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Survey of conformational isomerism in (*E*)-2-[(4-bromophenylimino)methyl]-5-(diethylamino)phenol compound from structural and thermochemical points of view

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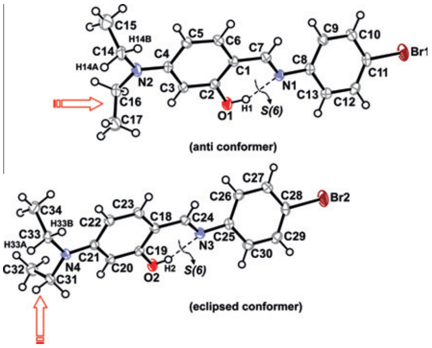
HIGHLIGHTS

- ▶ Isomerism and tautomerism are investigated.
- ▶ Isomerism is evaluated from thermochemical point of view.
- ▶ Tautomerism is investigated depending on solute–solvent interactions.

GRAPHICAL ABSTRACT



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ABSTRACT

In this study, (*E*)-2-[(4-bromophenylimino)methyl]-5-(diethylamino)phenol compound was investigated by mainly focusing on conformational isomerism. For this purpose, molecular structure and spectroscopic properties of the compound were experimentally characterized by X-ray diffraction, FT-IR and UV–Vis spectroscopic techniques, and computationally by DFT method. The X-ray diffraction analysis of the compound shows the formation of two conformers (anti and eclipsed) related to the ethyl groups of the compound. The two conformers are connected to each other by non-covalent C–H···Br and C–H···π interactions. The combination of these interactions is resulted in fused $R_2^2(10)$ and $R_2^4(20)$ synthons which are responsible for the tape structure of crystal packing arrangement. The X-ray diffraction and FT-IR analyses also reveal the existence of enol form in the solid state. From thermochemical point of view, the computational investigation of isomerism includes three studies: the calculation of (a) the rate constants for transmission from anti or eclipsed conformations to transition state by using Eyring equation, (b) the activation energy needed for isomerism by using Arrhenius equation, (c) the equilibrium constant from anti conformer to eclipsed conformer by using the equation including the change in Gibbs free energy. The dependence of tautomerism on solvent types was studied on the basis of UV–Vis spectra recorded in different organic solvents. The results showed that the compound exists in enol form in all solvents except ethyl alcohol.

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Introduction

o-Hydroxy Schiff bases derived from the condensation of primary amines with carbonyl compounds have a strong intramolecular hydrogen bond. These compounds are of interest because of their thermochromism and photochromism in the solid state, which can involve reversible intramolecular proton transfer from an oxygen atom to the neighboring nitrogen atom. Intramolecular proton transfer mechanism of both excited-state and ground-state is still the subject of intensive research. On the basis of thermochromic and photochromic Schiff bases, it was proposed that molecules exhibiting thermochromism are planar, while molecules exhibiting photochromism are non-planar [1,2]. Photochromic compounds are used as optical switches and optical memories, variable electrical current, ion transport through membranes [3]. In addition, they have widespread usage as ligands in the field of coordination chemistry [4] as well as in diverse fields of chemistry and biochemistry owing to their biological activities [5]. *o*-Hydroxy Schiff bases can exist in two tautomeric structures as enol and keto forms in the solid state [6,7]. *o*-Hydroxy Schiff bases were studied in solvent media and found to exist as both enol and keto form. While the absorption band at wavelength greater than 400 nm is observed in polar solvents, this band is not observed in apolar solvents. The absorption band at greater than 400 nm was found to belong to the keto form of *o*-Hydroxy Schiff bases [8,9].

In this study, (*E*)-2-[(4-bromophenylimino)methyl]-5-(diethylamino)phenol compound was studied mainly from the point of conformational isomerism. For this purpose, molecular structure and spectroscopic properties of the compound were experimentally characterized by X-ray diffraction, FT-IR and UV–Vis spectroscopic techniques, and computationally by DFT method.

Experimental and computational methods

Synthesis

The compound (*E*)-2-[(4-bromophenylimino)methyl]-5-(diethylamino)phenol (I) 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-bromoaniline (0.29 g, 2.59 mmol) in 20 mL ethanol. The reaction mixture was stirred for 1 h under reflux. The crystals of (*E*)-2-[(4-bromophenylimino)methyl]-5-(diethylamino)phenol suitable for X-ray analysis were obtained by slow evaporation from acetone (yield 82%; m.p. 380–381 K).

