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# Molecular structure, spectroscopic investigations, second-order nonlinear optical properties and intramolecular proton transfer of (*E*)-5-(diethylamino)-2-[(4-propylphenylimino)methyl]phenol: A combined experimental and theoretical study

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# 1. Introduction

# ABSTRACT

This work presents a combined experimental and theoretical study on an *ortho*-hydroxy Schiff base compound, (*E*)-5-(diethylamino)-2-[(4-propylphenylimino)methyl]phenol. The crystal structure and spectroscopic properties of the compound have been determined by using X-ray diffraction, IR and UV-vis spectroscopy techniques. The electronic structure, vibrational frequencies and electronic absorption spectra have been investigated from the calculative point of view. A relaxed potential energy surface scan has been performed based on the optimized geometry of OH tautomeric form to describe the potential energy barrier belonging to intramolecular proton transfer and to observe the effects of transfer on the molecular geometry. The second-order nonlinear optical properties have been investigated based on the first static hyperpolarizability ( $\beta$ ) by using the density functional theory.

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Molecules containing C=N double bond are known as Schiff bases and formed by a reaction of a primary amine and an aldehyde. Especially ortho-hydroxy Schiff base derivatives are the most commonly studied class of Schiff bases because of their interesting photochromic and thermochromic features in the solid state [1]. These features are caused by an intramolecular proton transfer associated with a change in  $\pi$ -electron configuration from the hydroxyl O atom to the imine N atom occurring under the influence of light for photochromic and temperature for thermochromic Schiff bases and the potential energy profile of this transfer shapes the photochromic and thermochromic features of the compound [2]. These features were investigated first time in 1909 by Senier and Shepheard [3,4]. It has been suggested that the molecules showing photochromism are non-planar and showing thermochromism are planar [5,6]. Many published research studies concern the related features of ortho-hydroxy Schiff base

\* Corresponding author at: Department of Science Education, Sinop University, Sinop 57010, Turkey. Tel.: +90 368 2715526; fax: +90 368 2715530. *E-mail addresses*: basak.kosar@gmail.com, bkosar@sinop.edu.tr (B. Koşar). compounds and the interest on this class of compounds continues for many years. They have wide application in many fields, e.g., as ligands in the field of coordination chemistry [7], as starting materials in synthesis of important drugs like antibiotics, antiallergics, antitumors and antifungals in pharmacy [8], as new organic materials in nanotechnology [9] and as elements for the design of various electronic devices such as optical switches and optical data storage devices through the agency of their non-linear optical properties [10].

Ortho-hydroxy Schiff bases exist either as OH (enol-imine) or NH (keto-amine) tautomeric forms in solid state and these forms can be distinguished easily by using the X-ray diffraction technique [11]. NH form is a resonance hybrid of two canonical structures, the zwitterionic and *cis*-quinoid forms [12]. The zwitterionic and *cis*-quinoid forms [12]. The zwitterionic and *cis*-quinoid forms are not just resonance structures of each other, they can also exist separately. The zwitterionics can differ easily from *cis*-quinoids with their N<sup>+</sup>—H bond distances and aromaticity of the rings [13]. The position of transferred proton determines the tautomeric form of compounds and the type of intramolecular hydrogen bonds. Three types of intramolecular hydrogen bonds are possible in *ortho*-hydroxy Schiff base compounds: O—H…N in OH forms, N—H…O in cis-quinoid NH forms and N<sup>+</sup>—H…O<sup>-</sup> in zwitterionic NH forms as can be seen from Fig. 1.

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Fig. 1. Possible tautomeric forms of (E)-5-(diethylamino)-2-[(4-propylphenylimino)methyl]phenol.

In conjunction with the development of technology, among the computational methods calculating the electronic structure of molecular systems, DFT has been a favorite one due to its great accuracy in reproducing the experimental values of in molecule geometry, vibrational frequencies, atomic charges, dipole moment, etc. [14]. In recent years, besides the experimental studies, an increase is seen in quantum chemical computational studies with DFT on tautomerism and intramolecular proton transfer process in *ortho*-hydroxy Schiff base compounds [15–18].

Concerning with the above mentioned phenomena, we present here the synthesis, crystallographic, spectroscopic and quantum chemical computational studies on the newly synthesized *ortho*-hydroxy Schiff base compound, (*E*)-5-(diethylamino)-2-[(4propylphenylimino)methyl]phenol.

#### 2. Materials and methods

#### 2.1. Synthesis of the title compound

The compound (*E*)-5-(diethylamino)-2-[(4-propylphenylimino)methyl]phenol was prepared by refluxing a mixture of a solution containing 5-(diethylamino)-2-hydroxybenzaldehyde (0.5 g, 2.59 mmol) in 20 mL ethanol and a solution containing 4-propylaniline (0.35 g, 2.59 mmol) in 20 mL ethanol. The reaction mixture was stirred for 1 h under reflux. The crystals of (*E*)-5-(diethylamino)-2-[(4-propylphenylimino)methyl]phenol suitable for X-ray analysis were obtained by slow evaporation from acetone (yield 65%; m.p. 353–355 K).

#### 2.2. Instrumentation

The melting point was determined by an electro-thermal melting point apparatus. FT-IR spectrum of the title compound was recorded on a Bruker 2000 spectrometer in KBr disk. Absorption spectra were recorded on a Unicam UV-Vis spectrometer using a 1 cm path length of the quartz cell. All diffraction measurements were performed at room temperature (296 K) using graphite monochromated Mo K $\alpha$  radiation ( $\lambda$  = 0.71073 Å) with a Stoe IPDS 2 diffractometer.

