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Synthesis, molecular structure, spectroscopic and theoretical studies on E-2-

ethoxy-4-[(4-ethoxyphenylimino)methyl]phenol

Celal Tuğrul Zeyrek^a*, Gökhan Alpaslan^b, Hamit Alyar^c, Mustafa Yıldız^d, Nefise Dilek^e, Hüseyin Ünver^{f**}

^aAnkara Nuclear Research and Training Center, Turkish Atomic Energy Authority, TR-06100 Besevler-Ankara, Turkey.

^bDepartment of Medical Services and Techniques, Vocational School of Health Services, Giresun University, TR-28200 Giresun, Turkey.

^cDepartment of Physics, Science and Art Faculty Karatekin University, TR-18100 Çankırı, Turkey.

^dDepartment of Chemistry, Faculty of Sciences and Arts, Çanakkale Onsekiz Mart University, TR-17100 Çanakkale, Turkey.

^eDepartment of Physics, Faculty of Sciences and Arts, University of Aksaray, TR-68100, Aksaray, Turkey.

^fDepartment of Physics, Faculty of Sciences, University of Ankara, TR-06100 Besevler-Ankara, Turkey.

*Corresponding author. Tel.: +90-312-2126230; fax: +90-312-2226421

E-mail address: zeyrek@taek.gov.tr, cteyrek@gmail.com

**Corresponding author. *Tel.*: +90-312-2126720 - 1106; fax: +90-312-2232395

E-mail address: unverh@ankara.edu.tr, huseyinunverr@gmail.com

Abstract

Synthesis, crystallographic characterization, spectroscopic (FT-IR) and density functional modelling studies of a new Schiff base E-2-ethoxy-4-[(4-ethoxyphenylimino)methyl]phenol $C_{17}H_{19}NO_3$ have been reported. The molecular structure obtained from X-ray single-crystal analysis of the investigated compound in the ground state has been compared using Hartree-Fock (HF) and density functional theory (DFT), B3LYP and B1B95 functional with the 6-311++G(d,p) basis set. In addition to the optimized geometrical structures, atomic charges, molecular electrostatic potential (MEP), natural bond orbital (NBO), nonlinear optical (NLO) effects and thermodynamic properties of the compound have been investigated by using DFT calculations. The electronic properties of the title compound in solvent media were also examined using the DFT calculations. The potential energy surface (PES) scans about important torsion angles are performed by using B3LYP/6-311++G (d,p) level of theoretical approximation for the compound. The experimental (FT-IR) and calculated vibrational frequencies (using DFT calculations) of the title compound have been compared. The predicted NLO properties of the compound which calculated by the B3LYP method with 6-31G(d), 6-31+G(d,p), 6-31++G(d,p), 6-311+G(d) and 6-31G(d), 6-31+G(d,p), 6311++G(d,p) basis sets are greater than ones urea. The standard thermodynamic functions were obtained for the title compound with the temperature ranging from 200 to 450 K.

Keywords: Schiff base; Crystal structure; PES scan; Density functional theory; FT-IR, Nonlinear

optical effects.

1. Introduction

Schiff-bases are known azomethines and they having a double C=N bond and usually synthesized from the condensation of primary amines and active carbonyl groups. Schiff bases exhibit mainly interest as corrosion inhibitors, catalyst carriers, thermo-stable materials, metal complexion agents and in biological systems and they have a wide range of applications, such as dyes and pigments [1–9]. Several Schiff bases have nonlinear optical (NLO) behavior [10-13]. They have been under investigation the last years, since their potential applicability in optical communications. We reported previously the spectroscopic studies, nonlinear optical (NLO) properties and crystal structures of several Schiff base compounds [14-20]. Density functional theory (DFT) is widely used methods in the computational quantum chemistry by using ab initio calculation of electronic structures of many-particle systems. Many molecular properties are calculated and revealed according to the development of better and better exchange-correlation functional method [21]. In the literature, the DFT calculations has a great accuracy in reproducing the experimental values in geometry, dipole moment, vibrational frequency, excited states of organic compounds [21-23]. Recently, the synthesis, structure, spectroscopic and DFT modelling studies of 1-[(4-ethoxyphenylimino)methyl]napthalene-2-ol has been studied by our research group [20]. In the present work, firstly we present the synthesis, crystal structure and Fourier transform infrared spectroscopy (FT-IR) of a new Schiff base E-2-ethoxy-4-[(4ethoxyphenylimino)methyl]phenol. The molecular structure, the potential energy surface (PES) scans, vibrational frequencies assignments, atomic charges, molecular electrostatic potential (MEP), natural bond orbital (NBO), nonlinear optical (NLO) effects and thermodynamic properties of the compound have been investigated by using DFT calculations. Theoretical geometrical parameters and frequencies were compared with the corresponding experimental results.

2. Materials and methods

2.1 General techniques

Elementary analyses were performed on a Vario EL III CHNS elemental analyzer. The infrared spectra of the investigated compound were recorded in the 4000–400 cm⁻¹ region using KBr pellets on a MATTSON-1000 model FT-IR spectrometer. A suitable single crystal of the title compound was mounted on goniometer and data were collected at 296 K on a Bruker Kappa APEXII CCD diffractometer using graphite monochromated MoK α radiation (λ =0.71073 Å).

2.2. Synthesis of the compound

3-Ethoxy-4-hydroxybenzaldehyde, 4-ethoxyaniline, CHCl₃, n-pentane and ethanol were purchased from Merck (Germany). A solution of 3-ethoxy-4-hydroxybenzaldehyde (0.005 mol, 0.83 g) in 50 mL pure ethanol was prepared and heated to the boiling temperature. 4-Ethoxyaniline (0.005 mol, 0.69 g) was dissolved in 60 mL hot ethanol. A mixture of the two solutions was then refluxed for 1 h. The yellow crystals were formed during the reflux. The yellow precipitate was collected by filtration, and then washed with cold ethanol. It was recrystallized from CHCl₃ : n-pentane (3:1). C₁₇H₁₉NO₃ (285.14): calcd. C 71.54; H 6.66; N, 4.90; found C 71.53, H 6.67, N 4.90. The chemical diagram of the molecule is shown in Figure S1 (supplementary material). The suitable single crystals were obtained directly from the synthesis of the compound. Formula; C₁₇H₁₉NO₃, Yield; 92 %. Carbon, nitrogen and hydrogen analyses were within \pm 0.4% of theoretical values.

2.3. X-ray structure determination

Cell parameters of the compound were determined by using SAINT software [24]. Absorption correction ($\mu = 0.08 \text{ mm}^{-1}$) was obtained by the multi-scan method via SADAPS V2012/1 [25] software. Details of the data collection conditions and the parameters of the

refinement process are given in Table 1. The compound is solved by direct methods using SHELXS-97 [26] and refined with SHELXL-97 [27]. The molecular figures are prepared by the help of Mercury and ORTEP3 program packages [28, 29]. The atoms of ethoxy groups are disordered over two positions. For C1A, C2A, C33A, C34A, O2A and O6A atoms the site occupancy factor is 0.656(9) and for C1B, C2B, C33B, C34B, O2B and O6B atoms the site occupancy factor is 0.344(9). Crystallographic data (excluding structure factors) for the structure reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as 19 Supplementary Publication No. CCDC 1036031¹.

2.4. Calculation details

The molecular geometry of the compound is directly taken from the X-ray diffraction experimental result of the geometry optimization. This result was used at in the Gaussian 09 software package and the Gauss-view visualization program [30,31] for the DFT calculations with Becke's Three-parameter Hybrid Functional Using the Lee-Yang-Parr (LYP) Correlation Functional B3LYP at the 6-31G(d), 6-31+G(d,p), 6-31++G(d,p), 6-311+G(d) and 6-311++G(d,p) basis sets by using the Berny method [32, 33]. The optimized structure parameters of the title compound were calculated by using Hartree-Fock (HF) and density functional theory (DFT) with the functional B3LYP and B1B95 using the 6-311++G(d,p) basis set.

The Mulliken atomic charges and natural population analysis (NPA) for the included H atoms of the compound were calculated at B3LYP/6-311++G(d,p) level by NBO analysis [34].

In order to investigate the solvent effect selected five kinds of solvent ($\epsilon = 4.9$, chloroform; ε =10.36, dichloroethane; ε =24.55, ethanol; ε =46.7, dimethylsulfoxide and ε =78.39 water), the atomic charge distributions of the compound were also calculated at B3LYP/6-311++G(d,p) level by using a Polarized Continuum (PCM) model [35].

To investigate the reactive sites and to identify sites of intra- and intermolecular interactions of the compound, molecular electrostatic potential surface was evaluated by using B3LYP/6-311++G(d,p) method.

The HOMO and LUMO are the main orbitals taking part in chemical stability. The HOMO represents the ability to donate an electron, LUMO as an electron acceptor representing the ability to obtain an electron. The total molecular energies, HOMO and LUMO energies and HOMO-LUMO band gaps were predicted by the B3LYP/6-311++G(d,p) level.

