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Spectroscopic investigations and quantum chemical computational study of (*E*)-4-methoxy-2-[(p-tolylimino)methyl]phenol

Basak Kosar*, Cigdem Albayrak

Department of Science Education, Sinop University, Sinop 57010, Turkey

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ABSTRACT

In this work the electronic structure of (*E*)-4-methoxy-2-[(p-tolylimino)methyl]phenol has been characterized by the B3LYP/6-31G(d) level by using density functional theory. The experimental infrared and electronic absorption spectra have been obtained and compared with the theoretically obtained ones. Molecular electrostatic potential map has been evaluated; natural bond orbital and frontier molecular orbitals analysis have been performed from the optimized geometry. The energetic behavior of the title compound has been examined in solvent media using polarizable continuum model. The non-linear optical properties have been computed with the same level of theory. In addition, the changes of thermodynamic properties have been obtained in the range of 100–500 K.

1. Introduction

Schiff bases are compounds having C=N double bond and formed by reaction of a primary amine and an aldehyde. The most commonly studied class of compounds are *o*-hydroxy Schiff base derivatives. *o*-Hydroxy Schiff bases have attracted the interest of chemists and physicist because of their photochromic and thermochromic features in the solid state [1]. These features are caused by an intramolecular proton transfer associated with a change in π-electron configuration from the hydroxyl O atom to the imine N atom and occur under the influence of light for photochromic and temperature for thermochromic Schiff bases. It has been suggested that the molecules showing photochromism are non-planar and showing thermochromism are planar [2,3]. Schiff bases are used as starting materials in the synthesis of important drugs such as antibiotics, antiallergics, antitumors and antifungals because of their biological activities [4,5]. They have also widely used as ligands in the field of coordination chemistry [6,7]. In addition, their non-linear properties have an importance for the design of various molecular electronic devices such as optical switches and optical data storage devices [8,9].

o-Hydroxy Schiff bases exist as enol [10,11], keto [12,13] or zwitterionic form [14,15] in solid state. Depending on their forms, three types of strong intramolecular hydrogen bonds are possible in *o*-hydroxy Schiff bases: (a) O–H···N in enol-imine and (b) N–H···O in keto-amine tautomers and (c) N^+–H···O^- in zwitterionic forms (see Fig. 1).

In recent years, among the computational methods calculating the electronic structure of molecular systems, DFT has been favorite one due to its great accuracy in reproducing the experimental values of in molecule geometry, vibrational frequencies, atomic charges, dipole moment, etc. [16–18]. The X-ray crystallography of (*E*)-4-methoxy-2-[(p-tolylimino)methyl]phenol has been studied in our previous publication [19]. Related to this phenomenon, we wish to present here the spectroscopic properties and electronic structure of (*E*)-4-methoxy-2-[(p-tolylimino)methyl]phenol.

2. Material and methods

FT-IR spectrum of the title compound was recorded on a Bruker 2000 spectrometer in KBr disk. Absorption spectra were recorded on a Thermo Scientific BioGenesis UV-Vis spectrometer using a 1 cm path length of the quartz cell at room temperature.

In computational procedure, the geometry optimization of the molecule leading to energy minima was achieved with the B3LYP hybrid exchange-correlation functional [20,21] and the 6-31G(d) basis set [22,23]. For the modeling, the calculations were started with the crystallographically obtained geometry of the molecule [19]. At the optimized geometry for the title molecule no imaginary frequency modes were obtained, so there is a true minimum on the potential energy surface was found. All calculations were carried out using the Gaussian03W software package [24] and GaussView visualization program [25] on a personal computer. In order to investigate the energetic behavior and dipole moments of the title compound in various solvents, we performed optimization in the

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* Corresponding author. Tel.: +90 538 9513150; fax: +90 368 2715530.
E-mail address: bkosar@sinop.edu.tr (B. Kosar).

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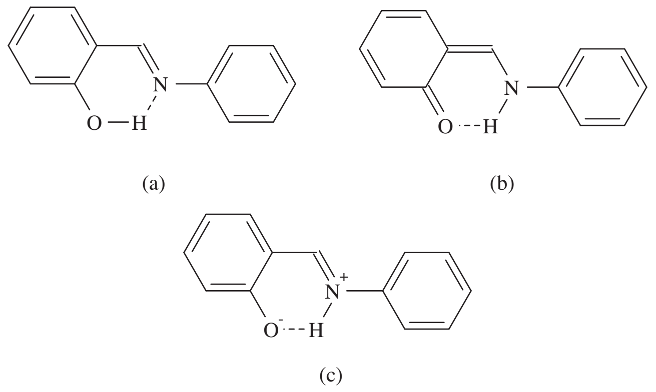

Fig. 1. (a) Enol, (b) keto and (c) zwitterionic forms of *o*-hydroxy Schiff bases.

four different kinds of solvent (dimethyl sulfoxide $\varepsilon = 46.7$, ethanol $\varepsilon = 24.3$, chloroform $\varepsilon = 4.8$ and benzene $\varepsilon = 2.3$) by using polarizable continuum model (PCM) for the molecule [26]. The reactive behavior of the molecule was examined with the help of the molecular electrostatic potential (MEP) map.

In order to show the non-linear optical (NLO) activity of the molecule, the linear polarizability and first hyperpolarizability were obtained by molecular polarizabilities using polar=ENONLY input to Gaussian03W with the same level of theory. Also, the frontier molecular orbitals (FMO) and natural bond orbital (NBO) analyses were performed because of their relationships with the non-linear optical activity of the molecule. For the NBO calculations NBO 3.1 program [27] as implemented in Gaussian03W package was used.