# 2.3. Crystal structure determination

A suitable sample of size  $0.62\,mm \times 0.53\,mm \times 0.46\,mm$  was chosen for the single crystal X-ray study. Reflections were collected in the rotation mode ( $\omega$  scanning mode) and cell parameters were determined by using X-AREA software [19]. Absorption correction  $(\mu = 0.07 \text{ mm}^{-1})$  was achieved by the integration method via X-RED32 software [19]. The structure was solved by direct methods using SHELXS-97 [20]. The refinement was carried out by fullmatrix least-squares method using SHELXL-97 on the positional and anisotropic temperature parameters of the non-hydrogen atoms, or equivalently corresponding to 424 crystallographic parameters [20]. All non-hydrogen atom parameters were refined anisotropically and all H atoms except for H1a and H1b were refined using a riding model. The C-H bond distances of these H atoms were fixed to 0.93 Å for CH, 0.96 Å for  $CH_3$  and 0.97 Å for  $CH_2$  groups. The  $U_{\rm iso}$  values of H atoms were also fixed to 1.2 times  $U_{\rm eq}$  value of parent atom for CH and CH<sub>2</sub> groups and 1.5 times U<sub>eq</sub> value of parent atom for CH<sub>3</sub> groups. Under the condition of  $I > 2\sigma(I)$  threshold, the structure was refined to  $R_{int} = 0.072$  with 3860 observed reflections. Other data collection conditions and parameters of refinement process are listed in Table 1.

# 2.4. Supplementary data

CCDC 772023 contains the supplementary crystallographic data for this paper. These data can be obtained free of

#### Table 1

Crystal data and refinement parameters of (*E*)-5-(diethylamino)-2-[(4-propylphenylimino) methyl]phenol.

CCDC	772023
Formula	C <sub>20</sub> H <sub>26</sub> N <sub>2</sub> O
Formula weight	310.43
Crystal color	Yellow
Crystal system	Orthorhombic
Space group	Pna2 <sub>1</sub>
Ζ	8
a, b, c	24.1689 (8), 8.0549 (4), 18.7206 (6) Å
α, β, γ	90°
V	3644.5 (2)Å <sup>3</sup>
Radiation type	Μο Κα
μ	$0.07 \mathrm{mm}^{-1}$
T <sub>max</sub> , T <sub>min</sub>	0.970, 0.855
Measured reflections	23,624
Independent reflections	7544
Reflections with $I > 2\sigma(I)$	3860
Number of parameters	424
$\theta_{\max}, \theta_{\min}$	26.5°, 1.7°
Scan range	-30 < h < 30, -10 < k < 9, -23 < l < 23
$R[F^2 > 2\sigma(F^2)]$	0.047
$wR(F^2)$	0.113
S	0.880
$\Delta ho_{ m max}$ , $\Delta ho_{ m min}$	0.10, –0.18e Å <sup>-3</sup>

charge via www.ccdc.cam.ac.uk/data\_request/cif, by emailing data\_request@ccdc.cam.ac.uk, or by contacting The Cambridge Crystallographic Data Centre, 12, Union Road, Cambridge CB2 1EZ, UK; fax: +44 1223 336033.

# 2.5. Computational details

In computational procedure, the geometry optimizations of tautomers of the title compound in gas phase and in different solvents leading to energy minima were performed using the analytical gradient methods of DFT with Becke's three parameters (B3) exchange functional together with the Lee–Yang–Parr (LYP) non-local correlation functional, symbolized B3LYP [21,22] by means of 6-31+G(d,p) basis set implemented in Gaussian 03W software

#### Table 2

Selected geometric parameters for (*E*)-5-(diethylamino)-2-[(4-propylphenyl imino)methyl]phenol.

package [23]. The calculations for geometry optimizations were started with the crystallographically obtained coordinates of OH tautomer and no imaginary frequency modes were obtained at the optimized geometries for the tautomers, so there are true minima on the potential energy surfaces were found for both. The vibrational frequencies were calculated at the same level of theory and the obtained frequencies were scaled by 0.9648 depends on the method and basis set used [24]. To investigate the energetic behaviors and changes of the geometric parameters of the tautomers in various environments, we performed optimizations in CHCl<sub>3</sub> ( $\varepsilon$  = 4.9), and DMSO ( $\varepsilon$  = 46.7), too by using polarizable continuum model (PCM) [25]. If there is no specific interaction such as hydrogen bond formation between the solute and solvent, this model is able to valid approximations of solvent effects on the molecule [26,27]. The absorption spectra of the tautomers were calculated using time-dependent density functional theory (TD-DFT) method started from the solution phase optimized geometries. A relaxed potential energy surface (PES) scan was performed based on the optimized geometry of the OH tautomeric form by varying the redundant internal coordinate (O1-H1 bond distance) from 1.00 to 1.70 Å with 15 steps of 0.05 Å in order to describe the potential energy barrier belonging to the intramolecular proton transfer and to observe the effects of transfer on the molecular geometry. In the scan process, all the remaining internal coordinates were fully optimized. With this kind of calculation it is possible to observe step by step the changes in the molecular geometry. In order to show the non-linear optical (NLO) activity of the molecule, the linear polarizability and the first static hyperpolarizability were obtained by molecular polarizabilities with the same level of theory.