The chemical hardness is useful to rationalize the relative stability and reactivity of chemical compounds. There are large HOMO–LUMO gap in the hard compounds and more stable and less reactive than soft compounds having small HOMO–LUMO gap [36]. The definitions of universal concepts of molecular structure stability and reactivity can be provided by using DFT method [37]. For definition of hardness η , following equation developed [38, 39];

$$\eta = \frac{1}{2}(I - A) \tag{1}$$

In the equation (1) I is the vertical ionization energy and A stands for the vertical electron affinity. According to the Koopmans theorem [40], the ionization energy and electron affinity can be equalized through HOMO and LUMO orbital energies:

$$EA = -\varepsilon_{HOMO}$$
(2)
$$IP = -\varepsilon_{LUMO}$$

According to the equation (2), the hardness corresponds to the gap between the HOMO and LUMO orbitals. Hence, the larger the HOMO-LUMO energy gaps the harder molecule.

$$\eta = \frac{1}{2} (\varepsilon_{LUMO} - \varepsilon_{HOMO}) \tag{3}$$

For the title compound, the chemical hardness (η) were calculated with the B3LYP/6-311++G(d,p) base sets.

The stabilization energies of the compound were computed by using second-order perturbation theory for examined the intra- and intermolecular interactions among bonds and also

investigated charge transfer and conjugative interactions in the molecular system of the investigated compound. The stabilization energy $E^{(2)}$ connected with electron delocalization between donor NBO_(i) and acceptor NBO_(i) were estimated as [41]

$$E^{(2)} = -q_i \frac{(F_{ij})^2}{\varepsilon_i - \varepsilon_i}$$
(4)

where q_i is the donor orbital occupancy, ε_i , ε_j are diagonal elements (orbital energies) and F_{ij} is the off-diagonal NBO Fock matrix element. B3LYP/6-311++G(d,p) level was used for second-order perturbation theory analysis of the Fock matrix.

Thanthiriwatte and Nalin de Silva were explained in detail previously that how is the calculations of the total dipole moment (μ_{tot}), linear polarizability (α_{ij}), and the first-order hyperpolarizability (β_{ijk}) from the Gaussian output file [42]. The total molecular dipole moment (μ_{tot}), linear polarizability (α_{ij}), and the first-order hyperpolarizability (β_{ijk}) was predicted by the B3LYP method with different base sets 6-31G(d), 6-31+G(d,p), 6-31++G(d,p), 6-311++G(d) and 6-311++G(d,p) for investigating the effects of basis sets on the NLO properties.

The natural bond orbital (NBO) analysis of the title compound was fulfilled at the B3LYP/6-311++G(d,p) level by means of the NBO 3.1 program within the Gaussian 09 package [43].

It is well-known that the vibrational wavenumbers obtained by DFT computations usually overestimate than their experimental counterpart. These discrepancies can be corrected either by computing anharmonic corrections or by introducing a scaled field. In order to compensate these systematic errors and also to get precise vibrational wavenumbers for the investigated compound in solid phase, we calibrated the vibrational wavenumbers by using a scale factor group for individual primitive internal coordinates at B3LYP/6-311++G(d,p) level of theory. The scale factor values used in the scaled quantum mechanics force field (SQMFF) methodology [44]. The assignments of each vibrational mode were defined from their potential energy distributions

(PED) which were calculated by using SQM program [45]. The visual check for the vibrational band assignments were also performed by using Gauss-View molecular visualization program.

Finally, the standard thermodynamic functions were obtained from statistical thermodynamics based on the vibrational frequency analysis at B3LYP/6-311++G(d,p) level at the Gaussian 09 software package.

3. Results and discussions

3.1. Description of the crystal structure

The title compound, an *Ortep-3* view which is shown in Figure 1, crystallizes in the monoclinic space group *Pbca* with Z = 16 in the unit cell. The asymmetric unit of the title compound contains two independent molecules, namely (I) and (II), which are linked by a O–H…N hydrogen bond. Both the molecules have an *E* conformation about the central C=N bond. While molecule (I) in the asymmetric unit is non-planar, molecule (II) is almost planar. The dihedral angles between the two phenyl ring systems are 27.79(6)° and 5.07(7)°, respectively, for molecules (I) and (II). In the azomethine groups, the N1–C9 distance is 1.269(3) Å for molecule (I) and N2–C26 distance is 1.271(3)Å for molecule (II). The bond lengths and bond angles of the title compound are in a good agreement with those of the related structures [46-50]. The obtained geometric parameters from X-ray study are given in Table 2. In crystal structure of the title compound, there are two intermolecular hydrogen bonds. The donor and acceptor distances are 3.454(3) Å for C12–H12…O3ⁱ [symmetry code (i): -*x*, -*y*+3, -*z*,] and 2.958(3) Å for O4–H4…N1ⁱⁱ [symmetry code (ii): *x*, *y*-1, *z*.], respectively (Figure 2 and Figure 3). The details of the hydrogen bonds are summarized in Table 3.

3.2. Optimized molecular structure

The molecular structure of *E*-2-ethoxy-4-[(4-ethoxyphenylimino)methyl]phenol has been experimentally determined. The optimized structure parameters such as bond lengths, bond angles,

and dihedral angles of the title compound were calculated by using Hartree-Fock (HF) and density functional theory (DFT) with the functional B3LYP and B1B95 using the 6-311++G(d,p) basis set. The calculated bond distances, bond angles and selected torsion angles are compared with the experimental values of the title compound (Table 2). The conformational discrepancies between the X-ray structure and optimized counterparts by using Hartree-Fock (HF), the B1B95 and the B3LYP functional with 6-311++G(d,p) basis set can be seen from Figure S2 (supplementary material).

As seen from Table 2 and Figure S2 (supplementary material), when the X-ray structure of the title compound is compared with its optimized counterparts, slight conformational discrepancies are observed between them. The most significant structural disparities are found in the orientation of 3-Ethoxy-4-hydroxybenzaldehyde ring (ring1) in the compound. This structural disparity is defined by torsion angles C5–C9–N1–C10 [172.97(19)°], C9–N1–C10–C15 [-17.9(3)°], and C6–C5–C9–N1 [173.4(2)°] for experimentally. These torsion angles are the orientation of the aldehyde ring (ring1) part with respect to the 4-ethoxyaniline ring (ring2) part, and have been calculated for the investigated compound at 178.236, -43.252, 178.626° for the HF/6-311++G(d,p) level, 176.454, -38.543, and 178.013° for the B1B95/6-311++G(d,p) level and 176.661, -37.503, and 178.460° for the B3LYP/6-311++G(d,p) level.

The ring1 part and ring2 part are inclined at the angle of $27.8(1)^{\circ}$ with respect to one another for experimentally, whereas this angle has been calculated as $44.1(6)^{\circ}$ for the HF/6-311++G(d,p) level, $41.1(6)^{\circ}$ for the B1B95/6-311++G(d,p) level, and $39.2(6)^{\circ}$ for the B3LYP/6-311++G(d,p) level.

The bond lengths of C9–N1 [1.269(3) Å] and C26–N2 [1.271(3) Å] have a double bond character. These bond lengths are predicted by the bond lengths of 1.2538 Å for HF, 1.2735 Å for B1B95 and 1.2791 Å for B3LYP level.

It is well known that DFT-optimized bond lengths are usually longer and more accurate than HF due to the inclusion of electron correlation [19, 20, 51]. According to our calculations

(Table 2), the biggest difference between experimental and calculated bond lengths is about 0.0242 Å for HF, 0.0320 Å for B1B95, and 0.0390 Å for B3LYP level, while the root mean square error (RMSE) is found to be 0.0235 Å for HF, 0.0252 Å for B1B95, and 0.0226 Å for B3LYP. According to the RMSE value, the bond lengths obtained by the B3LYP level show a good correlation with the experimental values. For bond angles, the opposite was observed. As can be seen from Table 2, both the biggest difference and the RMSE for the bond angles obtained by the DFT calculations (B1B95 and B3LYP level) are bigger than those determined by HF. A logical method for globally comparing the structures obtained from theoretical calculations is by superimposing the molecular skeleton on that obtained from X-ray diffraction [Figure S2 (supplementary material)]. According to these results, it may be concluded that the B3LYP calculation well reproduces the bond lengths, while the HF method is better at predicting the bond angles and 3D geometry of the title compound.

Whereas the most of the calculated bond lengths are slightly longer than the experimental values, as seen from Table 2, the calculated bond lengths and angles are in good agreement with the experimental values of the title compound and also similar compounds in the literature [19, 20, 46-50].

We noted that the experimental results belong to the solid phase whereas theoretical calculations belong to the gas-phase. The result in the differences of bond parameters between the calculated and experimental values depend on the existence of the crystal field along with the inter-molecular interactions connects the molecules together in the solid state [52]. The presence of the intermolecular hydrogen bonds (Table 3) appears as an important property of the title compound, stabilizing its conformation in the crystal, so the NBO analysis is also discussed as follows.

