EPSC
European Planetary Science Congress

Life Origination Hydrate Hypothesis (LOH-Hypothesis): the theory and procedure of simulation of basic DNA units in hydrate structure

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Abstract

Reasonable results concerning the arrangement of such elementary DNA units as nucleic bases, complementary pairs of bases, ribose, and nucleosides within the CH_4-hydrate structure II are simulated. The results provide a discussion on the origin of life and give new arguments in support of the «Hydrate hypothesis of living-matter origination» («LOH-Hypothesis») [1, 2].

1. Introduction

Clathrate hydrates are non-stoichiometric host–guest compounds, in which guest molecules of gases (or other chemical species of rather small dimensions) are held by van-der-Waals interactions within polyhedral cavities of the host water ice cage. It is the basic idea of the life emergence hypothesis [1, 2] that hydrates play the role of a template matrix (or a kind of 'nano-laboratory') to promote chemical self-assembling of primary DNA molecules. Previous arguments in support to this hypothesis were, in particular, based on the two-dimensional compatibility of the CH_4-hydrate and DNA structures [1, 2]. Here, we modify the earlier ideas and techniques [3–5] intended for three-dimensional computer simulations of crystallographic structures with the aim of creation of a procedure for housing single nucleic bases, their H-bonded pairs, ribose molecules and their complexes with bases, as well as of nucleosides within the cavities of hydrate crystals and testing the possibility of DNA housing within the three-dimensional H_2O-matrix of hydrate structure II.

2. Main technical improvements and testing of the procedure

Energy calculations for units of hydrate complexes were performed with semiempirical pair-wise atom–atom potential functions [3]. Interactions of host water molecules with each other were calculated with the TIP4P potential set [6] confirmed by MD simulations of solid ice polymorphs and liquid water. The 6-12 Lennard–Jones potentials proposed by Scheraga group [7] were used to model both the van-der-Waals interactions of H, C, N, and O atoms and N–H...O hydrogen bonding of guest units with one another and with water environment.

The aromatic nucleic bases were treated as rigid units, whereas ribose and deoxyribose molecules were regarded as flexible systems composed of several rigid fragments, such as $>CH_2$, $>CHO-$, and $-H$, connected with each other through a set of potentials of harmonic type. The long-range electrostatic forces were calculated with partial charges placed on atoms of all molecular units except water. The latter was modeled with a site charge shifted by 0.16 Å from the O-atom towards the molecular center-of-mass [6]. The atomic charges were derived by a least-square fit [3] from the quantum-mechanical electrostatic potential of the molecule calculated ab initio by the Hartree–Fock method with the basis function set 6-31G(d,p) [8]. Lattice energy sums were calculated with convergence acceleration [3, 9] by using the convergence constant $K_{conv} = 0.5$ and the cut-off parameters 9 Å and 0.5 Å^{-1} in direct and reciprocal spaces, respectively. Local energy minimizations were carried out with a quasi-Newton procedure [10]. The PMC program was used to perform energy calculations throughout the present work [11]. The host structures were based essentially on the experimental positions of O-atoms. A few thousand trial host configurations were built with molecular orientations selected at random from a list of 1080 sets of rotation matrices scanning total rotation space in a regular way and were minimized by energy. The energy minima were sorted by energy with all non-unique solutions screened out by using program CRYCOM [3]. All H-bonds demonstrated nearly linear geometry with the O...H distances very close to those observed in the water ice polymorphs.

The set of non-bonded potentials [6, 7] and harmonic force field parameters was assessed for prediction of the guanosine dihydrate crystal structure. The energy minimized structure was found to be close to the experimentally observed one. Thus, the r.m.s. change in the unit cell constants *a*, *b*, and *c* is -2.5%. On the whole, the test showed that the model works fairly well in the prediction of essential features of hydrated nucleoside structures.

The clathrate hydrate complexes were constructed in the following way. The ground-state hydrogen-ordered configuration of water molecules with both cubic (I and II) and hexagonal type of oxygen-atoms arrangement were used throughout the calculations as principal host structures. The mass center of a guest molecule was placed in the center of a polyhedron cavity. In the case of a nitrogen-base pair or a nucleoside molecule, two adjacent cavities were explored by filling them in with both components of the pair. The same operation was performed with single nucleoside molecules whose base and ribose components entered into separate adjacent cavities of large and small sizes, respectively. To prevent the occurrence of extremely short interatomic contacts on entering the guest molecule (giving rise to a collapse of minimization process at early iteration steps), the starting host structure was stretched out in three dimensions by a factor of 1.5, thus increasing all intermolecular distances. Such a trial structure was then energy-minimized, with the six unit cell dimensions and $6(N_w+N_f)$ rigid body parameters of N_w water molecules and N_f fragments of the guest molecule having been treated as independent optimized parameters. This procedure has been carried out with multiple trial models, which involved variation of mutual orientation of molecular units and torsion angles in ribose and nucleoside molecule.

3. Summary and Conclusions

Structure simulations of hydrates show the remarkable ability of polyhedral hydrogen bonded network to adapt its configuration in response to violations caused by entering of guest molecule into a host cavity. In particular, we find that the water molecules of the shell of the cavity and of the nearest environment rearrange themselves in a cooperative way to minimize stresses resulting from intermolecular contacts of water with guest. Notably, such a rearrangement does not destroy principal topology of the hydrogen-bonded network whereas particular geometric parameters partially modify. In the equilibrium state, the host–guest structure is stabilized over the parent host structure by host–guest van-der-Waals and electrostatic interactions.

Acknowledgements

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