#### 3. Results and discussion

3.1. Crystal structure, optimized geometries of tautomers and intramolecular proton transfer process

An ORTEP-3 [28] plot of the asymmetric unit of title compound is shown in Fig. 2. Displacement ellipsoids are drawn at the 30%

$ \begin{array}{ c c c c c c c c c c c c c c c c c c c$	
$ \begin{array}{ c c c c c c c c c c c c c c c c c c c$	
Bond lengths (Å)           C2 C7         1.419 (4)         1.422 (4)         1.438         1.438         1.438           C7 N1         1.295 (4)         1.276 (4)         1.298         1.301         1.303           C1 O1         1.365 (4)         1.350 (4)         1.345         1.351         1.355           N1 C8         1.415 (4)         1.411 (4)         1.406         1.408         1.409           N2 C5         1.352 (4)         1.353 (4)         1.379         1.374         1.372           C3 C4         1.352 (4)         1.357 (4)         1.381         1.380         1.381           C5 C6         1.404 (4)         1.407 (4)         1.412         1.417         1.418           O1 H1         0.930 (3)         0.930 (4)         1.000         1.005         1.007           N1 H1         -         -         -         -         -         -         -           Bond angles (°)         C1 O1 H1         107.0 (2)         108.0 (3)         107.2         106.8         106.6           C6 C1 O1         117.2 (3)         119.6 (3)         118.2         118.4         118.5         12           C2 C7 N1         123.7 (3)         123.6 (3)         122.5<	
C2 C71.419 (4)1.442 (4)1.4381.4381.4381.438C7 N11.295 (4)1.276 (4)1.2981.3011.303C1 011.365 (4)1.350 (4)1.3451.3511.355N1 C81.415 (4)1.411 (4)1.4061.4081.409N2 C51.352 (4)1.353 (4)1.3791.3741.372C3 C41.352 (4)1.357 (4)1.3811.3801.381C5 C61.404 (4)1.407 (4)1.4121.4171.418O1 H10.930 (3)0.930 (4)1.0001.0051.007N1 H1Bond angles (°)C1 O1 H1107.0 (2)108.0 (3)107.2106.8106.6C6 C1 O1117.2 (3)119.6 (3)118.2118.4118.512C2 C7 N1123.7 (3)123.6 (3)122.5122.2122.112C7 N1123.7 (3)123.6 (2)120.0101.6101.6101.6	
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C1 01 $1.365(4)$ $1.350(4)$ $1.345$ $1.351$ $1.355$ N1 C8 $1.415(4)$ $1.411(4)$ $1.406$ $1.408$ $1.409$ N2 C5 $1.352(4)$ $1.353(4)$ $1.379$ $1.374$ $1.372$ C3 C4 $1.352(4)$ $1.357(4)$ $1.381$ $1.380$ $1.381$ O1 H1 $0.930(3)$ $0.930(4)$ $1.000$ $1.005$ $1.007$ N1 H1       -       -       -       -       -         Bond angles (°)       C1 O1 H1 $107.0(2)$ $108.0(3)$ $107.2$ $106.8$ $106.6$ C6 C1 O1 $117.2(3)$ $119.6(3)$ $118.2$ $118.4$ $118.5$ $122.7$ C2 C7 N1 $123.7(3)$ $123.6(3)$ $122.5$ $122.2$ $122.1$ $122.7$	1.337
N1 C8       1.415 (4)       1.411 (4)       1.406       1.408       1.409         N2 C5       1.352 (4)       1.353 (4)       1.379       1.374       1.372         C3 C4       1.352 (4)       1.357 (4)       1.381       1.380       1.381         C5 C6       1.404 (4)       1.407 (4)       1.412       1.417       1.418         O1 H1       0.930 (3)       0.930 (4)       1.000       1.005       1.007         N1 H1       -       -       -       -       -       -         Bond angles (°)       C1 O1 H1       107.0 (2)       108.0 (3)       107.2       106.8       106.6         C6 C1 O1       117.2 (3)       119.6 (3)       118.2       118.4       118.5       12.2         C2 C7 N1       123.7 (3)       123.6 (3)       122.5       122.2       122.1       12.2	1.273
N2 C5 $1.352 (4)$ $1.353 (4)$ $1.379$ $1.374$ $1.372$ C3 C4 $1.352 (4)$ $1.357 (4)$ $1.381$ $1.380$ $1.381$ C5 C6 $1.404 (4)$ $1.407 (4)$ $1.412$ $1.417$ $1.418$ O1 H1 $0.930 (3)$ $0.930 (4)$ $1.000$ $1.005$ $1.007$ N1 H1       -       -       -       -       -         Bond angles (°)       -       -       -       -         C1 O1 H1 $107.0 (2)$ $108.0 (3)$ $107.2$ $106.8$ $106.6$ C6 C1 O1 $117.2 (3)$ $119.6 (3)$ $118.2$ $118.4$ $118.5$ $122.7 (3)$ C2 C7 N1 $123.7 (3)$ $123.6 (3)$ $122.5$ $122.2$ $122.1 1$ $122.1 1$ $122.1 1 122.1 1$	1.403
C3 C4 $1.352 (4)$ $1.357 (4)$ $1.381$ $1.380$ $1.381$ C5 C6 $1.404 (4)$ $1.407 (4)$ $1.412$ $1.417$ $1.418$ O1 H1 $0.930 (3)$ $0.930 (4)$ $1.000$ $1.005$ $1.007$ N1 H1 $     -$ Bond angles (°)       C1 O1 H1 $107.0 (2)$ $108.0 (3)$ $107.2$ $106.8$ $106.6$ C6 C1 O1 $117.2 (3)$ $119.6 (3)$ $118.2$ $118.4$ $118.5$ $122.7$ C2 C7 N1 $123.7 (3)$ $123.6 (3)$ $122.5$ $122.2$ $122.1$ $127.1$	1.379
C5 C6       1.404 (4)       1.407 (4)       1.412       1.417       1.418         01 H1       0.930 (3)       0.930 (4)       1.000       1.005       1.007         N1 H1       -       -       -       -       -       -         Bond angles (°)       C1 01 H1       107.0 (2)       108.0 (3)       107.2       106.8       106.6         C6 C1 01       117.2 (3)       119.6 (3)       118.2       118.4       118.5       12         C2 C7 N1       123.7 (3)       123.6 (3)       122.5       122.2       122.1       12	1.365
01 H1         0.930 (3)         0.930 (4)         1.000         1.005         1.007           N1 H1         -	1.396
N1 H1     -     -     -     -     -       Bond angles (°)       C1 01 H1     107.0 (2)     108.0 (3)     107.2     106.8     106.6       C6 C1 01     117.2 (3)     119.6 (3)     118.2     118.4     118.5     12       C2 C7 N1     123.7 (3)     123.6 (3)     122.5     122.2     122.1     12	-
Bond angles (°)         107.0 (2)         108.0 (3)         107.2         106.8         106.6           C6 C1 O1         117.2 (3)         119.6 (3)         118.2         118.4         118.5         12           C2 C7 N1         123.7 (3)         123.6 (3)         122.5         122.2         122.1         12	1.049
C1 01 H1         107.0 (2)         108.0 (3)         107.2         106.8         106.6           C6 C1 01         117.2 (3)         119.6 (3)         118.2         118.4         118.5         12           C2 C7 N1         123.7 (3)         123.6 (3)         122.5         122.2         122.1         12	
C6 C1 01         117.2 (3)         119.6 (3)         118.2         118.4         118.5         12           C2 C7 N1         123.7 (3)         123.6 (3)         122.5         122.2         122.1         12           C2 C7 N1         120.7 (3)         120.6 (3)         120.5         122.2         122.1         12	-
C2 C7 N1         123.7 (3)         123.6 (3)         122.5         122.2         122.1         12           C2 V1 C2         122.4 (2)         122.5         122.2         122.1         12	2.1
	2.3
L/NIL8 123.1 (3) 119.7 (3) 121.3 121.4 121.3 12	8.3
C5 N2 C17 122.8 (3) 121.3 (3) 122.0 122.1 122.1 12	2.8
C5 N2 C19 121.4 (3) 122.6 (3) 121.8 121.9 122.0 12	1.3
Torsion angles (°)	
C18 C17 N2 C5 87.2 (4) -89.6 (4) -89.3 -89.0 -88.9 -9	0.1
C20 C19 N2 C5 88.3 (4) -85.2 (4) -87.7 -87.7 -87.8 -8	7.8
C11 C14 C15 C16 -177.8 (4) -177.1 (4) -179.8 -179.9 -179.4 1	9.9
C3 C2 C7 N1 178.7 (3) -177.3 (3) -178.6 -178.8 -178.6 -1	9.9
C2 C7 N1 C8 177.8 (3) 179.5 (3) -176.9 -176.9 -176.9 -17	'9.0
C7 N1 C8 C9         -157.9 (3)         -141.5 (3)         -147.6         -148.8         -148.9         -17	2.8