The changes in the thermodynamic functions entropy, enthalpy and the heat capacity were investigated for the different temperatures from the vibrational frequencies calculations.

In addition, to calculate the excitation energies of the molecule, TD-DFT calculations started from gas phase and solution phase optimized geometries were carried out using the same level of theory. Also gas-phase vibrational frequency analysis of the molecule was performed with the same level of theory and the vibrational band assignments have been made using the GaussView visualization program.

3. Results and discussion

3.1. Optimized molecular geometry

(*E*)-4-Methoxy-2-[(p-tolylimino)methyl]phenol crystallize in monoclinic space group $P2_1/c$, the crystal structure parameters of the title molecule are $a = 21.1680(9)$ Å, $b = 4.7844(2)$ Å, $c = 12.2759(3)$ Å and $\beta = 92.859(3)°$, and molecule adopts the enol-imine tautomeric form rather than the keto-amine tautomeric form [19].

The selected optimized geometrical bond lengths, bond angles and torsion angles are listed in Table 1 with the X-ray experimental counterparts for comparison. As can be seen from Table 1, the maximum deviance from the experimental value is 24.79° and belongs to torsion angle C8–N1–C9–C14. The torsion angle C8–N1–C9–C14 is one of the angles controlling the planarity of molecule. Therefore, the aromatic ring orientations in two counterparts are different related to controller torsion angles. The dihedral angle between the ring C1/C6 and C9/C14 is 5.46(11)° for X-ray geometry and 34.42° for gas phase optimized geometry.

For a visual comparison, the molecular structure and superimposition of the experimental and theoretical molecule skeletons are shown in Fig. 2(a) and (b), respectively. In the title molecule, there is a strong hydrogen bond observed between the atoms O1 and N1 [19]. The geometry of this bond is also determined for the optimized geometry and the D–H, H···A, D···A and D–H···A values are 0.99 Å, 1.76 Å, 2.65 Å and 147.12°, respectively.

Table 1
Selected geometric parameters from X-ray diffraction and DFT calculation.

Parameters	X-ray[a]	B3LYP/6-31G(d)
Bond lengths (Å)		
C1–C8	1.4514 (16)	1.4517
C2–O1	1.3509 (15)	1.3466
C5–O2	1.3741 (15)	1.3714
O2–C7	1.4130 (17)	1.4163
C8–N1	1.2757 (15)	1.2918
N1–C9	1.4194 (15)	1.4079
Bond angles (°)		
O1–C2–C3	119.41 (11)	118.80
O1–C2–C1	121.45 (11)	122.41
C5–O2–C7	117.30 (11)	118.00
O2–C5–C4	124.94 (11)	124.82
O2–C5–C6	115.88 (11)	116.21
C1–C8–N1	122.08 (11)	122.41
C8–N1–C9	121.40 (10)	121.32
Torsion angles (°)		
C6–C1–C8–N1	177.85 (11)	−179.68
C1–C8–N1–C9	−179.19 (10)	−177.40
C8–N1–C9–C14	−173.10 (11)	−148.31

[a] Experimental values are taken from Ref. [19].

Against this background, despite the good harmony between the geometries of counterparts, somewhat differences were observed for bond length, bond angle and torsion angle values between the results from X-ray experimental study and DFT calculation. These differences are caused by handling the molecule in experimental and computational processes. While the experimental results belong to the solid-crystal phase, during theoretical calculations molecule is considered in gas phase.

Investigating the molecular electrostatic potential (MEP) generated in the space around a molecule by the charge distribution is very helpful in understanding the sites for electrophilic attacks and nucleophilic reactions for the study of biological recognition process [28] and hydrogen bonding interactions [29]. The electrostatic potential, $V(\vec{r})$ at any point $\vec{r}$ is given by Eq. (1) [28]:

$$V(\vec{r}) = \sum_A \frac{Z_A}{|\vec{R}_A - \vec{r}|} - \int \frac{\rho(\vec{r}\,')d\vec{r}\,'}{|\vec{r}\,' - \vec{r}|} \qquad (1)$$

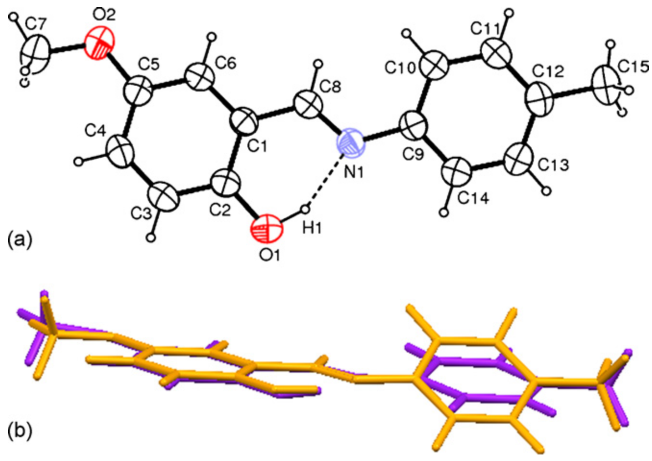

Fig. 2. (a) Atom numbering scheme [19] and (b) superimposition of the X-ray structure (purple) and calculated structure (orange) of the title molecule. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of the article.)