3.3. Potential energy surface (PES) scan

To investigate the conformational stability of the title compound, the potential energy surface (PES) scans about the link fragments of the aldehyde ring (ring1) part with respect to the 4-ethoxyaniline ring (ring2) part in the whole molecule (Figure 1). For this reason, the torsion angles T1(C9–N1–C10–C15) and T2(C6–C5–C9–N1) are relevant coordinates for conformational flexibility of the investigated molecule. The scans were obtained by minimizing the potential energy using B3LYP/6-311++G(d,p) level of theory in all geometrical parameters by varying the torsion angles at a step of 10° in the range of 0-360° rotation around the bond. The variations of potential energy change from its equilibrium with the torsional perturbation are presented in Figure S3 (supplementary material). Potential energy surface (PES) scan for torsion angles T1 show five minima positions at 37.503, 147.503, 217,503, 327.503 and -37.503 ° and T2 shows three minima positions at -178.460, 1.540 and 181.540°. Among these the deepest minima values correspond to the optimized molecular geometry [T1(C9–N1–C10–C15) = -37.503 and T2(C6–C5–C9–N1) = 178.460° using B3LYP/6-311++G(d,p) level] of the compound which is directly taken from the X-ray diffraction experimental result. The energy of the most stable conformation is -939.91536142 Hartree, respectively.

3.4. Vibrational spectra

The vibrational band assignments were performed at B3LYP/6-311++G(d,p) theory level combined with scaled quantum mechanics force field (SQMFF) methodology [44] to compare the experimental (FT-IR) and calculated vibrational frequencies of the title compound (Figure 4). The compound *E*-2-ethoxy-4-[(4-ethoxyphenylimino)methyl]phenol consists of N=40 atoms and hence 114 (3N-6) normal modes of vibrations. We have analyzed the normal vibrational frequencies and compared our calculated results of the investigated compound with the experimental ones on the basis of potential energy distributions (PED) and given in Table 4. The infrared spectra of the

investigated compound have some characteristic bands of the vibrations of the O – H, C – H, C = N, C – O, C – C, C – H₃ and C – H₂ groups.

O–*H* vibrations

The characteristic region of the O – H group vibrations spectrum in the Schiff bases, which have a free hydroxyl group or non-hydrogen bonded, is $3550 - 3700 \text{ cm}^{-1}$ [53]. In this study, the experimental O–H stretching vibration was observed at 3735 cm^{-1} . The O – H stretching vibration was calculated at 3582 cm^{-1} for B3LYP/6-311++G(d,p) level with the 100% contribution of PED. The experimental and theoretically predicted frequency for O–H vibration by B3LYP/6-311G(d,p) level shows excellent agreement with recorded spectrum as well as the literature data and also find support from PED values [54, 55]. The strong hydrogen bonding if present in the Schiff bases composed with 2-hydroxy-1-napthaldehyde system would reduce the O–H stretching band shifting to lower wavenumber 2900 cm⁻¹ [20, 36]. The in plane O–H bending vibration modes occur 1350± 50 cm⁻¹, while the out-of plane O–H bending vibration modes is $650\pm50 \text{ cm}^{-1}$ [56]. The inplane O–H bending vibration modes is observed at 1371 experimentally and calculated at 1355 cm⁻¹. The out-of-plane OH deformation appears at 456 experimentally and calculated at 448 cm⁻¹.

C-H vibrations

The aromatic structure shows the presence of C–H stretching vibrations in the region 3000 – 3125 cm⁻¹, which is the characteristic region for the identification of v(CH) stretching vibrations [36], But in this region, the bands are not appreciable affected by the nature of the substituent [57]. In the FT-IR spectrum of the title compound, symmetric C–H stretching vibrations are observed at 3223 and 3268 cm⁻¹. The calculated values of these symmetric C–H stretching vibrations are 3076, 3066, 3059 and 3058 cm⁻¹. The calculated values the asymmetric C–H stretching vibrations are 3043, 3038 and 3033 cm⁻¹. The asymmetric and the symmetric modes are almost pure modes with the 90-100% contribution of PED. Substitution sensitive C–H in-plane bending vibrations lie in

the region $1000 - 1300 \text{ cm}^{-1}$ [54]. In the title compound, four infrared bands at 1286, 1240, 1178 and 1123 cm⁻¹ with medium, very strong and very weak intensities are assigned to C–H in-plane bending vibrations. These vibrations are corresponding to 1296, 1239, 1180 and 1130 cm⁻¹ of calculated values. The C–H out-of-plane bending vibrations appear in the range 1000 – 675 cm⁻¹ [54, 58, 59]. The observed vibrations are 971, 946, 917 and 793 cm⁻¹ for the C–H out-of-plane bending vibrations. The bands at 940, 917, 908, 906, 875, 830, 808, 797 and 785 cm⁻¹ are assigned to the C–H out-of-plane bending vibrations for the investigated compound. As seen in Table 4, the C–H out-of-plane bending vibrations are assigned as mixed and pure modes, respectively.

C–H₂ vibrations

For the assignments of CH₂ group frequencies, basically six fundamentals can be associated to each CH₂ group namely, v_s (CH₂)-symmetric stretch, v_{as} (CH₂)-asymmetric stretch, sci(CH₂)- scissoring, and ρ (CH₂)-rocking modes which belong to in-plane vibrations. In addition to that w(CH₂)-wagging and Tw(CH₂)-twisting modes of CH₂ group would be expected to be out-of-plane bending vibrations. The asymmetric CH₂ stretching vibration is generally observed at the 2926 \pm 10 cm⁻¹, while the CH₂ symmetric stretch will appear 2855 \pm 10 cm⁻¹, cm⁻¹ [56]. The CH₂ asymmetric and symmetric stretching vibrations computed by B3LYP/6-311++G(d,p) at 2906 and 2873 cm⁻¹ are assigned to CH₂ asymmetric stretching and symmetric pure modes with the 98 and 99% contribution of PED. The calculated band at 2966 cm^{-1} is assigned to CH₂ asymmetric stretching mix modes with 68% contribution of PED. The other fundamental CH₂ group vibrations which are sci(CH₂)- scissoring, ρ (CH₂)-rocking, w(CH₂)-wagging and Tw(CH₂)-twisting modes appear in the expected wavenumber region of 1475-875 cm⁻¹ [60, 61]. In the investigated compound, scaled vibrational frequencies computed at 1514 and 1380 cm⁻¹ are assigned to sci(CH₂)-scissoring mix modes, while observed at 1564 cm⁻¹ in FT-IR spectrum. The computed wavenumbers at 1390 and 1366 cm⁻¹ are assigned to w(CH₂)-wagging vibration. The Tw(CH₂)twisting vibration observed 1286 cm⁻¹ as a very strong band in FT-IR spectrum is assigned to CH_2

twisting vibration. The calculated value of $Tw(CH_2)$ -twisting vibration is 1278 cm⁻¹, respectively. The $\rho(CH_2)$ -rocking mode appear at 846 cm⁻¹ experimentally and calculated at 818 cm⁻¹. The assignments of CH₂ group frequencies show good agreement with literature [60-62].

C–H₃ vibrations

The $v_s(CH_3)$ -symmetric stretching, $v_{as}(CH_3)$ -asymmetric stretching, $\delta(CH_3)_s$ -symmetric bending deformation (umbrella mode), $\delta(CH_3)_{as}$ -asymmetric bending deformation, and $\rho(CH_3)$ rocking frequencies are assigned for the CH₃ group in the investigated compound. The v_{as} (CH₃)asymmetric stretching vibration is generally observed at the 2962±10 cm⁻¹, while the $v_s(CH_3)$ symmetric stretching will appear 2872 \pm 10 cm⁻¹ [56]. The v_s(CH₃)-symmetric stretching vibrations are observed at 2909 and 2806 cm⁻¹, and assigned at 2911 and 2910 cm⁻¹ as pure modes with the 100% contribution of PED by B3LYP/6-311++G(d,p) level. The v_{as} (CH₃)-asymmetric stretching modes are assigned at 2991, 2982, 2973, and 2971 cm⁻¹. The $\delta(CH_3)_s$ -bending deformation (umbrella mode) show up at 1375 ± 10 cm⁻¹, while $\delta(CH_3)_{as}$ -asymmetric bending deformation show up at 1460±10 cm⁻¹ [56]. In our present study, the δ (CH₃)_s-bending deformation (umbrella mode) vibrations are assigned at 1409, 1405, and 1380 cm⁻¹, whereas $\delta(CH_3)_{as}$ -asymmetric bending deformation modes are assigned at 1496, 1495, 1493, 1486, and 1483 cm⁻¹. The δ (CH₃)_{as}asymmetric bending deformation is observed at 1472 cm⁻¹ as experimentally. The rocking vibrations of CH₃ group usually appear in region 1070-1010 cm⁻¹ [63]. The FT-IR spectrum at 1178 and 1123 cm⁻¹ are assigned to CH₃ rocking vibration. The rocking vibrations of CH₃ group are calculated at 1180, 1167, 1154, and 1115 cm⁻¹ by B3LYP/6-311++G(d,p) level.

