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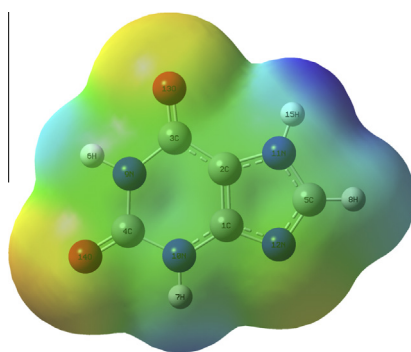
Investigation of solvent polarity effect on molecular structure and vibrational spectrum of xanthine with the aid of quantum chemical computations

Turgay Polat^{a,*}, Gurcan Yildirim^b^aKastamonu University, Department of Physics, Kastamonu 37100, Turkey^bAbant İzzet Baysal University, Department of Mechanical Engineering, Bolu 14280, Turkey

HIGHLIGHTS

- Strong intra-molecular charge transfer in the xanthine molecule.
- Role of different medium polarity on the geometric structure and vibrational spectra.
- Determination of the assignments of fundamental vibrational modes belonging to the title molecule.
- Improvement of the correlation between the theoretical and experimental geometric structure.

GRAPHICAL ABSTRACT



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ABSTRACT

The main scope of this study is to determine the effects of 8 solvents on the geometric structure and vibrational spectra of the title compound, xanthine, by means of the DFT/B3LYP level of theory in the combination with the polarizable conductor continuum model (CPCM) for the first time. After determination of the most-steady state (favored structure) of the xanthine molecule, the role of the solvent polarity on the SCF energy (for the molecule stability), atomic charges (for charge distribution) and dipole moments (for molecular charge transfer) belonging to tautomer is discussed in detail. The results obtained indicate not only the presence of the hydrogen bonding and strong intra-molecular charge transfer (ICT) in the compound but the increment of the molecule stability with the solvent polarity, as well. Moreover, it is noted that the optimized geometric parameters and the theoretical vibrational frequencies are in good agreement with the available experimental results found in the literature. In fact, the correlations between the experimental and theoretical findings for the molecular structures improve with the enhancement of the solvent polarity. At the same time, the dimer forms of the xanthine compound are simulated to describe the effect of intermolecular hydrogen bonding on the molecular geometry and vibrational frequencies. It is found that the C=O and N–H stretching vibrations shift regularly to lower frequency value with higher IR intensity as the dielectric medium enhances systematically due to the intermolecular N–H...O hydrogen bonds. Theoretical vibrational spectra are also assigned based on the potential energy distribution (PED) using the VEDA 4 program.

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Introduction

Xanthines, being a class of purine bases, are common agrochemical and therapeutic agents, and easily oxidized to uric acid

* Corresponding author. Tel.: +90 366 280 19 30; fax: +90 366 215 49 69.

E-mail address: tpolat@kastamonu.edu.tr (T. Polat).

and methyl uric acid [1]. Thus, they have pharmacologic properties stimulating the central nervous system and relax smooth muscles. Moreover, the xanthine compounds can be found in most human body tissues, fluids and other organisms. The unchecked level of xanthine in our human body may lead to kidney stone formation, urinary tract disease and muscle diseases. The treatments can be achieved avoiding the foods and drinks containing xanthine and its derivatives (coffee, tea and colas) [2], because a number of mild stimulants are derived from the xanthines such as caffeine, theophylline and theobromine. Even, the former (caffeine) is the most well-known natural psychoactive substance [3]. Xanthine derivatives are also occasionally found as the components of some pharmaceutical preparations such as formulations being used to alleviate neonatal apnea; or to treat the asthmatic manifestations and chronic obstructive pulmonary disease [4]. In the literature, the researchers have been interested in both experimental and theoretical studies on the xanthine and its derivatives for several years [5–13]. For example; Uçun et al. have calculated the molecular structures, vibrational frequencies and corresponding vibrational assignments of xanthine and its methyl derivatives [14]. In 2011, the vibrational wavenumbers, geometrical parameters, modes of vibrations and other thermodynamic parameters of xanthine molecule were investigated by the scientists, Arivazhagan and Jeyavijayan [2]. To the best of our knowledge, there have been no theoretical DFT calculations including the solvent effects on the molecular structure and vibrational spectra of xanthine and its dimers. Furthermore, solvent-induced vibrational frequency shifts have attracted interest for many years owing to the existence of significant information on chemical bonding and solute–solvent interactions. As well known, the intra-molecular frequency shifts are determined by the normal coordinate-dependent parts of the attractive and repulsive interactions between solute and solvent molecules [15]. At the same time, the tautomeric equilibria affecting the chemical and biological properties of the organic molecules are significantly sensitive to the environmental influences [16–20]. In the exhaustive work, we survey not only the tautomerism mechanism but also the solvent effects on the optimized molecular structure and vibrational spectra of the xanthine compound in detail. The changes of dipole moments and charges on atoms are also investigated both in the gaseous phase and in different solvents. The dimeric forms of xanthine are also analyzed to deduce the effect of intermolecular hydrogen bonding on the molecular geometry and vibrational frequencies. Further, the vibrational modes are assigned based on the potential energy distribution (PED) using the VEDA 4 program.