**Fig. 2.** Atom numbering scheme of (*E*)-5-(diethylamino)-2-[(4-propylphenyl imino)methyl]phenol with the relative positions of the two independent molecules. Dashed lines indicate the intramolecular hydrogen bonds.

Table 3

probability level and hydrogen atoms are shown as small spheres of arbitrary radii.

The asymmetric unit of title compound contains two independent identical molecules, labeled A and B. The imine frames and the six-membered rings (C1/C6 and C8/C13) of the molecules can be seen in Fig. 2. The molecular geometry of the title compound is non-planar with the dihedral angle between the rings of  $24.50^{\circ}$ for molecule A and  $42.13^{\circ}$  for molecule B. According to the value of dihedral angle, the title compound displays photochromic features as mentioned in introduction. Selected geometrical parameters both molecule A and B are listed in Table 2.

As can be seen from their values in Table 2, the C7=N1 double, C2-C7 single and C1-O1 single bonds point out that the compound adopts the OH tautomeric form rather than the NH form in the solid state. These bond lengths are in agreement with the corresponding values in the literature [29,30]. In the OH tautomeric form, both rings of compound must be aromatic (see Fig. 1). In order to provide the further verification of OH form, we calculated the harmonic oscillator model of aromaticity (HOMA) indices for both rings by using following equation [31,32]:

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

where *n* is the number of bonds in the molecular fragments interested (in our case n is equal to 6 for the six-membered rings),  $\alpha_i$ normalization constant is equal to 257.7 and  $R_{opt}$  is equal to 1.388 Å for C—C bonds. The HOMA index is equal to 1 for the purely aromatic systems and equal to 0 for non-aromatics [33,34]. It is expected that the HOMA index of C1/C6 and C8/C13 rings should be in the range of 0.800–0.990 if the rings are aromatic and 0.500–0.700 if the rings are non-aromatic. While the calculated indexes of C1/C6 rings are 0.898 for molecule A and 0.782 for molecule B, indexes of C8/C13 rings are 0.929 for molecule A and 0.915 for molecule B. This result also indicates that the independent molecules of the title compound show OH tautomerism in solid state.