C=N vibrations

The C=N stretching vibrations were assigned in the region 1500-1600 cm⁻¹ by Silverstein [63]. In the present study, the C=N stretching vibration band observed at 1616 in FT-IR. This band

is calculated at 1621 cm⁻¹ with B3LYP/6-311++G(d,p) level. The PED for this mode is 51%. The PED for this mode suggests that this is a mixed mode (Table 4).

C-C and C=C vibrations

The ring C=C stretching vibrations for aromatic group generally appear 1430-1625 cm⁻¹ [64] and usually assigned to C=C stretching modes in 1400-1650 cm⁻¹ [65]. For title compound, the C–C and C=C stretching vibrations are observed at 1616, 1564, 1427, and 1371 and 1286 cm⁻¹ in FT-IR spectrum. The mean difference between theoretical and experimental frequencies is about 7 cm⁻¹. It shows the good agreement between theoretical and experimental the ring C–C and C=C stretching vibrations for aromatic group.

C–O vibrations

The C–O stretching vibrations appear in the spectral range 1168-1310 [66]. The C–O stretching vibrations are observed at 1240, 1178 and 1123 cm⁻¹ in FT-IR spectra respectively, and assigned values of these modes are 1239, 1180 and 1130 cm⁻¹ by the DFT calculations. The C–O stretching vibrations are also calculated at 1222, 1130, 115, 1027, 963 and 917 cm⁻¹ with 10-43% contributions of PED. The phenolic C–OH stretching vibration was observed at 1291 cm⁻¹ and calculated at 1273 cm⁻¹ [20]. For title compound, the phenolic C–OH stretching vibration is observed at 1240 cm⁻¹ and assigned at 1239 cm⁻¹ with 25% contributions of PED.

The calculated values of other group vibrations show good agreement with the experimental results. The other experimental and calculated vibrational values can be seen in Table 4. To make a comparison with the experimental observation, we present correlation graphics in Figure S4 (supplementary material). The relations between the calculated unscaled (v_{ucal}) and experimental (v_{exp}) wavenumbers and also the calculated scaled (v_{cal}) and experimental (v_{exp}) wavenumbers are linear and described by the following equations:

$$v_{ucal} = 1.03856 v_{exp} - 8.30142, \quad R^2 = 0.99664 \tag{5}$$

 $v_{cal} = 0.98862 v_{exp} - 14.99685, \ R^2 = 0.99688$ (6)

According to the fitting results of the equation (1) and (2), the general scale factor value was found to be 0.96287 for 6-311++G(d,p). As a result, the scaled fundamental vibrationals are in good consistency with experimental results and are found a good agreement above the predicted literature.

3.5. Atomic charge distributions, energy and dipole moment behavior in the gas and the solution phases

The calculation of atomic charges plays a significant role in the application of quantum mechanical calculations to molecular systems because of atomic charges affect some properties of molecular systems including dipole moment and molecular polarizability. The atomic charges have been also used to describe the MEP surfaces [20, 67, 68]. The total atomic charges of the Mulliken population analysis and the natural population analysis (NPA) were listed in Table S1 (supplementary material). The calculated Mulliken atomic charges for gas and solvent phase were illustrated in Figure S5 (supplementary material). According to the calculated Mulliken atomic charges and, the C5 atom has a largest positive atomic charge and C8 atom has a largest negative atomic charge. As can be seen in Figure S5 and Table S1 (supplementary materials), all of the hydrogen atoms have net positive charge. The obtained atomic charge was showed that the H10 atom has bigger positive atomic charge (0.30164) than the other hydrogen atoms. The imine N1 atom has positive atomic charge and O1, O2 and O3 atoms have a large negative atomic charge in the gas phase. These behavior may be result of the intermolecular N-H···O hydrogen bond. On the other hand, as shown in Figure S5 and Table S1 (supplementary materials), the negative atomic charge values of the O atoms in solution phase are becoming more negative while the positive atomic charge of N1 is decreasing with the increase of the polarity of the solvent.

According to these results, NBO's net charges (NPA) are slightly longer than Mulliken charges. The intention is to accurately model partial charge magnitude and location within a molecule.

The total energies and dipole moments of the compound calculated with B3LYP/6-311++G(d,p) level for five solvents (ε =4.9, chloroform; ε =10.36, dichloroethane; ε =24.55, ethanol; ε =46.7; dimethylsulfoxide and ε =78.39 water), in order to evaluate the difference of total energy and dipole moment behavior of the title compound in solvent media. The results are given in Table 5. As can be seen from Table 5 and Figure S6 (supplementary material), the dipole moments which are calculated by the PCM method in the various solvents increase with increasing solvent polarity. The energy difference between the gas phase and solvent media and dipole moments are shown in Figure S6 (supplementary material). According to the results, we can say that the obtained total energy of the compound decreases with the increasing polarity of the solvent. The lessening in total energy of the title molecule increases the stability. We can conclude that according to the results, the investigated molecule in the gas phase more reactive than in the solution phase.

3.6. Molecular electrostatic potential surface

To investigate reactive sites for electrophilic and nucleophilic attack, the regions of the MEP for the title compound was composed by DFT calculation using the optimized geometry at the B3LYP/6-311++G(d,p). As shown Figure S7 (supplementary material), red and yellow colors indicated for the negative regions of the MEP are related to electrophilic reactivity, while blue colors indicated for positive regions to nucleophilic reactivity. As can be seen from Figure S7 (supplementary material), the compound has three possible sites for electrophilic attack. The oxygen atoms O1 of the aldehyde ring and the N1 and O3 atoms of the 4-ethoxyaniline ring have negative region. The maximum negative molecular electrostatic potential value is 0.033 a.u. for the mainly region of the O1 atom. The H10 atom of the O1 have positive region to nucleophilic attack with a maximum value. According to these calculated results, the region of MEP shows that

the negative potential sites are on electronegative atoms as well as the positive potential sites are around the hydrogen atoms. The determining of MEP region is best suit for identifying sites for intra- and intermolecular interactions [69]. According to the MEP surface of the compound, the weak negative region associated with O1 atom and also the weak positive region by the nearby H10 atom. It can be indicative of an intermolecular (O1–H10^{···}N2) hydrogen bonding in the compound (Figure 2 and Figure 3).

3.7. Relation between the HOMOs – LUMOs gap and the chemical hardness

The highest occupied molecular orbital (HOMO) and the lowest unoccupied molecular orbital (LUMO) are the very important parameters for quantum chemistry. These orbitals play an important role in the electric properties and determine the way the molecule interacts with other species [70–72]. Both the HOMO and the LUMO are the main orbital taking part in chemical reaction. While the energy of the HOMO is directly related to the ionization potential, LUMO energy is directly related to the electron affinity. Frontier molecular orbitals (HOMO and LUMO) may be used to predict the adsorption centers of the inhibitor molecule for corrosion of metal surfaces [73]. To provide a reasonable qualitative indication of the excitation properties, HOMO and LUMO for the title compound were investigated. The total molecular energies, HOMO and LUMO energies and HOMO-LUMO band gaps were predicted by the B3LYP method with 6-311++G(d,p). The calculated values of HOMO and LUMO energies and HOMO-LUMO band gaps of the title compound were listed in Table 5. The HOMO-LUMO energy gap value was found to be 3.9288 eV at B3LYP/6-311++G(d,p) in gas phase. The frontier molecular orbital distributions and energy levels of the HOMO and LUMO, which computed at B3LYP/6-311++G(d,p) level of the title compound are shown in Figure S8 (supplementary material). The frontier molecular orbital shows π molecular orbital characteristics and visualized in Figure S8 (supplementary material). Except for ethoxy group atoms in the aldehyde and aniline rings of the

structure, the LUMO is mainly localized on the whole structure, whereas except for CH_2 and CH_3 atoms in the structure, the HOMO is localized on the whole structure as seen from Figure S8 (supplementary material). The HOMO and LUMO are mostly the π -antibonding type molecular orbitals in the structure.

The chemical hardness is useful to rationalize the relative stability and reactivity of chemical compounds. For the title compound, the chemical hardness (η) were calculated with the B3LYP/6-311++G(d,p) base sets The results are given in Table 5. The value of energy separation between the HOMO and LUMO is 3.9288 eV and the value of hardness is 1.9644 eV for the title molecule. From Table 5, in going from the gas phase to the solvent phase, the chemical hardness increases in parallel with the increasing value of the energy gap and molecule becomes more stable. These results are in a good agreement with those of the related structures [74-76].

3.8. Natural Bond Orbital (NBO) Analysis

The natural bond orbital occupancies of the title compound are listed in Table S2 (supplementary material). The double bond character of the N1–C9 has revealed by the NBO analysis. In the aniline ring, consist of C3, C4, C5, C6, C7 and C8 atoms and rings of the aldehyde part, consist of C10, C11, C12, C13, C14 and C15 atoms are typically single-double arrangement that form the conjugate structure. Also, as seen from Table S2 (supplementary material), the NBO occupancies of single O2–C2 and O3–C16 are same level in the ethoxy part. The calculated results from the NBO analysis are consistent with the obtained from X-ray structure analysis of the compound. So, NBO analysis can be a very useful method for molecular modelling.

