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The nature of hydrogen bonds with divalent selenium compounds

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ABSTRACT

Electronic structure of hydrogen bonded complexes of several organoselenium compounds was studied by means of the quantum chemistry methods (HF, DFT, MP2). Energy, geometric and spectral properties of the complexes justify the formation of weak hydrogen bond with selenium atom. However, the detailed analysis of orbital characteristics and the features of electronic distribution by means of topological parameters and integrated atomic properties included in Koch–Popelier criteria of hydrogen bond formation revealed similarities and differences in the properties of complexes with the Se...H bonds in comparison with traditional H-complexes, in which electronegative atoms of the second-row act as proton acceptors. The observed peculiarities of Se...H contacts can be explained by unusual electrostatic repulsion between Se and H atoms opposite to classical N...H or O...H contact and greater stabilization effect of charge transfer in the former. Se...H interaction is also characterized by greater covalence in comparison with conventional H-bonds.

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1. Introduction

At present organoselenium compounds attract great attention, mostly because of their high biological activity and promising applications in medicine [1,2]. There is no doubt that high biological activity of organoselenium compounds is tightly connected with their participation in intermolecular interactions, in particular with their complex formation ability. Also an amount of works devoted to theoretical investigations of complexation of organoselenium compounds has significantly increased [3,4].

Despite of the fact that great interest has recently arisen in the nature of unconventional hydrogen bonds [5–8], only a few thorough theoretical works are available where hydrogen bonds with selenium atoms of Se...H type are studied, and the nature of the interaction is characterized [3]. In our opinion, H-complexation with selenium atom should be more comprehensively investigated, since just the intermolecular interactions of this type play important role in biological systems. We are interested in clarification of the general and specific features in the structure of H-complexes of organoselenium compounds in comparison with ordinary proton acceptors.

In this work, we studied complexes of organic compounds of divalent selenium – dimethylselenide (I), methylselenocyanate (II), dimethyldiselenide (III) – with methanol, where selenium atom is (or potentially can be) the proton acceptor and methanol – proton donor. In the organoselenium compounds one of the substituents – methyl group – is constant and the other one varies

with the aim to estimate and analyze the influence of the structure factors on the ability of organoselenium compounds to be electron donor in the reactions of complexation. Classical molecular orbital approach, natural bonding orbital (NBO) method [9] and Bader's quantum theory of atoms in molecules [10] were used.

2. Computational details

Quantum-chemical calculations were performed with the Gaussian 03 program package [11] and GAMESS US package [12] by Density Functional Theory [13–16], *ab initio* Hartree–Fock and Møller–Plesset second-order perturbation methods [17] with different basis sets. All the structures of individual selenides and their complexes were obtained in the course of full geometry optimization; stationary points were characterized as minima by corresponding eigenvalues of the energy hessian. Searching for global minima by geometry optimization was performed with the use of numerous initial geometries acceptable from chemical point of view. The most representative results for isolated molecules and complexes are collected in Tables S1 and S2 in Supplementary data.

Electron density analysis in the framework of the quantum theory of atoms in molecules (QTAIM) was performed by AIMAll 10.05.04 program package [18] and MORPHY98 program [19]. Natural bonding orbitals analysis was performed by standard procedure implemented in Gaussian 03 [20].

Basis set superposition error in complexes was taken into account with counterpoise (CP) correction method of Boys and Bernardi [21] in the process of geometry optimization [22]. Geometry, frequencies and electronic density distribution calculations at the MP2/6-311++G(d,p) level discussed in the paper were carried

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