Computational details

Density functional theory (DFT) calculations lead to the prediction of more accurate molecular structure and vibrational frequencies than the conventional ab initio Hartree-Fock calculations [21–24]. The B3LYP method based on Becke's three parameter hybrids functional combined with the Lee–Yang–Parr correlation functional (B3LYP) of DFT yields a good definition of harmonic vibrational frequencies for small and medium sized molecules [25–27].

All the calculations are performed using Gaussian 09 program [28] with GaussView 5 molecular visualization program package [29]. The optimized structure parameters and vibrational frequencies are calculated by using B3LYP method at 6-311++G (d,p) basis set. The values of the natural bond orbital (NBO) [30] atomic charges on the atoms and dipole moments are obtained with the B3LYP method in the Gaussian 09 package. The nonspecific solvent effects of the solvent medium are studied by means of the conductor-polarizable continuum model (CPCM) [31].

Force field scaling is exerted via the selective scaling in the natural internal coordinate representation based on SQM procedure [32–35]. Besides, VEDA-4 program [36] is preferred to determine

the transformation of the force field and subsequent normal coordinate analysis including the least square refinement of the scaling factors, calculations of the potential energy distribution (PED) and the prediction of IR and Raman intensities.

At the same time, Raman activities (A_R) are converted to the relative Raman intensities (I_{IR}) by means of the following equation inferred from the basic theory Raman scattering [37,38],

$$I_i = \frac{f(v_0 - v_i)^4 S_i}{v_i [1 - \exp(-hc v_i / KT)]}$$

where h , c and k present the universal constants and f is properly chosen as common normalization factor for the intensities when v_0 (cm^{-1}) denotes the exciting frequency and v_i depicts the vibrational wave number of the normal mode.

Results and discussion

Energy analysis and tautomeric stability

As well known, the different molecular structures belonging to a compound affect seriously its physical and chemical properties [39]. In the comprehensive study, the molecular energies of 28 tautomeric and conformer forms of the xanthine molecule are computed by means of the B3LYP/6-311++G (d,p) calculation level to find the favored conformation (most steady state) of the title compound as given in Fig. 1. The characteristic parameters such as the total energy (in Hartrees), ZPE corrected energy, relative energy ($\text{kcal}\cdot\text{mol}^{-1}$), dipole moment (Debye) and imaginary frequency values are listed in Table 1. Of the 28 structures for xanthine molecule, the lowest energy value of $E_{\text{Hartree}} = -562.607505$ a.u. in gas phase is attributed to the tautomer-10. In forthcoming sections, the theoretical values belonging to the favored tautomer-10 will thus be taken for correlation and further discussions. Fig. 2 shows the molecular structure along with the atom-numbering scheme for the tautomer studied.

Fig. 3 shows the calculated potential energy curves for the tautomers and conformations of xanthine. The shape of the potential energy as a function of the hydrogen atom transferring is illustrated in Fig. 3. Generally, the potential energy curve of a molecule is plotted as a function of the dihedral angle from 0° to 360° using a step of 10° . In this work, the main difference between the most stable two tautomers is a hydrogen atom transferring from N12 atom to N11 one, which increases the total energy value. Therefore, in order to investigate the most stable tautomer of xanthine, potential energy scans are performed without the dihedral angle. It is to be mentioned here that the differences between the energy parameters of the most stable two tautomers (tautomer-10 and tautomer-1) are found to be about $9.12 \text{ kcal mol}^{-1}$ for the total energy and $8.60 \text{ kcal mol}^{-1}$ for zero point corrected energy, respectively. The energy difference stems from a hydrogen atom transferring from N12 atom to N11 one. The main difference between the most stable and less stable tautomers is 0.058333 Hartree. At first glance, the main reason of the energy distribution seems to be the hydrogen atom orientation relative to the nearest group. For this reason, we investigated whether the most stable tautomer-10 result from formation of $\text{H}\cdots\text{O}$ contact (intramolecular hydrogen bonding-like interaction) or not. Because the calculated $\text{H}\cdots\text{O}$ distances are approximately 2.4 \AA , we have concluded that hydrogen bonding-like interactions does not responsible for stability of tautomer-10 but hydrogen atom transferring and long-range electrostatic interactions can be responsible for it due to the fact.

The dipole moment values are also different from each other as a consequence of the change of the charge distribution in the molecule is another interesting point. The dipole moment values of each tautomer studied in this work are tabulated in Table 1. It is

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