The synthesis, characterization and theoretical study on nicotinic acid [1-(2,3-dihydroxyphenyl)methylidene]hydrazide

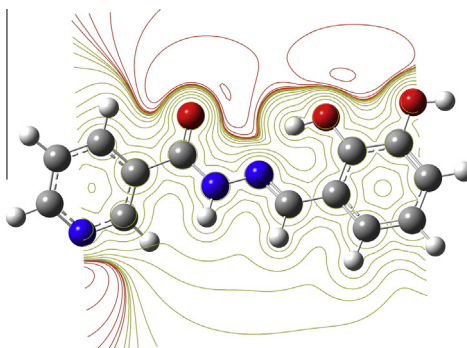Necmi Dege [a], Nuray Şenyüz [b], Hümeyra Batı [b], Nergin Günay [c], Davut Avcı [c,*], Ömer Tamer [c], Yusuf Atalay [c]

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HIGHLIGHTS

- The title compound was solved by means of X-ray diffraction, FT-IR and NMR.
- HOMO–LUMO analysis, charge distributions and the total electron density were investigated.
- The NLO and NBO analysis were carried out.
- This paper presents a combined experimental and theoretical investigation.

GRAPHICAL ABSTRACT

The contour map of electrostatic potential (ESP) surfaces for nicotinic acid [1-(2,3-dihydroxyphenyl)methylidene]hydrazide (obtained from B3LYP/6-311++G(d,p) level).

ARTICLE INFO

ABSTRACT

In this study, we reported a combined experimental and theoretical study on nicotinic acid [1-(2,3-dihydroxyphenyl)methylidene]hydrazide ($C_{13}H_{11}N_3O_3$) molecule. The title compound was prepared and characterized by ^1H and ^{13}C FT-NMR, FT-IR and single-crystal X-ray diffraction. The compound crystallizes in the monoclinic space group $P2_1/c$ with $a = 6.2681(3)$ Å, $b = 16.5309(7)$ Å, $c = 12.4197(6)$ Å, $\alpha = 90°$, $\beta = 111.603(4)°$, $\gamma = 90°$ and $Z = 4$. In addition, the molecular geometry, vibrational frequencies, gauge including atomic orbital (GIAO), continuous set of gauge transformations (CSGT), individual gauges for atoms in molecules (IGAIM) ^1H and ^{13}C NMR chemical shift values, natural bond orbital (NBO), nonlinear optical (NLO) and HOMO–LUMO analyses, molecular electrostatic potentials (MEPs) and thermodynamic properties of the title compound in the ground state were investigated by using Hartree–Fock (HF) and density functional theory (DFT/B3LYP) methods with 6-311++G(d,p). Besides, the hardness and electronegativity parameters were obtained from HOMO and LUMO energies. Obtained results indicate that there is a good agreement between the experimental and theoretical data.

Introduction

Compounds which include XC = NY structure are known as Schiff bases, which are usually synthesized from the condensation of primary amines and active carbonyl groups. Schiff bases are used as starting materials in the synthesis of important drugs, such as antibiotics and antiallergic, antiphlogistic, and antitumor substances [1]. In recent years, schiff bases have been intensively investigated in many fields of chemistry and biochemistry, because of their coordination properties, diverse applications and versatile metal binding ability [2,3].

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Hydrazones have been utilized for the determination of carbonyl compounds [4,5] and they play an important role in inorganic chemistry, because they easily form stable complexes with many of the transition metal ions. Interest in hydrazone complexes has risen with the development of the field of bioinorganic chemistry, since it was recognized that many of these complexes may serve as models for biologically important species [6]. It is reported that hydrazones (R-CO—NH—N=CH-R′) derived from condensation of isonicotinic acid hydrazide and pyridine aldehydes exhibit better antitubercular activity than INH [7–9]. In this study, we present the crystal structure of the title compound, which is a product of the condensation reaction of isonicotinic acid hydrazide with pyridine aldehydes.

We present the results of a detailed investigation of the synthesis and structural characterization of nicotinic acid [1-(2,3-dihydroxyphenyl)methylidene]hydrazide using single crystal X-ray, FT-IR, NMR and quantum chemical methods. The GIAO, CSGT, IGAIM ^{1}H and ^{13}C NMR chemical shifts of the title compound in the ground state have been calculated by using the HF and DFT/B3LYP methods with 6-311++G(d,p) basis set. The calculated geometric parameters (bond lengths and bond angles), vibrational frequencies, ^{13}C and ^{1}H NMR chemical shifts values for the mentioned compound are consistent with the experimental data. Furthermore, the highest occupied molecular orbital (HOMO) and the lowest unoccupied molecular orbital (LUMO) have been simulated, and the transition states, energy band gaps and molecular electrostatic potential (MEP) maps for the title compound have been determined using *ab initio* calculations. Additionally, we also report NBO, NLO and thermodynamic properties of the title compound.