Instrumentation

The melting point was determined by StuartMP30 melting point apparatus. FT-IR spectrum of the compound was recorded in the 4000–400 cm^{-1} region with a Bruker 2000 spectrometer using KBr pellet. UV–Vis absorption spectra were recorded on a Thermo scientific BioGenesis UV–Vis spectrometer using a 1 cm path length of the cell. Diffraction experiment was carried out at 130 K with an Xcalibur diffractometer using graphite monochromated MoK$_{\alpha}$ radiation. The structure was solved by direct methods using SHELXS-97 [10]. The refinement was carried out by full-matrix least-squares method. All non-hydrogen atoms were refined anisotropically. The H atoms except those bonded to O atoms were placed in geometrically idealized positions and refined by a riding model with $U_{iso}(H) = 1.2\,U_{eq}(C)$ and $U_{iso}(H_{methyl}) = 1.5\,U_{eq}(C)$. The relevant crystal data, experimental conditions and final refinement parameters can be obtained from Cambridge Structural Database (CCDC: 801848).

Computational procedure

All computations were performed using GAUSSIAN 03W [11]. Full geometry optimization of the title molecule was performed by using DFT method with Becke's three-parameters hybrid exchange-correlation functional (B3LYP) [12] employing 6-311G(d,p) basis set [13–15]. The ground state geometry optimization of the title compound for gas phase was calculated using DFT method with B3LYP adding 6-311G(d,p). The ground state geometry optimization of the title compound in gas phase for TS structure was performed with the same level of theory. A computational study was carried out from global minimum through a transition state to local minimum for the title compound. Vibra-

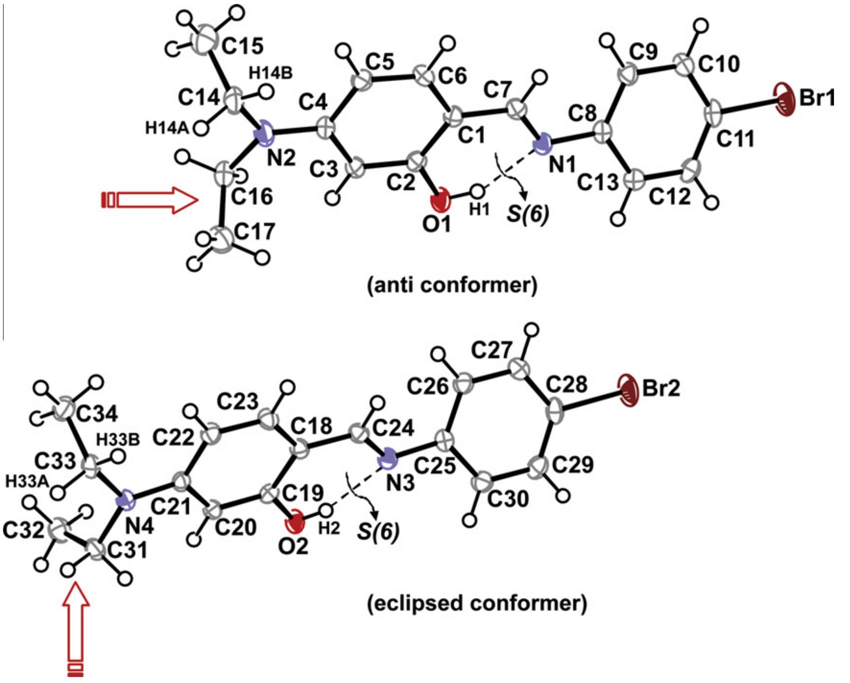

Fig. 1. A view of the title compound, showing anti and eclipsed conformers. H atoms not involved in non-covalent interactions were not labeled for clarity.

Table 1
Bond distances (Å), angles (°) and non-covalent interactions in anti and eclipsed conformers of the title compound.