The title compound displays strong intramolecular interactions including the atoms O1 and N1 as a common feature of *o*-hydroxysalicylidene systems [35,36]. The geometries of intramolecular hydrogen bonds can be seen in Table 3. The crystal structure is stabilized by weak van der Waals interactions in three-dimensional network.

Besides observed geometrical parameters, B3LYP/6-31+G(d,p) calculated geometrical parameters in gas phase for OH and NH forms and in various solvents for OH form were listed in Table 2. There are no significant differences between the experimental and calculated geometrical parameters of OH form, except for the torsion angles controlling the planarity of molecular geometry. The dihedral angles between the rings are 36.59° for gas phase optimized OH form and 8.12° for gas phase optimized NH form according to the DFT calculations. The differences which observed between the geometries of counterparts are caused by underestimating the intermolecular interactions. DFT and similar calculations cannot take the intermolecular hydrogen bond formations into account, and consider molecules in the gas phase (*in vacuo*), but in real, the experimental results belong to the solid state consists of interacting molecules.

For a visual comparison, superimposition of the experimental (black) and theoretical (gray) molecule skeletons with r.m.s. deviation of 0.782 Å is shown in Fig. 3.

We have investigated the intramolecular proton transfer in the gas phase for the title compound by performing a PES scan process at the B3LYP/6-31+G(d,p) level so as to take a closer look to its effects on the molecular geometry. Process was started from the gas phase optimized OH geometry by assigning the O1–H1 bond as redundant internal coordinate. The relative energy versus the redundant coordinate O1–H1 bond distance in PES scan process can be seen in Fig. 4. The relative energy values are calculated with respect to the energy of stable OH tautomer.

Hydrogen bonding geometry of (*E*)-5-(diethylamino)-2-[(4-propylphenylimino) methyl]phenol.

D—H···A	<i>D</i> —Н (Å)	H···A (Å)	$D \cdot \cdot \cdot A$ (Å)	D— $H$ ··· $A$ (°)
O1a—H1a…N1a	0.93 (3)	1.75 (3)	2.595 (3)	149 (3)
O1b—H1b…N1b	0.93 (4)	1.78 (4)	2.603 (4)	145 (4)



Fig. 3. Superimpositions of the experimental (black) and theoretical (gray) geometries of the title compound.



Fig. 4. Relative energy versus the redundant coordinate in PES scan process.

As seen in Fig. 4, there are two minima representing the stable forms. While the first and deeper one is a global minimum and corresponds to stable OH form, second one is a local minimum and corresponds to stable NH form of the title compound. The potential energy barrier was determined as 4.957 kcal mol<sup>-1</sup> for the transition from the OH tautomeric form to the NH tautomeric form.

The effects of the intramolecular proton transfer on the molecular geometry can be seen better via examining the changes in HOMA index of C1/C6 ring and indicative bond lengths for every steps in the scan process. Fig. 5 reflects that the changes occurred in the lengths of C7=N1 double, C2-C7 single and C1-O1 single bonds during the transfer process. Bond lengths of C7=N1 (1.298 Å),



Fig. 5. Indicative bond lengths versus the redundant coordinate in PES scan process.

C2–C7 (1.438 Å) and C1–O1 (1.345 Å) belonging to stable OH tautomer were found as 1.337, 1.391 and 1.272 Å at the fourteenth step of scan where the stable NH tautomer was observed. The figure clearly indicates that the intramolecular proton transfer affects the double and single characters of these indicative bonds.

The HOMA indexes of C1/C6 and C8/C13 rings were calculated at every step of the scan process and Fig. 6 shows the changes of HOMA indexes in terms of scan coordinate. It is seen from the figure that the aromaticity level of C1/C6 ring is decreasing with the scan coordinate going from 1.00 Å to 1.70 Å. On the other hand, HOMA index of C8/C13 ring is nearly constant at 0.955 and the ring holds its aromaticity during the process, as expected.

#### 3.2. Vibrational frequencies

FT-IR spectrum of the title compound was given for comparison with the calculated IR spectrum in Fig. 7.

The first remarkable absorption band in experimental spectrum is in 2000–3000 cm<sup>-1</sup> region and can be attributed to the O–H stretching. It is well known that the intramolecular and intermolecular hydrogen bond formations affect the O–H stretching vibration. Due to the formation of strong intramolecular hydrogen bond between the O1 and N1 atoms, the experimental-based vibrational frequency of O–H stretching is shifted and widened to the 2000–3000 cm<sup>-1</sup> range. At this point, a notable difference is seen in the figure for the O–H stretching. The corresponding theoretical value (3012 cm<sup>-1</sup>) is very sharp because the intra- and intermolecular hydrogen bonds formations have not taken into account by the DFT calculations. The O–H in plane and out of plane bending vibrations are located at 1342 cm<sup>-1</sup> and 790 cm<sup>-1</sup>, respectively. The second one is located at 1623 cm<sup>-1</sup> and can be attributed to C=N



**Fig. 6.** HOMA indexes of C1/C6 and C8/C13 rings versus the redundant coordinate in PES scan process.



Fig. 7. The comparison of the experimental IR spectrum (black) with theoretical IR spectrum (blue). (For interpretation of the references to color in this figure legend, the reader is referred to the web version of the article.)

stretching. The spectrum shows also the presence of C—O stretching at 1243 cm<sup>-1</sup> cm. The absorption bands located at 2971–2865 cm<sup>-1</sup> region are belonging to aliphatic C—H stretching. The other remarkable vibrational frequencies and scaled computational vibrational frequencies of compound can be seen and compared in Table 4. These frequency values are in good agreement with the literature [37]. The DFT-based IR results show a good agreement with the experimental values except for the O—H stretching.

