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

Mehrdad Dadsetani [a], Ahmad Abdolmaleki [a], Abedin Zabardasti [b,*]

[a] Department of Physics, Lorestan University, Khorramabad, Iran
[b] Department of Chemistry, Lorestan University, Khorramabad, Iran

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ABSTRACT

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

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* Corresponding author.
E-mail address: zebardasti@yahoo.com (A. Zabardasti).

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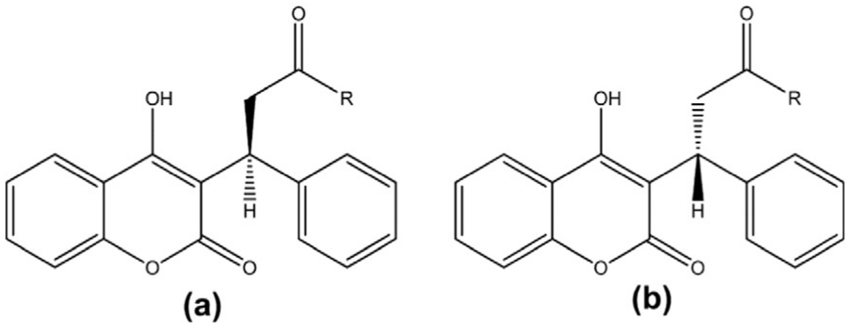

Fig. 1. Structure of (a) *S*-warfarin and (b) *R*-warfarin.

and in this way, 9 different initial geometries for SW-water hydrogen bond complexes were built and optimized.

1.1. Computational methods

Calculations were performed using the Gaussian 03 package [44]. In order to predict the optimized geometries of isolated *S*-warfarin (SW) and water molecules as well as SW-water complexes, the Density Functional Theory (DFT) hybrid method with the Becke's three-parameter exchange functional and gradient-corrected functional of Lee, Yang and Parr (B3LYP) [45–48] was used. The geometries were optimized using the following standard basis set: 6-311++G(d,p), valence triple zeta plus diffuse and polarization functions of d and p type. It is generally recognized that for an accurate description of hydrogen bonds at least double zeta quality basis augmented with a set of polarization and diffuse functions set is needed. Therefore a somewhat better geometry description is expected with 6-311++G(d,p) standard basis set. All geometry optimizations were followed by calculations of frequencies in order to confirm obtained structures as energy minima (no imaginary frequencies) and also to evaluate zero-point vibrational energies (ZPVE). The counterpoise procedure [49–51] was used to correct the interaction energy for basis set superposition error (BSSE). NBO analysis of all structures was done using NBO [52–54] program as implemented in the Gaussian program package. The atoms in molecules (AIM) theory [55,56] implemented within Multiwfn [57] package are applied here to analyze the characteristics of the intermolecular interactions and bond properties in studied complexes. The energy decomposition analysis (EDA) was done at the B3LYP-D3/TZP level of theory using the program package ADF (2010.2) [58,59], which is based on the work by Ziegler and Rauk [60] and Morokuma [61].

The nonlinear optics (NLO) activity provide the key functions for frequency shifting, optical modulation, optical switching and optical logic for the developing technologies in areas such as communication, signal processing and optical interconnections [62,63]. Nonlinear optics deals with the interaction of applied electromagnetic fields in various materials to generate new electromagnetic fields, altered in wavenumber, phase, or other physical properties [64]. It is well known that the higher values of dipole moment, polarizability, and hyperpolarizability are important for more active NLO properties. The components of β_0 are defined as the coefficients in the Taylor series expansion of the energy in the external electric field. When the external electric field is weak and homogeneous this expansion becomes:

$$E = E_0 - \mu_i F_i - \frac{1}{2}\alpha_{ij} F_i F_j - \frac{1}{6}\beta_{ijk} F_i F_j F_k + \ldots$$

where E_0 is the energy of the unperturbed molecules, F_i is the field at the origin and μ_i, α_{ij}, β_{ijk} are the components of dipole moment, polarizability, and first hyperpolarizability respectively. The total dipole moment (μ_0), the mean polarizability ($|\alpha_0|$), the anisotropy of the polarizability ($\Delta\alpha$) and the total first hyperpolarizability (β_0) using x, y, z components are defined as [65]

$$\mu_0 = \left(\mu_x^2 + \mu_y^2 + \mu_z^2\right)^{\frac{1}{2}}$$
$$|\alpha_0| = \frac{1}{2}\left(\alpha_{xx} + \alpha_{yy} + \alpha_{zz}\right)$$
$$\Delta\alpha = \frac{1}{\sqrt{2}}\left[\left(\alpha_{xx} - \alpha_{yy}\right)^2 + \left(\alpha_{yy} - \alpha_{zz}\right)^2 + \left(\alpha_{zz} - \alpha_{xx}\right)^2 + 6\alpha_{xy}^2 + 6\alpha_{xz}^2 + 6\alpha_{yz}^2\right]^{\frac{1}{2}}$$
$$\beta_0 = \left(\beta_x^2 + \beta_y^2 + \beta_z^2\right)^{\frac{1}{2}}$$

where

$$\beta_i = \beta_{iii} + \frac{1}{3}\sum\nolimits_{i \neq j}\left(\beta_{ijj} + \beta_{jij} + \beta_{jji}\right).$$

The polarizability and hyperpolarizability tensors were obtained by a polar job in Gaussian.

For the calculation of the optical absorption spectra, the time-dependent density functional theory (TDDFT) method using a frequency-domain Casida [66] model as implemented in the real space, pseudopotential code Octopus [67], was employed. The spacing parameter of 0.125 Å and a spherical box with radius of 4 Å for each atom has been used in all the calculations. The GGA/PBE [68] exchange-correlation functional and Troullier-Martins pseudopotential [69] are used. We used 90 unoccupied orbitals in Casida calculation.

2. Results and discussions

Association of one molecule of warfarin with one molecule of water leads to the formation of 1:1 dimer complexes which assigned as F1–F5. The optimized geometries of considered adducts are depicted in Fig. 2.

DFT calculation was performed for the SW and the optimized structure is in good agreement with another computational work as listed in Table 2.

The zero point vibrational energies (ZPVE), the basis set superposition errors (BSSE) and the corrected and uncorrected stabilization energies of all of the structures are given in Table 1. The most stable complex is F1 and also the other complexes are numbered in order of their stabilization energies. As it can be seen, all stabilization energies are negative, so the SW-water complexes are more stable than separate isolated SW and water molecules.

The bond lengths of optimized geometries are given in Table 2. Major geometrical variations for SW in different complexes are at middle rings (R2) and the branch contain C2═O3 bond. Also the most number of variations was occurred in the backbone of the most stable complex, i.e. F1.

According to NBO analysis, in F1, the electron density from the lone pairs of O40 atom of water transferred to the σ^* orbital of O23-H39 bond of SW. This charge transfer leads to a reduction in the strength of O23-

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