The results of second-order perturbation theory analysis of the Fock matrix at B3LYP/6-311++G(d,p) level of theory and the stabilization energies larger than 12.55 kJ/mol are given Table S3 (supplementary material). The stabilization energy $E^{(2)}$ value increases with the strong interaction between electron donors and electron acceptors. Also, the larger stabilization energy $E^{(2)}$ values, the greater the extend of the conjugation of the whole system. As seen from Table S3

(supplementary material), the strong intramolecular hyperconjugative interaction of the σ and π electrons of C – C to the anti C – C bond of the aromatic rings results to stabilization of some part of the rings, such as the intramolecular hyperconjugative interaction of the σ (C13 – C14) distribute to σ^* (C13 – C12) stabilization of 16.95 kJ/mol. This enhanced further conjugate with antibonding orbitals π^* of the C12 – C11 and C15 – C10 which results to strong delocalization of 69.20 and 86.94 kJ/mol, respectively. The results from the NBO analysis indicate that the C12 – C11, C10 – C15, C6 – C5, C8 – C7 and C4 – C3 bonds have the same kind interaction, as seen from Table S3 (supplementary material).

The donor orbitals LP(2) of O1 and O3 have strongest interaction energies resulting stabilization of 120.92 and 122.47 kJ/mol. This important interaction reveals the existence of intermolecular hydrogen bonding in the compound. The N1 LP(1) with antibonding orbital $\sigma^*(C9 - H9)$ causes to moderate stabilization of 54.73 kJ/mol, respectively.

The NBO analysis provides an efficient method for studying intra- and intermolecular bonding such as $O-H^{...}N$ and $C - H^{...}O$ interactions. These interactions and bonds significantly influence the crystal packing of this molecule.

3.9. Nonlinear Optical (NLO) Effects

To investigate the nonlinear optical properties of the molecules is very important because of the key functions of frequency shifting, optical modulation, optical switching, optical logic and optical memory for the emerging technologies in areas such as in telecommunications, signal processing and optical interconnections [77].

The total molecular dipole moment (μ), linear polarizability (α), and the first-order hyperpolarizability (β) were calculated by the B3LYP method with each of 6-31G(d), 6-31+G(d,p), 6-31++G(d,p), 6-311+G(d) and 6-311++G(d,p) basis sets to investigate the effects of basis sets on the NLO properties. The calculated values of the μ_{tot} , α_{tot} and β_{tot} are listed in Table 9. From the Table 9, it can be seen that the calculated values of the μ_{tot} , α_{tot} and β_{tot} slightly depend

on the size of basis sets. The obtained values of the μ_{tot} , α_{tot} and β_{tot} with 6-31G(d) basis set are smaller than those obtained with the large size of basis sets. It was found that the calculated results for the basis sets from 6-31+G(d) to 6-311++G(d,p) have minor differences from each other.

It can be seen from the Table 9, the calculated values of β_{tot} for the title compound are greater than urea (the β_{tot} of urea is 0.373×10^{-30} cm⁵/esu obtained by using B3LYP/6-31G(d) basis set). When it is compared with the similar Schiff base compounds in the literature, the calculated values of β_{tot} in the compound are larger than that of N-(2,5-methylphenyl)salicylaldimine (I) (β_{tot} =3.752x10⁻³⁰ cm⁵/esu) [19], while smaller than that of 2-[2,4-dimethylphenyl)iminomethyl]-3,5cm⁵/esu) $=8.256 \times 10^{-30}$ [78] dimethoxyphenol] (β_{tot}) and 1-[(4ethoxyphenylimino)methyl]napthalene-2-ol ($\beta_{tot} = 33.231 \times 10^{-30} \text{ cm}^{5}/\text{esu}$) [20] calculated with B3LYP/6-311++G(d,p) method. The calculated value of $\beta_{tot} = 7.0934 \times 10^{-30}$ cm⁵/esu in the gas phase, which is greater than that of urea ($\beta_{tot} = 0.592 \times 10^{-30}$ cm⁵/esu obtained by using B3LYP/6-311++G(d,p) method). Especially, the first-hyperpolarizability value of the investigated compound is 11.98 times more than that of urea at the same level B3LYP/6-311++G(d,p) base set.

3.10. Thermodynamic Properties

The standard thermodynamic functions: heat capacity $(C_{p,m}^{0})$, entropy (S_{m}^{0}) and enthalpy (H_{m}^{0}) based on the vibrational analysis using the B3LYP/6-311++G(d,p) level to investigate thermodynamical properties of the title compound were calculated and listed in Table 10. The standard heat capacities, entropies, and enthalpies increase at any temperatures from 200 to 450 K for the compound, by reason of the intensities of the molecular vibration increase with increasing temperature. The correlations between the thermodynamic properties $C_{p,m}^{0}$, entropy S_{m}^{0} and enthalpy H_{m}^{0} and temperatures T are described and shown in Figure S9 (supplementary material), according to the data in Table S5 (supplementary material).

The correlation equations between these thermodynamic properties and temperature T are as follows:

$H_m^o = -0.02739 + 0.01058T + 0.00011T^2$	$(R^2=1)$	(7)
$C^o_{p,m} = 3.09925 + 0.2587T - 0.00006T^2$	(R ² =0.99991)	(8)
$S_m^o = 70.30779 + 0.29039T - 0.00005T^2$	$(R^2=1)$	(9)

The values of $C_{p,m}^{0}$, S_{m}^{0} and H_{m}^{0} can easily be obtained at any temperatures using these relationships and these results will be helpful for the further studies of the title compound.

4. Conclusion

synthesized *E*-2-ethoxy-4-[(4-ethoxyphenylimino)methyl]phenol has been and characterized by FT-IR and X-ray single crystal diffraction. DFT studies of the Schiff base ligand have been also reported in this study. The calculated geometric parameters by using the Hartree-Fock (HF) and density functional theory (DFT) with the 6-311++G(d,p) basis set are in good agreement with the X-ray structure, in spite of the observed differences, in general. The result in the differences of bond parameters between the calculated and experimental values depend on the existence of the crystal field along with the inter-molecular interactions connects the molecules together in the solid state. The potential energy surface (PES) scans two torsion angles are performed by using B3LYP/6-311++G(d,p) level of theoretical approximation for the compound. The energy of the most stable conformation is -939.91536142 Hartree. The total molecular energies obtained by the PCM method decrease with the increasing polarity of the solvent and the stability of the title compound increase in going from the gas phase to the solution phase. The lessening in total energy of the title molecule increases the stability. We can conclude that according to the results, the investigated molecule in the gas phase more reactive than in the solution phase.

The vibrational band assignments were performed at B3LYP/6-311++G(d,p) theory level to compare the experimental (FT-IR) and calculated vibrational frequencies of the title compound. The calculated vibrations show good agreement with the experimental results. The Mulliken atomic charges for the included H atoms of the compound were calculated at B3LYP/6-311++G(d,p) level. The obtained atomic charge was showed that the H10 atom has bigger positive atomic charge (0.301642) than the other hydrogen atoms. The imine N1 atom has positive atomic charge and O1, O2 and O3 atoms have a large negative atomic charge in the gas phase. These behaviors may be result of the intermolecular dipole-dipole interactions once again because of the partial positive hydrogen (H10) and partial negative nitrogen (N) atoms. According to the MEP surface of the compound, the weak negative region associated with O1 atom and also the weak positive region by the nearby H10 atom. It can be indicative of an intermolecular (O1-H10^{...}N2) hydrogen bonding in the compound. The HOMO–LUMO energy gap value was found to be 3.9288 eV at B3LYP/6-311++G(d,p) in gas phase. The frontier molecular orbital shows π molecular orbital characteristics. According to the value of energy separation between the HOMO and LUMO and the value of hardness is 1.9644 eV for the title molecule, in going from the gas phase to the solvent phase, the chemical hardness increases in parallel with the increasing value of the energy gap and molecule becomes more stable. The bond characters and inter-intramolecular interactions of the investigated molecule has revealed by the NBO analysis. The calculated results from the NBO analysis are consistent with the obtained from X-ray structure analysis of the compound. The total molecular dipole moment (μ), linear polarizability (α), and the first-order hyperpolarizability (β) were calculated by the B3LYP method with different basis sets to investigate the effects of basis sets on the NLO properties. Our computational results yield that β_{tot} for the title compound is greater than those of urea. So the HOMO-LUMO gap is also related to the polarizability of a molecule and the investigated compound is a good candidate as a nonlinear optical material. The thermodynamic properties heat capacity $\binom{0}{p_{p,m}}$, entropy $\binom{S_m^0}{s_m}$, enthalpy $\binom{H_m^0}{s_m}$ and temperatures T were also obtained. The results show that the standard thermodynamic

functions increase at any temperatures from 200 to 450 K, because the intensities of the molecular vibration increase with increasing temperature.