# 3.3. Energetic behavior and electronic absorption spectra

The interactions between the solute and solvent molecules influence the molecular geometry, vibrational frequencies, total energy, electronic spectrum, etc. [38,39]. So, the solvents are good helpers for the investigation of compounds showing tautomerism. Table 5 reflects the total energies, frontier molecular orbital energies and dipole moments of both tautomeric forms of the title compound in gas phase and various solvents.

It is clear from Table 4 that while the calculated total energies of tautomers decreases, the dipole moments of tautomers increases with the increasing polarity of solvent. The energy gap ( $\Delta E$ ) between the highest occupied molecular orbital (HOMO) and the lowest-lying unoccupied molecular orbital decreases for the OH form and increases for the NH form when an increase occurs in polarity of solvent. In CHCl<sub>3</sub> and gas phase OH form is more

Table 4
The experimental and calculated vibrational frequencies of IR spectra $(cm^{-1})$

Assignments <sup>a</sup>	Experimental	DFT/B3LYP/6-31+G(d,p)
Uaromatic(C-H)	3062-3021	3087-3055
U(O-H)	3000-2000	3012
$v_{aliphatic}(C-H)$	2971-2865	2991-2914
v(HC=N)	1623	1607
$v_{aromatic}(C=C)$	1581-1520	1551-1504
$\gamma_{aliphatic}(C-H)$	1449-1427	1452-1443
γ( <b>O</b> —H)	1342	1376
U(C-0)	1243	1289
$\gamma_{aromatic}(C-H)$	1132	1142
$\zeta_{aromatic}(C-H)$	826	910
ζ(Ο—Η)	790	858

<sup>a</sup>  $\upsilon$ : stretching,  $\gamma$ : bending and  $\zeta$ : out of plane bending.

stable than the NH form by 3.451 and 0.439 kcal mol<sup>-1</sup>, respectively. It is not surprising because the OH form has two aromatic rings correspond to a more delocalized  $\pi$ -electronic system and generally o-hydroxy salicylideneanilines are observed as OH tautomeric form. But the calculations also point out that the NH form of compound is more stable than the OH form by 1.066 kcal mol<sup>-1</sup> in DMSO by contrast with the situations in CHCl<sub>3</sub> and gas phase. In fact, according to the DFT the NH form is favored this time. So, keto form is easily stabilized by the polar solvents and this result is in accordance with the literature [40].

The UV–vis electronic spectra of title compound in CHCl<sub>3</sub> and DMSO were recorded within 200–500 nm range at the room temperature. The theoretical electronic excitation energies, oscillator strengths and nature of the first 10 spin-allowed singlet–singlet excitations were calculated by the TD-DFT method for the same solvents. The major contributions of the transitions were designated with the aid of SWizard program [41]. The experimental and calculated results of UV–vis spectral data are compared in Table 6. In addition, the characteristic UV–vis absorption bands of title molecule can be seen in Fig. 8.

In the UV-vis spectra of *ortho*-hydroxy Schiff base compounds, the presence of an absorption band at <400 nm indicates the OH

#### Table 5

Calculated energies, frontier orbital energies and dipole moments for (E)-5-(diethylamino)-2-[(4-propylphenylimino) methyl]phenol in gas phase and various solvents.

	Gas	CHCl <sub>3</sub>	DMSO
OH $E_{\text{total}}$ (a.u.) $E_{\text{LUMO}}$ (eV) $E_{\text{HOMO}}$ (eV) $\Delta E$ (eV) $\mu$ (D)	-962.6041 -1.4988 -5.2673 3.7685 3.7517	-962.6141 -1.5916 -5.2991 3.7075 4.9356	-962.6189 -1.6471 -5.3351 3.6880 5.5424
NH $E_{\text{total}}$ (a.u.) $E_{\text{LUMO}}$ (eV) $E_{\text{HOMO}}$ (eV) $\Delta E$ (eV) $\mu$ (D)	-962.5986 -1.8291 -5.2904 3.4613 3.3589	-962.6134 -1.9211 -5.4238 3.5026 4.9209	-962.6206 -1.9815 -5.5064 3.5249 5.8578



Fig. 8. The comparison of the experimental UV-vis spectra (black) with calculated transitions (blue). (For interpretation of the references to color in this figure legend, the reader is referred to the web version of the article.)

tautomeric form. On the other hand, compounds adopt NH tautomeric form show a new absorption band at >400 nm [42,43].

It is clear from the Table 6 and Fig. 8 that there is no absorption band observed at >400 nm region in any solvent for the title compound. This behavior can be explained with the pure enol-imine tautomeric form of the molecule even in solution. According to the experimental absorption spectra, for all of the solvents, the

Table 6Experimental and calculated electronic transitions in gas phase and various solvents.