Experimental procedure

Synthesis

Nicotinic acid hydrazide (0.20 g, 1.5 mmol) was dissolved in hot anhydrous ethanol (15 ml). To this solution was added dropwise 2,3-dihydroxy benzaldehyde (0.21 g, 1.5 mmol) in anhydrous ethanol (15 ml) and one drop of triethylamine. The reaction mixture was refluxed for 4 h. A yellow product formed was separated by filtration and washed with ethanol. The solid product was recrystallized from methanol-acetonitrile (2:1) to give crystals of the title compound (yield 35%, m.p. 198–200 °C).

Materials and measurements

Elemental analyses were performed using standard methods at TUBİTAK (The Turkish Scientific Research Centre). The IR spectrum was recorded on a Vertex 80v sample Compartment RT-DLaTGS spectrophotometer operating within 4000–500 cm^{-1}. ^{1}H NMR and ^{13}C NMR spectra were obtained using BRUKER DPX-400, 400 MHz High Performance Digital FT-NMR spectrometer in *DMSO-d_6* solvent.

X-ray crystal structure determination

A pale yellow crystal of size $0.55 \times 0.43 \times 0.20$ mm^3 was chosen for crystallographic study and then carefully mounted on goniometer of a STOE IPDS II diffractometer. All diffraction measurements were performed at 296 K using graphite monochromated Mo Kα radiation (λ = 0.71073 Å).

Data collection

X-AREA [10]; the cell parameters were determined by using X-AREA software; data reduction: X-RED32 [10]; the crystal structure was solved by direct methods using SHELXS-97 [11]; program(s) used to refine structure: SHELXL97 [12]; molecular plot was pre-

pared with ORTEP III for Windows [13]; WinGX software [14] was used to prepare material for publication. All H atoms attached to C atoms and N atoms were fixed geometrically and treated as riding with C—H = 0.97 Å (methyl), N—H = 0.90 Å (amino), N—H = 0.860 Å and C—H = 0.930 Å, Uiso(H) = 1.1 Ueq (CH$_2$, NH$_2$, NH and CH). Details of the data collection conditions and parameters of refinement process are given in Table 1.

Computational procedure

In this study, all calculations were carried out with the GaussView [15] molecular visualization program and Gaussian 03W [16] package program on personal computer. The optimized molecular structure, vibrational frequencies, ^{1}H and ^{13}C NMR chemical shifts of the title compound in ground state have been calculated by using HF and B3LYP (Becke's three-parameter hybrid model using the Lee-Yang Parr correlation functional) [17,18] methods with 6-311++G(d,p) basis set. Additionally, NBO analysis, transition energy (HOMO–LUMO) and thermodynamic properties of the title compound have been calculated using B3LYP/6-311++G(d,p) level. The optimized structural parameters are used in the vibrational frequency calculations at HF and DFT levels. The calculated positive values of vibrational wavenumbers indicate that the optimized molecular structures are stable, but the wavenumber values obtained at these levels contain the systematic errors [19]. Therefore, the calculated vibrational wavenumbers were scaled by 0.9555 and 0.9970 for HF/6-311++G(d,p) and B3LYP/6-311++G(d,p) methods, respectively [20]. At the same time, the orbital shapes (HOMO and LUMO) and the MEPs of the mentioned compound in 3D (3-dimensional) were plotted at B3LYP/6-311G(d,p) level. Furthermore, the NBO charge plot of the title compound was plotted at B3LYP/6-311++G(d,p) level. Also, the dipole

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

Crystal data	
Chemical formula	$C_{13}H_{11}N_3O_3$
M_r	257.25
Temperature (K)	293
Wavelength (Å)	0.71073
Cell setting	Monoclinic
Space group	$P2_1/c$
a (Å)	6.2681 (3)
b (Å)	16.5309 (7)
c (Å)	12.4197 (6)
α (°)	90.00
β (°)	111.603 (4)
γ (°)	90.00
V (Å^3)	1196.50 (10)
Z	4
Radiation type	Mo Kα
μ (mm^{-1})	0.11
Crystal form, color	Prism, pale yellow
Crystal size (mm^3)	$0.55 \times 0.43 \times 0.20$
Data collection	
Diffractometer	STOE IPDS 2
Data collection method	Rotation method
Measured reflections	19619
Independent, observed reflections	2745, 2368
Criterion for observed reflections	$I > 2\sigma(I)$
θ_{max}, R_{int}	27.5°, 0.027
T_{min}, T_{max}	0.937, 0.982
Refinement	
$R[F^2 > 2\sigma(F^2)]$, $wR(F^2)$, S	0.035, 0.097, 1.06
Reflections	2745
Parameters	217
Extinction method	SHELXL
Extinction coefficient	0.012 (2)
$\Delta\rho_{max}$ (e/Å^{-3})	0.21
$\Delta\rho_{min}$ (e/Å^{-3})	−0.14