Experimental (X-ray, IR and UV–vis.) and DFT studies on cocrystallization of two tautomers of a novel Schiff base compound

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A B S T R A C T

In this study, the structure of 4-(((2-methyl-3-nitrophenyl)imino)methyl)benzene-1,2,3-triol was investigated with experimental (X-ray single crystal technique, UV–vis. and FT-IR spectroscopic techniques) and theoretical (DFT) methods. X-ray studies show that there are two independent molecules in asymmetric unit and coexist both keto-amin and enol-imine tautomeric forms. Theoretical studies were carried out in B3LYP with CAM-631G(d,p). The data obtained from calculation were compared with experimental data.

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1. Introduction

Schiff bases (RHC=NR) obtained by the condensation reaction of primary amines with aldehydes or ketones under proper circumstances are named after Hugo Schiff [1–3]. Schiff base derivatives have received considerable attention due to its easy to obtain and multiple uses [4]. The versatility of applications derives from the presence of carbon-nitrogen double bond [5]. Schiff bases have a wide variety of applications in many areas such as analytical, biological, and inorganic chemistry [6]. In the literature, the Schiff bases possess biological activity such as anti-fungal, anti-bacteria, anti-microbial have been reported [2,5–10]. Moreover, Schiff bases are used in the control and measurement of radiation intensity, display systems, optical devices, and widely as a ligand in the co-ordination chemistry [9,11,12].

There are many studies about tautomerization of the Schif bases. In general, Schiff bases have two possible tautomeric forms, the enol-imine (OH) and the keto-amine (NH) forms. Depending on the tautomers, two types of intramolecular hydrogen bonds are observed in Schiff bases: O—H⋯N in enol-imine and N—H⋯O in keto–amine tautomers. Another form of Schiff base compounds is zwitterionic form that is rarely seen. The characteristic property of this form is the presence of ionic N$^+$—H⋯O hydrogen bond [13–16].

In the present study, the molecular structure of the title compound is revealed by using X-ray diffraction technique. When the data obtained from diffraction are evaluated, it is seen that enol-imine tautomer and keto-amine tautomer are coexist in the asymmetric unit.

Additionally, we studied the title compound by using spectroscopic technics (FT-IR and UV–vis.) and theoretical technic [DFT-CAM-B3LYP/6-31G(d,p)]. The CAM (Coulomb-attenuating method)-B3LYP is a functional combines the hybrid features of B3LYP and the long-range correction [17]. The functional was designed to get over the difficulties including: (i) the polarizability of long chains, (ii) excitations for Rydberg states, (iii) charge-transfer excitations [17–19].

2. Experimental

2.1. Synthesis of the compound

2,3,4-trihydroxybenzaldehyde (0.02 g, 0.012 mmol) was added to a solution of 2-methyl-3-nitroaniline (0.019 g, 0.012 mmol) in ethanol (100 ml). The reaction mixture was stirred for 18 h under reflux. Single crystals suitable for X-ray analysis were obtained

from ethyl alcohol by slow evaporation (yield 65%; m.p. 213 °C) (Fig. 1).

FT-IR spectrum of the title compound was recorded on a Bruker 2000 spectrometer using KBr pellet. UV–vis absorption spectrum was recorded on a Thermo scientific BioGenesis UV–vis. spectrometer using a 1 cm path length of the cell.

Single crystal X-ray data were collected on an Agilent SuperNova diffractometer with an Eos CCD detector using Mo Kα radiation ($\lambda = 0.71073$ Å). The CrysAlisPro software [20] was used for data collection, cell refinement and data reduction. The structure was solved by direct methods using the program SHELXS97 [21]. All non-hydrogen atoms were refined anisotropically by full-matrix least-squares methods. Hydrogen atoms except hydrogen bonded to O1B were placed in geometrically idealized positions and refined as riding atoms with $U_{iso}(H) = 1.2U_{eq}(C, N)$ and $U_{iso} = 1.5U_{eq}(C)$. Program(s) used to refine the structure: SHELXL97 [21]; molecular graphic: ORTEP-3 for Windows [22] and Mercury [23]; prepare material for publication: WINGX [22]. Details of crystal data, data collection, structure solutions and refinements were given in Table 1.

2.2. Computational procedure

All calculations in this work have been done Gauss View molecular visualization program and Gaussian 09 [24,25] program package. Starting geometry of molecule was taken from X-ray refinement data. The molecular structure of the crystal in the ground state was optimized by using Coulomb Attenuating Method (CAM-B3LYP) [17] and basis set 6-31G(d,p).