Experimental	DFT/B3LYP/6-31+G(d,p)	
$\lambda$ (nm) [A] <sup>a</sup>	λ (nm) [f] <sup>b</sup>	Major contributions <sup>c</sup>
Gas		
-	356 [1.169]	$H \rightarrow L(81\%)$
-	312 [0.014]	$H-1 \rightarrow L(80\%)$
		$H \rightarrow L + 3 (9\%)$
-		
CHCl₃		
350 [0.791]	371 [1.336]	$H \rightarrow L(84\%)$
246 [0.105]	284 [0.015]	$H \rightarrow L + 1 (77\%)$
		$H-3 \rightarrow L(17\%)$
216 [0.170]	273 [0.054]	$H \rightarrow L + 2 (77\%)$
		$H-1 \rightarrow L(6\%)$
	261 [0.016]	$H-3 \rightarrow L(68\%)$
		$H \rightarrow L + 1 (18\%)$
		$H-2 \rightarrow L+1$ (6%)
	249 [0.058]	$H-4 \rightarrow L(46\%)$
		$H \rightarrow L + 5 (17\%)$
		$H \rightarrow L + 4 (14\%)$
DMSO		
356 [1.016]	373 [1.347]	$H \rightarrow L(84\%)$
246 [0.111]	284 [0.014]	$H \rightarrow L + 1 (78\%)$
		$H-3 \rightarrow L(17\%)$
	274 [0.059]	$H \rightarrow L + 2 (75\%)$
		$H-2 \rightarrow L(6\%)$
		$H-1 \rightarrow L(5\%)$
	262 [0.016]	$H-3 \rightarrow L(32\%)$
		$H \rightarrow L + 4 (28\%)$
		$H \rightarrow L + 3 (24\%)$
		$H \rightarrow L + 1$ (7%)
	248 [0.059]	$H-4 \rightarrow L(46\%)$
		$H \rightarrow L + 5 (13\%)$
		$H \rightarrow L + 4 (11\%)$

<sup>a</sup> A: absorbance.

<sup>b</sup> *f*: oscillator strength.

<sup>c</sup> H: HOMO; L: LUMO.

molecule exhibits absorption bands at near 350 and 240 nm. The results obtained by the TD-DFT calculations show the absorption bands at near 370 and 280 nm. In view of calculated absorption spectra of OH form, the maximum absorption wavelength corresponds to the electronic transition from the highest occupied molecular orbital HOMO to lowest unoccupied molecular orbital LUMO with 84% contribution. The other wavelengths with major contributions can be seen in Table 6.

Natural Bond Orbital (NBO) analysis is a helpful tool for understanding of delocalization of electron density from occupied Lewis-type (donor) NBOs to properly unoccupied non-Lewis type (acceptor) NBOs within the molecule [44]. Table 7 displays the second-order perturbation theory analysis of Fock matrix in NBO basis for the OH form of compound and it is clear that the  $\pi \rightarrow \pi^*$ interactions were common in the molecule. Then, we can say that the electronic transitions are mainly derived from the contribution of bands  $\pi \rightarrow \pi^*$ . The most important result obtained from the experimental and calculated electronic absorption spectra is the absence of band associated with the NH tautomeric form.

#### 3.4. Second-order non-linear optical (NLO) properties

The quantum chemistry based prediction of non-linear optical properties of a molecule has an important role for the design of materials in modern communication technology, signal processing and optical interconnections [45]. Organic molecules are commonly studied because of their larger NLO susceptibilities arising  $\pi$ -electron cloud movement from donor to acceptor, fast NLO response times, high laser damage thresholds and low dielectric constants. Although the organic molecules have these advantages, they have several NLO disadvantages, too: they have generally low thermal stability and they may undergo a facile relaxation to random orientation [46]. In addition, in the UV-vis region, the low energy transitions result in a trade-off between the non-linear efficiency and optical transparency [47,48]. But the usage of organic molecules as ligands can overcome these disadvantages. Schiff base compounds are the commonly investigated class of them because they are widely used as ligands [49].

The total static dipole moment  $\mu_{tot}$ , the average linear polarizability  $\bar{\alpha}$  and the first hyperpolarizability  $\beta$  can be calculated by using the Eqs. (2), (3) and (4), respectively [45]:

$$\mu_{tot} = \left(\mu_x^2 + \mu_y^2 + \mu_z^2\right)^{1/2} \tag{2}$$

#### Table 7

Selected second-order perturbation energies  $E^{(2)}$  associated with  $i \rightarrow j$  delocalization in gas phase for OH form.

Donor (i)	Acceptor (j)	$E^{(2) a}$ (kcal mol <sup>-1</sup> )	$\varepsilon_j - \varepsilon_i^{b}$ (a.u.)	<i>F</i> ( <i>i</i> , <i>j</i> ) <sup>c</sup> (a.u.)
BD(2) C1-C6	BD*(2) C2—C3	11.79	0.28	0.053
BD(2) C1-C6	BD*(2) C4—C5	26.46	0.27	0.079
BD(2) C2-C3	BD*(2) C1—C6	25.28	0.27	0.074
BD(2) C2-C3	BD*(2) C4—C5	14.09	0.26	0.056
BD(2) C2—C3	BD*(2) C7—N1	27.89	0.26	0.078
BD(2) C4—C5	BD*(2) C2—C3	31.09	0.27	0.083
BD(2) C4—C5	BD*(2) C1—C6	12.43	0.27	0.053
BD(2) C7—N1	BD*(2) C8-C9	10.77	0.36	0.060
BD(2) C12-C13	BD*(2) C8-C9	19.43	0.28	0.067
BD(2) C12-C13	BD*(2) C10-C11	18.98	0.29	0.067
BD(2) C8—C9	BD*(2) C7—N1	10.56	0.26	0.048
BD(2) C8—C9	BD*(2) C12—C13	19.21	0.28	0.066
BD(2) C8—C9	BD*(2) C10-C11	20.50	0.28	0.068
BD(2) C10-C11	BD*(2) C12-C13	20.59	0.27	0.067
BD(2) C10-C11	BD*(2) C8—C9	21.01	0.27	0.068
LP(1) N1	BD*(1) O1—H1	45.37	0.52	0.149
LP(2) O1	BD*(2) C1—C6	37.90	0.33	0.105

<sup>a</sup> Stabilization energy.

