COMPARATIVE MOLECULAR DYNAMICS OF DIPEPTIDES AND THEIR HYDROCARBONACEOUS ANALOGUES

A.A. Belyakov and K.V. Shaitan
M.V. Lomonosov Moscow State University

Pairs of aminoacids residues, meeting in proteins, have a number of the specific dynamic characteristics distinguishing them from analogues, relatives on chemical structure compounds. For example, nonlinear collective modes formed with dihedral angles, existence of the large number isomorphic conformational degrees of freedom concern to such characteristics. Similar characteristics are caused by a specific structure of a hypersurface of free energy of these molecular structures. The contributions of various interactions to the structure of energy surface are unequal. It is obviously important to allocate interactions and the features of molecular structure giving the greatest contribution, and so causing special dynamic characteristics of natural aminoacids and their combinations.

In the present work the comparative analysis of some natural dipeptides and their hydrocarbonic analogues - the molecular systems having identical spatial structure, but consisting from only atoms of carbon - is carried out. It was chosen homodipeptides AlaAla, ValVal, LeuLeu, IleIle.

Calculations of dipeptides and their analogues have been carried out with use of packages of molecular dynamics PUMA and MoDyp, in forcefield AMBER96. Results received by two packages coincide with a high degree of accuracy. Calculations have been carried out at temperature 2500K with use collision thermostat and Berendsen's thermostat with step of integration 0.001 ps. The length of trajectories is 5000 ps. Such parameters of calculation allow to receive ergodic trajectories, therefore it is lawful to use estimations of average on time as estimations of average on ensemble.

Comparison of autocorrelation functions of dipeptides with hydrocarbonic analogues finds out existence of isomorphism on angles φ, χ. On angles ψ isomorphism it is not observed. It is possible to explain it increase of periodic factor of dihedral angles ψ from the two up to three at transition from dipeptides to hydrocarbonic analogues.

Crosscorrelation functions find out coincidence in two cases:

1) at absence crosscorrelation both at dipeptide, and at correspond analogue, and 2) in pairs angles $\varphi 1$-$\psi 1$, $\varphi 1$-$\chi 1$ at LeuLeu and its analogue. Crosscorrelation functions of angles $\varphi 1$-$\psi 1$, $\varphi 1$-$\chi 1$, $\varphi 2$-$\psi 2$, $\varphi 2$-$\chi 2$ IleIle, $\varphi 1$-$\psi 1$, $\varphi 2$-$\psi 2$ ValVal and their analogues have different signs. As a rule, crosscorrelation, if it is present, it is more expressed at dipeptides.

The analysis of maps of density of probability finds out regular structure of energy surfaces in analogues. Maps of natural dipeptides are more various topologically; there are "isthmuses" between sites. Such "isthmuses" cause presence marked crosscorrelations. The basic differences of maps of dipeptides from maps of the appropriate analogues are:

1) Splitting sites in the hydrocarbons, caused by increase of periodic factor of an angle ψ, 2) occurrence additional sites in hydrocarbons, 3) formation ring-shaped structures between sites of dipeptides.

On the whole, dipeptides have more different dynamic types then their hydrocarbonic analogues

Similar change of behaviour it is possible to explain both absence a carbonic dipole in peptide bond at hydrocarbonic analogues (in various versions of AMBER forcefield charges on atoms of carbon and oxygen have the order 0.59e and-0.56e accordingly), and change of periodic factor of torsion angles.

Comparison of dynamic characteristics charged dipeptides and dipeptides without charges finds out absence of conclusive influence of charges on symmetry in the present systems. It is possible to assume, that the leading part in infringement of symmetry and change of dynamic characteristics at transition from natural dipeptides to hydrocarbonic analogues belongs to decrease of periodic factor of torsion angles (mainly, corners $\psi 1$ and $\psi 2$).