In DFT calculations, hybrid functional was also used, the Becke's three parameter functional (B3) [26,27] which defines the exchange functional as the linear combination of Hartre-Fock, local and gradient corrected exchange terms. The B3 hybrid functional was used in combination with the correlation functional of Lee, Yang and Parr [28]. Vibrational frequencies of the molecule were computed by using CAM-B3LYP/6-31G(d,p) level. The calculated frequencies were scaled by 0.9587 [29]. For UV–vis. computations, the optical band gaps in ethanol solvent were calculated using the time dependent DFT (TD-DFT) method at the CAM-B3LYP/6-31G(d,p) level [30–32]. In addition, the distributions and energy levels of HOMO-LUMO orbitals were calculated using DFT method and with similar hybrid functional and basis set.

3. Results and discussion

3.1. Crystal structure and aromaticity

There are two crystallographically independent molecules labeled as A and B in the asymmetric unit (Fig. 2). The unit contains two well-known tautomeric forms for Schiff bases, synchronously. This is an uncommon situation but there are little study in the literature [12,33,34]. C7–N1 and C1–O1 bond distances that are indicative for Schiff bases are 1.321(5) and 1.292(4) for molecule A, 1.303(5) and 1.322(5) for molecule B. These bond distances show that while molecule A has keto-amine character, molecule B has enol-imine character. The selected geometric parameters were

Table 1
Crystal data and structure refinement parameters for the title compound.

Empirical formula	$C_{14}H_{12}N_2O_5$
Formula weight	288.26
Temperature (K)	296
Crystal system, Space group	Monoclinic, $P2_1/n$
a (Å)	12.4396 (6)
b (Å)	14.5655 (6)
c (Å)	14.4251 (7)
β (°)	94.910 (4)
V (Å^3)	2604.1 (2)
Z	8
Absorption coefficient (mm^{-1})	0.11
Dcalc (Mg m^{-3})	1.470
Theta range for data collection (°)	3.6–30.4
Measured reflections	12245
Independent reflections	5114
Absorption correction	multi-scan (based on symmetry-related measurements)
R_{int}	0.020
$R[F^2-2\sigma(F^2)]$	0.089
$wR(F^2)$	0.290
S	1.07
$\Delta\rho_{max}(e\ Å^{-3})$	1.50
$\Delta\rho_{min}(e\ Å^{-3})$	−0.74

given in Table 2. The dihedral angles between the aromatic rings for A and B molecules are 7.03 (11)°, 8.13 (12)°, respectively.

HOMA (Harmonic Oscillator Model of Aromaticity) is a geometric approach to the aromaticity concept. The value of HOMA index is calculated depending on the experimental CC-bond lengths in the ring.

$$HOMA = 1 - \frac{\alpha}{n} \sum_{i=1}^{n} \left(R_i - R_{opt}\right)^2 \qquad (1)$$

where R_i and R_{opt} represent experimental and optimum bond distances of ith ring bond for the studied ring, respectively. The n is the number of the bonds in the ring and the α is a normalization factor which provides that HOMA equal to 1 for aromatic compounds and 0 for non-aromatic Kekuè structures. In the present study, the molecular moiety studied on aromaticity is benzene ring. The optimum C–C bond distance is 1.388 Å and α is 257.7 [35–37].

Harmonic oscillator model of aromaticity (HOMA) index is also an important parameter to define tautomer. In the OH tautomeric form, the index of o-hydroxy benzene ring closes to 1 which means that the ring is aromatic. However, the index deviates from 1 in NH tautomeric form. In the present study, the indexes of C1/6 and C8/13 rings were calculated as 0.759 and 0.975 for molecule A, 0.912 and 0.948 for molecule B. It is understood from these values that, while the benzene ring includes O atom in o-position of molecule A wanders from aromaticity, other rings are aromatic. These findings are also support that molecule A has keto-amine tautomeric form and molecule B has enol-imine tautomeric form.

Intra-molecular N1A–H1A···O1A and O1B–H1B···N1A hydrogen bonds which are characteristic for Schiff bases generate S(6) rings. Intra-molecular O2–H2···O1 and O3–H3···O2 hydrogen bonds between hydroxy parts of molecules generate S(5) rings
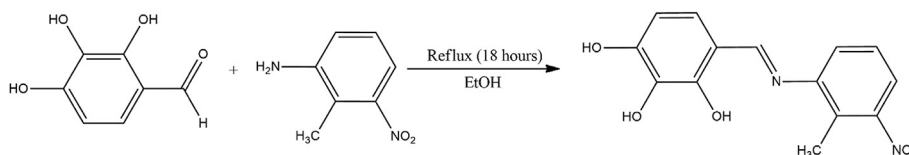

Fig. 1. Synthesis of 4-(((2-methyl-3-nitrophenyl)imino)methyl)benzene-1,2,3-triol.