We hope that the synthesis, crystallographic and spectroscopic characterization and DFT studies of E-2-ethoxy-4-[(4-ethoxyphenylimino)methyl]phenol will be helpful for the design and synthesis of new materials.

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Appendix A. Supplementary material

Supplementary data associated with this article can be found, in the online version, at http://dx.doi.org/

Note

 Further information may be obtained from: Cambridge Crystallographic Data Center (CCDC), 12 Union Road, Cambridge CB21EZ, UK, by quoting the depository number CCDC 1036031, e-mail: deposit@ccdc.cam. ac.uk.

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The figures captions:

Figure 1. Ortep-3 diagram of the title compound. Displacement ellipsoids are drawn at the 20% probability level. The intermolecular hydrogen bond is shown as a dashed line.

Figure 2. Intermolecular C12–H12···O3ⁱ hydrogen bonding interaction (i; -x, -y+3, -z).

Figure 3. Intermolecular O4–H4…N1ⁱⁱ hydrogen bonding interaction (ii; x, y-1, z).

Figure 4. Comparison of the experimental and calculated FT-IR spectra of the investigated compouns: (a) Observed

spectra; (b) Theoretical spectra at B3LYP/6-311++G(d,p) level.













Table 1. Crystallographic data and structure refinement for the title compound.

Chemical formula	Cu ₂ H ₁₀ NO ₂
Crystal shape/color	Prism/Yellow
Formula weight	285.33
Crystal system	Orthorhombic
Space group	Phea
Unit cell parameters	a = 21.9691(6) Å
enit een puruneters	h = 11,2079(3) Å
	c = 25.0951 (6) Å
Volume	$6179 1 (3) Å^3$
7	16
$D_{\rm r}$ (Mg cm ⁻³)	1 227
$U_x(\text{mm}^{-1})$	0.08
μ (mm)	2432
Crystal size (mm ³)	$0.40 \times 0.38 \times 0.23$
Data collection	0.+0×0.30×0.23
Diffractometer/meas meth	Bruker APEX-II CCD/w and a
scans	Druker Ar EA-II CCD/ W and V-
Absorption correction	Multi-scan
T min T	0.982
No of measured independent	41007 6076 4475
and observed reflections	1007, 0070, 1175
Criterion for observed	$I > 2\sigma(I)$
reflections	1 > 20(1)
R:	0.028
A A	26.0
Refinement	20.0
Refinement on	F^2
$R[F^2 > 2\sigma (F^2)] wR S$	0.057 0.158 1.03
No of reflection	6076
No of parameters	442
Weighting scheme	$w=1/[\sigma^2(F_0^2)+(0.0694P)^2]$
weighting selectic	$P = (F_0^2 + 2F_0^2)/3$
$\Delta \Omega_{\text{max}} = \Delta \Omega_{\text{min}} (e \text{\AA}^{-3})$	0.48 - 0.22

Table 2. Selected experimental and optimized (HF, B1B95 and B3LYP/gas phase) with 6-311++G(d,p) level geometric parameters of the title compound Bond distances (Å) and angles (°) with estimated standard deviations (e.s.d.s) in parentheses.

Parameters	Experimental (I)	Parameters	Experimental (II)	HF	B1B95	B3LYP
Bond lengths (Å)		Bond lengths (Å)				
C8–O1	1.351(2)	C25–O4	1.357(2)	1.3419	1.3473	1.3580
C5–C9	1.450(3)	C22–C26	1.454(3)	1.4738	1.4555	1.4624
C9-N1	1.269(3)	C26-N2	1.271(3)	1.2538	1.2735	1.2791
N1-C10	1.417(2)	N2-C27	1.423(3)	1.4093	1.3987	1.4053
C4–C5	1.395(3)	C22–C21	1.401(3)	1.4003	1.4008	1.4085
C5–C6	1.388(3)	C22–C23	1.385(3)	1.3800	1.3904	1.3981
C13–O3	1.366(2)	C20–O5	1.363(2)	1.3485	1.3556	1.3660
O3–C16	1.425(3)	O5–C19	1.442(3)	1.4040	1.4153	1.4286
C16-C17	1.486(3)	C18–C19	1.472(4)	1.5140	1.5069	1.5168
C13–C14	1.374(3)	C30–C31	1.358(5)	1.3822	1.3900	1.3970
Max. difference ^a				0.0242	0.0320	0.0390
RMSE				0.0235	0.0252	0.0226
Bond angles (°)		Bond angles (°)				
01	119.29(19)	O4–C25–C24	119.73(18)	119.887	120.522	120.192
O3-C13-C14	124.92(18)	O5–C20–C21	125.99(18)	124.898	124.555	124.763
O3-C16-C17	108.9(2)	O5-C19-C18	107.8(2)	107.905	107.786	107.736
N1-C9-C5	123.97(18)	N2-C26-C22	124.2(2)	123.137	123.140	123.099
C11-C10-N1	117.80(17)	C28-C27-N2	117.3(2)	118.066	118.565	118.061
	CC					

C11-C10-C15	117.01(19)	C28–C27–C32	117.7(2)	118.147	118.127	118.026
C6–C5–C9	120.43(18)	C23-C22-C26	119.78(19)	119.708	119.680	119.802
Max. difference ^a				1.092	1.435	1.227
RMSE				0.731	0.944	0.780
Torsion angles (°)		Torsion angles (°)				
C5-C9-N1-C10	172.97(19)	C22-C26-N2-C27	179.63 (18)	178.236	176.454	176.661
C9-N1-C10-C15	-17.9(3)	C26-N2-C27-C32	-21.8(3)	-43.252	-38.543	-37.503
C6-C5-C9-N1	173.4(2)	C23-C22-C26-N2	163.1(2)	178.626	178.013	178.460
C6C7C8O1	-178.0(2)	C23-C24-C25-O4	-179.43 (17)	-179.909	179.993	-179.954
C17-C16-O3-C13	-169.1(2)	C18-C19-O5-C20	-167.4 (2)	-179.476	-178.546	-179.694
O3-C13-C14-C15	-179.4(2)	O5-C20-C25-C24	-179.31(17)	-179.950	-179.696	179.972

^aRMSE and maximum differences between the bond lengths and angles computed using theoretical methods and those obtained from X-ray diffraction.

s computed u.

· · · · ·	D-H (A)	H···A (Å)	D…A (Å)	$D-H\cdots A(^{o})$
C12–H12…O3 ⁱ	0.93	2.53	3.454(3)	171
D1–H10…N1 ⁱⁱ	0.87(3)	2.19(3)	2.958(3)	153(3)
A= acceptor, D=de	onor atom.			
ymmetry codes (i):- <i>x</i> , - <i>y</i> +3, - <i>z</i> , ((ii) : <i>x</i> , <i>y</i> -1, <i>z</i> .		
			G	0
			Y	
		~ <u>P</u> .		
		O R.		
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	0			
	, (

Table 3. Hydrogen-bond^a geometry for the investigated compound.

Mode	Experimental	B3LYP/6-311G(d,p)		Potential Energy Distributions (PED)
	IR	Unscaled freq.	Scaled freq.	Description (%)
114	3735	3726	3582	$v_{s}(OH)(100)$
113	3223	3214	3076	v_{s} (CH) _{rine1} (100)
112	3068	3203	3066	$v_{s}(CH)_{rine2}(99)$
111		3195	3059	$v_{s}(CH)_{cincl}(99)$
110		3194	3058	$v_s(CH)_{max}(99)$
109		3178	3043	
108		3174	3038	$v_{\rm av}({\rm CH})_{\rm ring}$ (98)
107		3168	3033	vas(CH) ingl(90)
106		3125	2991	$\sum_{i=1}^{n} \frac{1}{(n+1)(n+1)(n+1)(n+1)(n+1)(n+1)(n+1)(n+1)$
105		3115	2982	$-a_{\alpha} \left(\frac{1}{2} \right) \left(\frac{1}$
104		3106	2973	$u_{\rm esc}({\rm CH}_2)(100)$
103		3104	2971	$-\alpha (1-\beta)(1-\beta)$
102		3099	2966	$u_{\rm ex} = (CH_2)(68) + n_{\rm ex} (CH_2)(31)$
101		3051	2920	$u_{\rm esc}(1-2)(98)$
100	2909	3041	2911	$\mu_{\rm c}({\rm Hz})(100)$
99	2806	3040	2910	$u_{\rm c}({\rm H}_2)(100)$
98	2000	3036	2906	$\mathcal{D}_{\mathcal{S}}(\mathcal{O}(\mathcal{S}))$
97	2733	3008	2879	$P(C^{23} \rightarrow H)(100)$
96	2155	3001	2873	$u(CL) H_1(00)$
95	1616	1682	1621	$v_{0}(c=12)(2/2)$
94	1010	1648	1594	u(C) = (5.1)
93		1637	1584	$\mathcal{O}(\mathbb{C}^{n})$, $\mathcal{O}(\mathbb{C}^{n+1})$, $\mathcal{O}(\mathbb$
92		1633	1577	u(CC), $(33)+u(C=N)(23)$
91		1607	1555	$u(CC)_{ring}((35)+b(CCH)) = (10)$
90	1564	1544	1514	
90 80	1504	1544	1510	
09		1540	1406	$S_{1}(CH_{2})(2\delta)$
87		1535	1490	$\delta(CH_3)_{ac}(24)^{-5} SC(CH_2)(12)$
86		1515	1493	$0(CH_{13})_{16}(53)^{15}C(CH_{2})(20)$
85		1515	1495	$0(CC)_{\text{ring}}(13)+0(C-026)(3)+0(CH3)_{as}(22)+0(CCH)_{\text{ring}}(3)+s0(CH2)(6)$
83	1472	1502	1480	$0(C_{fing}(2)) + 0(C_{0}) + 0(C_{0})_{a}(24) + 0(C_{0})_{fing}(10) + sc(C_{0})(8)$
04 92	1472	1502	1403	$O(CH_3)(30)$
83		1474	1403	$O(CH_3)(30)$ $O(CH_3)(30)$
02		14/4	1455	$0(CC)_{ring1}(3) + 0(C-O2)(3) + 0(CCH)_{ring1}(18) + 0(CO-H10)(4)$
81	1407	1430	1418	$0(CC)_{ring2}(29)+0(CCH)_{ring2}(27)$
80 70	1427	1436	1409	$O(CH_3)_s(\text{uniblena}(09)+W(CH_2)(0)$
79		1430	1405	$O(CH_{3})_{s}(\text{umbrelia})(SO)$
70		1420	1390	$0(CC)_{ring2}(19)+0(C-0.54)(5)+0(CO-1010)(10)+0(C-1010)(0)+0(CC-19)(5)+0(CH_2)(11)$
77		1412	1380	$(C(U_2)(5))^+(C(U_3)(22))$
76	1271	1405	1300	$U(CC)_{ingl}(3)+U(N=C)(3)+o(C=NH)(18)+o(CC-H9)(12)+W(CH_2)(23)$
75	1371	1397	1355	$v(CC)_{ring1}(10)+\delta(CO-H30)(18)+\delta(C=NH)(12)+\delta(CCH)_{ring1}(19)$
			*	

