes of proteins with phospholipids;
- complexes of nucleotide triphosphates with proteins;
- complexes of dehydrogenases with nicotinamide cofactors;
- complexes of cyclic monophosphates with receptors;
- phosphoproteins.

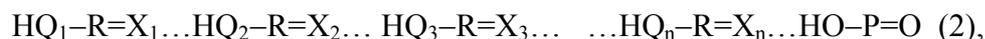
A question arises about the role of O–P=O-groups associated with CIHBS. Investigation of model crystals formed by analogs of phospholipids [2] may elucidate it. We obtained crystals of isobutyl-2-aminoethyl phosphate hydrochloride (IPE-HCl) and hydrobromide (IPE-HBr) and investigated them by means of X-ray analysis. The analysis revealed the occurrence of the following CIHBS's-zones in these crystals (scheme 1):



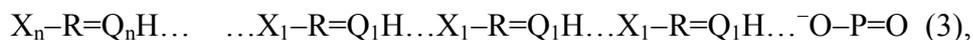
We studied electrophysical properties of the crystals. They manifested abnormally high dielectric permittivity (10^6) and low values of activation energy (0,7-1,3 eV for (IPE-HCl) and 0,4-0,6 eV for IPE-HBr at 20-70°C [2]. "Hopping" mechanism of conductivity, compatible with the model of energy transfer along SCIHB [1], was proposed to account for conductivity of the crystals.

Recently [3] the electronic structure of IPE-HCl crystal was calculated by Hartree-Fock (HF) LCAO non-empirical method as realized for periodic systems in the computer code CRYSTAL. The calculation showed that hydrogen atoms in systems of HO–P=O-groups possess the greatest positive value (+0.6e). The value of the positive charge of hydrogen atoms in the other groups of the molecule is significantly less (from 0.1e to 0.3e). The high value of the positive charge of hydrogen atoms in HO–P=O-groups suggests that these atoms are rather protons than covalently bonded atoms. Hence, they

should exhibit high mobility in such systems. Incorporation of HO–P=O-groups into CIHBS according (2):



or according (3) in case of $\text{O}^-\text{-P=O}$ -groups:



imparts greater mobility not only to protons contributing to bonding in $\text{R}=\text{X}_1\text{...HO-P=O}$ (scheme 2) or $\text{R-Q}_1\text{H...O}^-\text{-P=O}$ (scheme 3), but, due to cooperativity of CIHBS, also to those in all systems containing resonance groups. Thus, HO–P=O-groups can function as activating modules which render CIHBS potential channels for charge transfer. In addition, degradation of nucleotide triphosphates (ATP, GTP), accompanied by generation of negative charge, will contribute to delivery of the latter to CIHBS. We believe that it was just ignoring the role of HO–P=O-groups in CIHBS of proteins which caused skepticism about the idea of charge transfer along CIHBS. Undoubtedly, any artificially constructed bionic nanostructure should include HO–P=O-groups as important constituents.

Литература:

1. Karasev V.A., Luchinin V.V., Stefanov V.E. A model of molecular electronics used on the concept of Conjugated Ionic-Hydrogen Bond Systems. – Adv. Mater. Opt. Electron., 1994, V.4, pp. 203-218.
2. Karasev V.A., Korovnikova N.A., Miroshkin V.P., Luchinin V.V., Fundamensky V.S., Bannova I.I., Stefanov V.E. Crystals of phospholipids analogues as plausible material for molecular electronics. – Adv. Mater. Opt. Electron., 1996, V.6, pp. 1-14.
3. Evarestov R.A., Stefanov V.E., Karasev V.A., Bandura A.V. Quantum chemical calculations of crystalline model of biomembrane. – Int. J. Quant. Chem., 2004, V.96, pp. 106-115.