Theoretical study of optical activity of 1:1 hydrogen bond complexes of water with S-warfarin

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The molecular interaction between S-warfarin (SW) and a single water molecule was investigated using the B3LYP method at 6-311+ +G(d,p) basis set. The vibrational spectra of the optimized complexes have been investigated for stabilization checking. Quantum theories of atoms in molecules, natural bond orbitals, molecular electrostatic potentials and energy decomposition analysis methods have been applied to analyze the intermolecular interactions. The intermolecular charge transfer in the most stable complex is in the opposite direction from those in the other complexes. The optical spectra and the hyperpolarizabilities of SW-water hydrogen bond complexes have been computed.

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1. Introduction

Coumarin and its derivatives have great therapeutic potential and pharmacological activities [1–5]. Additionally, coumarin and its derivatives have been used as chromophores of fluorescent ion indicators in biological systems [6], optical brightening agents [7], dyes for lasers and dye-sensitized solar cell [8]. So, they are of significant interest because of their capacity to fluorescence. Although coumarin itself has a fairly low fluorescence [9], the use of different substituents on the coumarin structure can greatly influence its fluorescence properties [10–13]. The nature and position of substituents is important for the fluorescence behavior of these compounds, and many spectroscopic and theoretical studies have been undertaken to characterize the photophysical behavior of these substances [14–16].

Warfarin is a fluorescent coumarin derivative which has great clinical significance and is the highly potent anticoagulant [17,18]. It acts on the liver to block recycling of vitamin K and inhibit the vitamin K-dependent blood clotting factor synthesis [19].

Warfarin belongs structurally to the 3-substituted-4-hydroxy coumarins which consist of a benzene ring fused with a pyrone ring. The carbonyl group is attached at C-2 position, substitution group in position 3 and hydroxyl group in position 4. The substitution in making warfarin is methyl styryl ketone (or benzylideneacetone). As it is seen in the Fig. 1, warfarin has an asymmetric carbon atom and is mainly available as a racemic mixture of R-warfarin and S-warfarin. Activity and metabolism are markedly dissimilar for the two enantiomers and it is well demonstrated that S-warfarin is 3–5 times more potent than R-warfarin in producing an anticoagulant response [20,21]. Also, it is more stable than R-warfarin [22].

As mentioned above, the interaction of warfarin with other materials, such as a range of proteins and model systems [23–33], is highly interesting, because, for instance, the therapeutic efficacy, the specific biological activities and pharmacological properties of the warfarin were found to be influenced by interaction with metal ions or other materials and drugs. Various quantum chemical calculations for warfarin have been previously reported in literature [22,32,34–38].

In many chemical and biochemical systems, one of the most important interactions is hydrogen bond, which is responsible for the formation and function of cell membranes [39,40]. A hydrogen bond is defined as an interaction between two electronegative atoms, donor and acceptor, via an intermediate hydrogen atom that is covalently connected to the donor [41]. The properties of hydrogen bonds have been widely investigated, both theoretically and experimentally [42,43].

In this work influence of hydrogen bond interaction of a single water molecule on the S-warfarin structural and optical properties in Density Functional Theory (DFT) method has been studied. Since probability to access to the global minimum of potential energy surface or the most stable geometry of this compound by a single simple optimization is low, and with respect to that the possible interactions are hydrophilic and hydrogenic interactions, so it was tried to put water molecule near different sites with the most probability of hydrogen bonding.