Table 4. The vibrational assignments of the title molecule by normal mode analysis based on SQM force field calculations.

Table 4 continued

Mode	Experimental	B3LYP/6-311G(d,p)		Potential Energy Distributions (PED)
	IR	Unscaled	Scaled	Description (%)
74		1338	1301	$\delta(O2CH)(36) + \delta(C1CH)(33)$
73		1333	1296	$\upsilon(CC)_{ring2}(5) + \delta(CCH)_{ring2}(78)$
72		1325	1281	$v(CC)_{ring2}(53)+v(C-O3)(5)$
71	1286	1318	1278	$Tw(CH_2)(48)$
70		1307	1264	$\upsilon(CC)_{ring1}(23) + \upsilon(CC)_{ring2}(20) + \delta(CCH)_{ring1}(37)$
69		1301	1254	$\upsilon(CC)_{ringl}(75) + \delta(CCH)_{ringl}(5)$
68	1240	1275	1239	$v(C-O1)(25)+v(C-C9)(5)+\delta(CCH)_{ring1}(17)+\delta(CO-H10)(10)+\delta(CCC)_{ring1}(7)$
67		1265	1222	$v(C13-O3)(41)+v(CC)_{ring2}(21)+\delta(CCH)_{ring2}(6)$
66		1243	1203	$v(C10-N1)(26)+v(CC)_{ring}(18)+v(C3-O2)(4)+\delta(CCH)_{ring2}(18)$
65	1178	1216	1180	$\upsilon(CC)_{ring1}(9) + \upsilon(C3-O2)(6) + \rho(CH_3)(26) + \delta(CCH)_{ring1}(14) + \delta(CO-H10)(13)$
64		1201	1167	$\upsilon(CC)_{ring1}(10) + \upsilon(C9-C5)(7) + \rho(CH_3)(37) + \delta(CO-H10)(9)$
63		1192	1156	$\upsilon(CC)_{ring1}(10) + \upsilon(C10-N1)(4) + \delta(CCH)_{ring2}(58)$
62		1186	1154	$\rho(CH_3)(23) + \delta(O3 - CH_2)(61)$
61	1123	1168	1130	$\upsilon(CC)_{ring1}(17)+\upsilon(C9-N1)(15)+\upsilon(C3-O2)(15)+\upsilon(C2-O2)(6)+\delta(CCH)_{ring1}(19)$
60		1145	1115	$v(C16-O3)(11)+v(C17-C16)(10)+\rho(CH_3)(41)+\delta(C17-C16-O3)(11)$
59		1144	1111	$\upsilon(CC)_{ring1}(21)+\upsilon(C2-O2)(5)+\delta(CCH)_{ring1}(53)$
58		1132	1099	$\upsilon(CC)_{ring2}(23) + \delta(CCH)_{ring2}(54)$
57		1113	1083	$\upsilon(C1-C2)(14)+\upsilon(C2-O2)(4)+\gamma(CH_3)(51)+\delta(C1-C2-O2)(12)$
56		1068	1027	v(C17-O3)(43)+v(C16-C17)(41)
55		1056	1020	$v(C2-O2)(37)+v(C1-C2)(30)+v(CC)_{ring1}(3)+\delta(CCH)_{ring1}(4)$
54		1024	1001	$\upsilon(CC)_{ring2}(36) + \delta(CCH)_{ring2}(33) + \delta(CCC)_{ring2}(28)$
53	971	996	974	$\gamma(C9-H9)(76)+\tau(CCC-N1)(8)$
52		992	963	$\upsilon(CC)_{rine1}(27) + \upsilon(C3-O2)(12) + \upsilon(C1-C36)(12) + \upsilon(C5-C9)(8) + \delta(C-C9-N1)_{rine}(7)$
51	946	961	940	$\gamma(CH)_{ring2}(91)$
50	917	939	917	$p(C6-C4)(13)+p(C6-Q7)(8)+v(CH)_{ring2}(48)+v(C6-CH_3)(7)$
49		938	908	$v(CH)_{inst}(89)$
48		927	906	$p(C16-C17)(18)+p(C16-O3)(13)+y(CH)_{time}(41)$
47	890	905	879	$v(C1-C2)(27) \pm v(C2-C2)(11) \pm v(C2-CH)(11) \pm \delta(N-C-C5) = (6)$
46	070	894	875	v(CH) = (82)
45		873	848	$p(CC) + p(C10-N1)(0) + p(C2-O2)(8) + p(C1-C2)(7) + \delta(CCC) + p(8)$
43		850	830	u(CC) = u(CH) = u(CH) = u(A8)
43	846	830	818	v(C16 CH)(40) + v(CH)(rag2(48))
42	040	820	810	$\gamma(C_{10}^{-}C_{113})(4) + \rho(C_{12})(50)$ $\gamma(C_{20}^{-}C_{113})(4) + \rho(C_{20}^{-}C_{113}) + \rho(C_{20}^{-}C_{113})(4)$
41		827	810	v(CII) = (81)
41		817	707	$\gamma(CH)_{\text{ring1}}(\delta I)$
40	702	804	795	γ (C2-Cn ₃)(55)+ ρ (Cn ₂)(29)
39	195	804	185	$\gamma(CH)_{ring2}(75)$
			7	