<sup>b</sup> Energy difference between *i* (donor) and *j* (acceptor) NBO orbitals.<sup>c</sup> Fock matrix element of *i* and *j* NBO orbitals.

#### Table 8

Calculated dipole moments (*D*), polarizability (Å<sup>3</sup>) and the first hyperpolarizability ( $\times 10^{-30}$  esu) components for (*E*)-5-(diethylamino)-2-[(4-propylphenylimino) methyl]phenol.

Components	OH	NH
components	011	INII
$\mu_x$	-2.8685	1.0548
$\mu_y$	-2.2887	-3.0713
$\mu_z$	0.7790	0.8579
$\alpha_{xx}$	80.8582	86.1568
$\alpha_{xy}$	1.6397	1.1587
$\alpha_{yy}$	35.5604	36.0159
$\alpha_{xz}$	-1.2749	-1.8246
$\alpha_{yz}$	0.2576	-1.3018
α <sub>zz</sub>	25.0896	24.3544
$\beta_{xxx}$	44.3237	23.6349
$\beta_{xxy}$	-1.7955	-4.3662
$\beta_{xyy}$	-3.7174	-4.4285
$\beta_{yyy}$	-0.9624	-0.9377
$\beta_{xxz}$	-0.8781	-0.7466
$\beta_{xyz}$	0.8747	0.8671
$\beta_{yyz}$	0.2671	-0.0187
$\beta_{xzz}$	-0.6844	-0.7428
$\beta_{yzz}$	-0.5447	-0.5185
$\beta_{zzz}$	0.2681	0.2111

$$\bar{\alpha} = \frac{1}{3}(\alpha_{XX} + \alpha_{yy} + \alpha_{ZZ}) \tag{3}$$

$$\beta = \left[ \left( \beta_{xxx} + \beta_{xyy} + \beta_{xzz} \right)^2 + \left( \beta_{yyy} + \beta_{xxy} + \beta_{yzz} \right)^2 + \left( \beta_{zzz} + \beta_{xxz} + \beta_{yyz} \right)^2 \right]^{1/2}$$
(4)

In order to investigate the NLO properties of the title compound, the components of dipole moment, polarizability and the first hyperpolarizability have been calculated using polar = ENONLY input to Gaussian03 at the level of B3LYP/6-31+G(d,p) in gas phase. The components and calculated values of total static dipole moment  $\mu$ , the average linear polarizability  $\bar{\alpha}$  and the first hyperpolarizability  $\beta$  are listed in Table 8. The calculated values of components show difference depend on the size of basis sets used. But it is difficult to decide which basis set generates the reliable values because there are no reported experimental values for the title compound in literature. For this reason, we used the basis set 6-31+G(d,p) as in all this work. The calculated  $\beta$  components have been converted into electrostatic units (esu) (1 a.u. = 8.6393 × 10<sup>-33</sup> esu).

The values of  $\mu_{tot}$ ,  $\bar{\alpha}$  and  $\beta$  obtained by Sun and friends with the B3LYP/6-31G(d) method for urea are 1.373 D, 3.831 Å<sup>3</sup> and 0.372 × 10<sup>-30</sup> esu, respectively [50] and generally used for the comparison. In another paper,  $\beta$  value has been computed as  $34.797 \times 10^{-30}$  esu for a Cu(II) Schiff base complex by

Donmez et al. [51]. In our present work, their values are 3.751 D, 47.169 Å<sup>3</sup>, 40.059 × 10<sup>-30</sup> esu for OH form and 3.358 D, 48.842 Å<sup>3</sup>, 19.367 × 10<sup>-30</sup> esu for NH form. If we recall Table 7,  $\pi$ -electron cloud movement must be responsible for the non-linear optical properties of the tautomers. According to the high values of the first hyperpolarizability of the tautomeric forms, the title compound can really be a good applicant in the development of NLO materials.

# 4. Conclusions

In this study, we have synthesized a Schiff base compound, (E)-5-(diethylamino)-2-[(4-propylphenylimino)methyl]phenol and characterized by spectroscopic and structural techniques as well as the theoretical methods. X-ray, FT-IR and UV-vis methods confirm the OH form of the title compound. The PES scan process in gas phase shows that the potential barrier is 4.957 kcal mol<sup>-1</sup> to transition from the OH tautomeric form to the NH tautomeric form. This intramolecular proton transfer affects the molecular geometry by changing the aromaticity of C1/C6 ring and lengths of the indicative bonds. In addition, according to the calculated results, the increased polarity of solvent brings about proton transfer in intramolecular hydrogen bonding. And finally, the high values of the first hyperpolarizabilities of tautomers show that the title compound is a good applicant for NLO.

We hope the results of this study will help researchers to design and synthesis new materials.

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