Bond distance				Bond angle				Torsion angle			
Anti		Eclipsed		Anti		Eclipsed		Anti		Eclipsed	
N2–C4	1.360(2)	N4–C21	1.366(2)	N2–C14–C15	111.1(2)	N4–C33–C34	113.9(1)	C4–N2–C16–C17	89.6(2)	C21–N4–C31–C32	−88.8(2)
N2–C16	1.360(2)	N4–C31	1.461(2)	N2–C16–C17	112.9(2)	N4–C31–C32	114.1(2)	C4–N2–C14–C15	96.8(2)	C21–N4–C33–C34	76.8(2)
N2–C14	1.487(2)	N4–C33	1.467(2)	C14–N2–C16	116.4(1)	C31– N4–C33	116.9(1)	C1–C7–N1–C8	174.0(2)	C18–C24–N3–C25	178.6 (2)
C14–C15	1.494(3)	C31–C32	1.516(2)	C4–N2–C14	121.4(1)	C21–N4–C33	120.6(1)	C3–C4–N2–C14	166.2(2)	C20–C21–N4–C33	−175.1(2)
C16–C17	1.508(3)	C33–C34	1.518(2)	C4–N2–C16	122.0(2)	C21–N4–C31	122.2(1)	C3–C4–N2–C16	−9.4(3)	C20–C21–N4–C31	−0.9(2)
C2–O1	1.361(2)	C19–O2	1.361(2)	C3–C4–N2	121.7(2)	C20–C21–N4	122.1(2)	O1–C2–C1–C7	1.1(3)	O2–C19–C18–C24	−3.5(3)
N1–C7	1.296(2)	N3–C24	1.294(2)	C5–C4–N2	121.0(2)	C22–C21–N4	120.8(2)	N1–C7–C1–C6	−177.9(2)	N3–C24–C18–C23	−179.7(2)
N1–C8	1.411(2)	N3–C25	1.413(2)	C7–N1–C8	120.8(1)	C24–N3–C25	119.6(1)	C7–N1–C8–C9	−28.5(2)	C24–N3–C25–C26	−33.6(2)
C11–Br1	1.898(2)	C28–Br2	1.896(2)	C1–C2–O1	120.3(2)	C18–C19–O2	120.2(2)	C7–N1–C8–C13	156.4(2)	C24–N3–C25–C30	148.8(2)
D–H···A				**d(D–H)**		**d(H···A)**		**d(D···A)**		**<DHA**	
O1–H1···N1				0.839		1.821		2.598		153.3	
O1–H2···N3				0.765		1.933		2.630		151.4	
[a]C14–H14A···Br2^{i}				0.990		2.882		3.724		143.5	
[a]C33–H33A···Br1^{ii}				0.989		3.077		3.867		137.7	
X–H				**Cg**		**d(H···Cg)**		**d(X···Cg)**		**<XHCg**	
[a]C14–H14A				Cg1^{iii}		3.183		3.782		120.4	
[a]C33–H33A				Cg2^{iii}		2.970		3.587		122.0	

[a] Symmetry codes: (i) $-1+x, -1+y, z$; (ii) $-1+x, -1+y, -1+z$; (iii) $1-x, 1-y, 1-z$. Cg represents ring centroid. There are no s.u values in geometric parameters of non-covalent interactions since most of H atoms were placed in geometrically idealized positions.

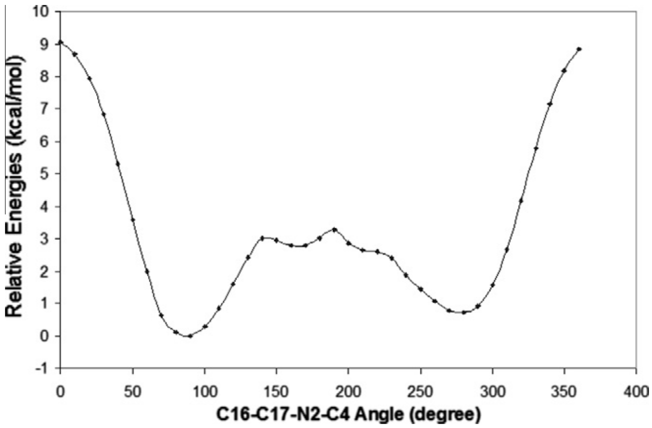

Fig. 2. Variations of the relative energies of the title compound against the torsional angle θ_1(C16–C17–N2–C4).

tional frequencies were obtained for characterization at stationary points called global and local minima for which all eigenvalues of the Hessian are positive and transition state corresponding to only one imaginary frequency [16,17]. The thermodynamic properties were obtained in the range of 100–500 K at the corresponding optimized geometries using the same theory level.

Results and discussion

Structure determination

Two independent molecules exist in the asymmetric unit, which correspond to two conformers of the compound (Fig. 1). The two conformers are resulted from rotation about C16–N2 single bond of ethyl group. In conformer I (anti conformer), the ethyl groups are positioned in the opposite directions. On the other hand, the ethyl groups in conformer II (eclipsed conformer) are in the same directions. The torsion angle C4–N2–C16–C17 = 89.6(2)° in anti conformer while its corresponding value in eclipsed conformer is −88.8(2)°. The characteristic bond distances and angles related to two conformers are comparatively given in Table 1. The compound prefers enol form in both conformers. The C=N double bond and C–O single bond distances compare well with previously reported values for similar compounds [18,19]. Both conformers adopt *E* configuration about the C=N double bond (Fig. 1). The strong intramolecular interactions between the phenolic atoms (O1, O2) and nitrogen atoms (N1, N3) constitute six-membered rings defined as *S*(6) in Etter's notation [20]. These hydrogen bonds are characterized by O1···N1 and O2···N3 distances of 2.598(2) and 2.630(2) Å (Table 1), being shorter than the sum of the van der Waals' radii for N and O [21].