Table 4 continued

Mode	Experimental	B3LYP/6-311G(d,p)		Potential Energy Distributions (PED)
	IR	Unscaled	Scaled	Description (%)
38		789	770	$v(C13-O3)(11)+v(C8-O1)(7)+v(CC)_{ring2}(6)+v(CC)_{ring1}(6)+v(C22-N25)(11)+\delta(CCC)_{ring2}(5)$
37	742	746	732	$\tau(\text{CCCC})_{\text{ring2}}(4)$
36		738	729	$\tau(CCCC)_{ring1}(23) + \tau(CCCH)_{ring1}(14) + \tau(O2-CC-O1)_{ring1}(6)$
35	683	726	718	$\tau(\text{CCCC})_{\text{ring2}}(34)$
34	649	655	648	$\upsilon(CC)_{ring2}(16)+\delta(CCC)_{ring2}(57)$
33		628	622	$\delta(CCC)_{ring2}(12) + \delta(CCC)_{ring1}(9) + \delta(C16 - O3 - C13)(6) + \delta(N1 - C9 - C5)(6) + \delta(C10 - N1 - C9)(5)$
32	617	623	617	$\tau(\text{CCCH})_{\text{ring}}(22) + \tau(\text{CCCC})_{\text{ring}}(20) + \tau(\text{O2-CC-O1})(8) + \tau(\text{C5-CC-O2})(8) + \tau(\text{C5-CC-N1})(5)$
31		575	572	$\upsilon(CC)_{ring1}(5) + \upsilon(C2-O2)(5) + \delta(C3-O2)(15) + \delta(C3-O2-C2)(13) + \delta(C10-N1-C9)(10) + \delta(C6-C5-C9)(10)$
30	554	556	549	$v(C3-O2)(12)+v(CC)_{ring1}(10)+\delta(CCC)_{ring1}(13)+\delta(C3-C8-O1)(10)+\delta(C7-C8-O1)(7)$
29		542	535	$\delta(C3-O2-C2)(4) + \tau(CCCH)_{ring2}(36) + \tau(CCCC)_{ring2}(8) + \tau(CC-O3-C16)(5) + \tau(C15-C10-N1-C9)(5)$
28	523	518	515	$v(C8-O1)(7)+\delta(CCC)_{ring1}(17)+\delta(C3-O2-C2)(11)+\delta(C3-C8-O1)(7)+\delta(C11-C10-N1)(6)$
27		491	489	δ(C15-C10-N1)(17)+δ(C11-C10-N1)(7)+δ(C4-C5-C9)(6)+δ(C10-N1-C9)(6)+δ(N1-C9-C5)(5)
26		469	465	$\delta(C1-C2-O2)(6) + \tau(CCCC)_{ring1}(33) + \tau(CCCH)_{ring2}(14) + \tau(CCC-O2)(8) + \tau(CC-O1-H10)(6)$
25	456	457	448	τ(C3-C8-O1-H10)(44)+τ(C7-C8-O1-H10)(40)
24		442	439	δ(C12-C13-O3)(10)+δ(C1-C2-O2)(7)+δ(C14-C13-O3)(6)+τ(C7-C8-O1-H10)(14)+τ(C3-C8-O1-H10)(6)
23	427	430	427	$\tau(CCCC)_{ring1}(45) + \tau(CCCH)_{ring1}(19) + \tau(C15 - C14 - C13 - O3)(6) + \tau(C14 - C15 - C10 - N1)(5)$
22		417	415	$\delta(C1-C2-O2)(14)+\tau(C11-C10-C13-O3)(8)+\tau(C12-C11-C10-N1)(7)+\delta(C7-C8-O1)(6)+\tau(C6-C7-C8-O1)(6)$
21		408	406	$\delta(C1-C2-O2)(10) + \delta(C12-C13-O3)(9) + \delta(C13-O3-C16)(8) + \delta(C7-C8-O1)(6) + \tau(C10-N1-C9-C5)(6)$
20		372	369	$\tau(N1-CC-C12)(13)+\tau(CCC-O3)(12)+\tau(C6-C7-C8-O1)(9)+\tau(C9-CC-C7)(6)+\tau(C4-C3-C8-O1)(6)$
19		349	345	υ(C13-O3)(9)+υ(C5-C9)(5)+δ(C17-C16-O3)(28)+δ(C14-C13-O3)(9)
18		327	324	$\upsilon(C2-O2)(5) + \upsilon(C3-O2)(4) + \delta(C2-O2-C3)(22) + \delta(C1-C2-O2)(13) + \delta(CCC)_{ring1}(6) + \tau(C2H_2-C1H_3)(15)$
17		282	281	$\delta(\text{C7-C8-O1})(10) + \delta(\text{C8-C3-O2})(7) + \delta(\text{C7-C8-O1})(6) + \delta(\text{C4-C5-C9})(6) + \delta(\text{C11-C10-N1})(5)$
16		256	251	$\delta(C8-C3-O3)(7)+\delta(C4-C3-O2)(5)+\tau(C16H_2-C17H_3)(48)$
15		251	248	$\delta(C8-C3-O2)(6) + \delta(C4-C3-O2)(4) + \tau(C17H_3-C16-O3)(29) + \tau(C16H_2-C17H_3)(4) + \tau(C1-C2-O2-C3)(4)$
14		235	233	$\tau(C5-C4-C3-O2)(9)+\tau(C9-N1-C0-15)(6)+\tau(C6-C7-C8-O1)(6)+\tau(C9-C5-C4-C3)(6)$
13		208	207	δ(C13-O3-C16)(7)+τ(C6-C5-C9-N1)(18)+τ(C9-N1-C10-C11)(15)+τ(C9-N1-C10-C15)(12)+τ(C6-C5-C9-H9)(12)
12		193	191	$v(C5-C9)(6)+\delta(C10-N1-C9)(10)+\tau(C19-C12-C13-O3)(5)+\tau(C15-C14-C13-O3)(5)+\tau(CCCC)_{ring}(5)$
11		183	181	$\delta(C4-C3-O2)(5) + \delta(C8-C3-O2)(4) + \delta(C3-O2-C2)(20) + \tau(O2-C2-CH_3)(36) + \tau(C2H_2-CH_3)(6)$
10		170	170	δ(C13-O3-C16)(25)+δ(O3-C16-C17)(10)+δ(C12-C9-O3)(9)+δ(C14-C13-O3)(6)+δ(C10-N1-C9)(6)+τ(C10-N1-C9)(4)
9		120	119	$\delta(C9-C5-C4)(10) + \delta(C13-O3-C16)(7) + \delta(N1-C9-C5)(7) + \delta(C6-C5-C9)(6) + \tau(C3-O2-CH_2)(13) + \tau(C1-C2-O2-C3)(11) + \tau(C1-C2-C3)(11) + \tau(C1-C3)(11)
8		113	112	τ(C14-C13-O3-C16)(27)+τ(C12-C13-O3-C16)(23)+τ(C13-O3-CH ₂)(15)+τ(C13-O3-C16-C17)(14)
7		100	99	δ(C13-O3-C16)(7)+τ(C9-N1-CC)(16)+τ(C14-C13-O3-C16)(12)+τ(C12-C13-O3-C16)(11)+τ(C9-C5-CC)(7)
6		86	85	δ(C2-O2-C3)(9)+δ(C10-N1-C9)(7)+τ(C2H ₂ -O2-C3)(24)+τ(C1-C2-O2-C3)(24)+τ(C13-O3-C16-C17)(12)
5		56	56	$\tau(C13-O3-C16-C17) (19) + \tau(C12-C13-O3-C16) (17) + \tau(C1-C2-O2-C3) (14) + \tau(C2H_2-O2-C3) (14) + \tau(C13-O3-C16-H) (12)$
4		49	48	$\tau(C2-O2-C3-C8) (36) + \tau(C2-O2-C3-C4) (32) + \tau(C9-N1-C10-C11) (12) + \tau(C9-N1-C10-C15) (10) + \tau(C6-C5-C9-N1) (6)$
3		39	38	$\delta(C10-N1-C9)(19) + \tau(C10-N1-C9-C5)(17) + \tau(C6-C5-C9-N1)(13) + \tau(C2-O34-C3-C4)(12) + \tau(C2-O2-C3-C8)(11)$
2		30	29	$\delta(C10-N1-C9) (12) + \tau(C9-N1-C10-C11) (19) + \tau(C2-O2-C3-C4) (15) + \tau(C2-O2-C3-C8) (14) + \tau(C9-N1-C10-C11) (11)$
1		24	23	$\tau(C10-N1-C9-C5) (14) + \tau(C4-C5-C9-N1) (11) + \tau(C9-N1-C10-C11) (8) + \tau(C10-N1-C9-H) (7) + \tau(N1-C10-C15-C14) (17)$

v: bond stretching, δ : in-plane angle bending, γ : out-of-plane angle bending, sci: scissoring, Tw: twisting, w: wagging, ρ : rocking, τ : torsion, as: asymmetric and s: symmetric.

Method	Gas phase	Chloroform	Dichloroethane	Ethanol	Dimethylsulfoxide	Water	
PCM		CHCl	CH ₂ ClCH ₂ Cl	C ₂ H ₅ OH	(DMSO) (CH3) ₂ SO	H ₂ O	
Dielectric constant (ε)	1	4.9	10.36	24.55	46.7	78.39	
Energy (a.u)	-939.91536142	-939.92196893	-939.92348366	-939.92438258	-939.92471544	-939.92486852	
E_{HOMO} (eV)	-5.5383	-5.3419	-5.3253	-5.3182	-5.3160	-5.3152	
$E_{LUMO} (eV)$	-1.6096	-1.4066	-1.3881	-1.3799	-1.3774	-1.3764	
$\operatorname{Gap}^{a}(\mathrm{eV})$	3.9288	3.9353	3.9372	3.9383	3.9386	3.9389	
η (eV)	1.9644	1.9677	1.9686	1.9692	1.9693	1.9694	
ΔE^{b} (kcal/mol)		4.1463	5.0968	5.6609	5.8697	5.9658	
μ (Debye)	1.5713	2.4734	2.5562	2.6030	2.6144	2.6278	
${}^{a}\text{Gap} = /E_{HOMO} - E_{LUMO} / \\ {}^{b}\Delta E = E_{solvation} - E_{gas} $							

Table 5. Calculated total energies, frontier orbital energies, hardnesses and dipole moments of the title compound in different solvents.



Highlights

- (E)-2-Ethoxy-4-[(4-ethoxyphenylimino)methyl]phenol has been synthesized. _
- The molecular structure obtained from X-ray single-crystal analysis. _
- Density functional modelling studies of the title compound have been reported. _
- The calculated vibrations show good agreement with the experimental results. _
- The molecule more reactive in the gas phase than in the solution phase. _

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