The crystal packing of the compound is mainly stabilized by C–H···Br interactions between methylene groups and bromide atoms (Table 1). The repetition of intermolecular C14–H14A···Br2^{i} (i: $-1+x$, $-1+y$, z) and C33–H33A···Br1^{ii} (ii: $-1+x$, $-1+y$, $-1+z$) interactions is resulted in $C_2^2(28)$ chains (Fig. S1). Further analysis of non-covalent interactions shows that the crystal packing are also supported by C14–H14A···Cg1^{iii} (iii: $1-x$, $1-y$, $1-z$) and C33–H33A···Cg2^{iii} interactions which involve the same methylene groups (Fig. S1). The geometry of these interactions are characterized by the H···Cg distances of 2.970 and 3.183 Å involving methylene groups and centroid of phenyl rings. It is seen that the two conformers are connected by these interactions. Thus, the $C_2^2(28)$ polymeric chains are linked to each other, generating fused $R_2^2(10)$ and $R_2^4(20)$ synthons in (0 1 0) plane. This arrangement of ring motifs is resulted in a tape structure in the crystal packing.

In order to determine the conformational energy profiles for different arrangements, the energy values as a function of the torsion angle θ_1(C4–N2–C16–C17) were calculated by DFT method. The calculated molecular energy profile as a function of θ_1 is given in Fig. 2. The molecular energy profile shows two minima at 90° and 280° which correspond to anti and eclipsed conformers, respectively. The energies of two conformers are close to each other. The eclipsed conformer is slightly higher than that of anti conformer by 0.73 kcal/mol due to the steric hindrance. After determining the both stable conformers, the geometry optimizations pertaining to both stable conformers of title compound were performed again by DFT method with B3LYP adding 6-311G(d,p) basis set in order to compare the results obtained for two conformers. The rate of conformational isomerism was studied by calculating the rate constants for both anti and eclipsed conformers. In the transition state theory, reactants are considered to pass through a transition state to form the final product. The transition state optimization was carried out in order to calculate the rotation rate

Table 2
The rate constants calculated at different temperatures.

T (K)	Anti conformer		Eclipsed conformer	
	$\Delta G^{\neq}$ (kcal/mol)	k (s^{-1})	$\Delta G^{\neq}$ (kcal/mol)	k (s^{-1})
100	7.498	8.48×10^{-5}	6.766	3.40×10^{-3}
200	7.824	1.17×10^{4}	7.166	6.16×10^{4}
298.15	8.246	5.56×10^{6}	7.656	1.51×10^{7}
300	8.256	6.04×10^{6}	7.666	1.60×10^{7}
400	8.756	1.37×10^{8}	8.234	2.64×10^{8}
500	9.308	8.90×10^{8}	8.852	1.41×10^{9}

Table 3
The Gibbs free energy, enthalpy, entropy changes and equilibrium constants calculated at different temperatures.

T(K)	ΔH (kcal/mol)	ΔS (cal/molK)	ΔG (kcal/mol)	K_{eq}
100	0.805	0.754	0.730	0.025
200	0.800	0.705	0.659	0.190
298.15	0.794	0.681	0.591	0.369
300	0.794	0.682	0.589	0.372
400	0.789	0.669	0.521	0.519
500	0.786	0.661	0.455	0.633

between the two conformers observed in the crystal structure of the compound.

$$\text{anti conformer} \leftrightarrow \text{TS} \leftrightarrow \text{eclipsed conformer} \tag{1}$$

The rate constant for TS formation from the reactant can be calculated using Eyring equation [22,23]:

$$k = \frac{k_B T}{h} e^{-\frac{\Delta G^{\neq}}{RT}} \tag{2}$$

where k is the reaction rate for TS formation, k_B and h are Boltzmann and Planck constants, respectively. $\Delta G^{\neq}$ is the change in free energy of activation between TS and reactant. $\Delta G^{\neq}$ and k constant were calculated to investigate the isomerism from anti conformer to TS in different temperatures. The rate constant increases when the temperature is increased from 100 to 500 K. The calculated results are given in Table 2. As seen from Table 2, the transmission rate from anti conformer to TS increases upon an increase in temperature. The same procedure was repeated for TS formation from eclipsed conformer and the results were compared. It was concluded that the transmission rate to TS of eclipsed conformer is more than that of anti conformer.

The relationship between the rate constant and temperature is given by Arrhenius equation [24] as follows:

$$k = Ae^{-E_a/RT} \tag{3}$$

where E_a and A are activation energy and integration constant, respectively. It is seen that the activation energy (E_a) needed for isomerism can be determined from the slope of the graph lnk-1/T. Therefore, we plotted lnk-1/T graphs to calculate activation energies for transmissions from anti or eclipsed conformers to TS (Fig. S2). While the activation energy from anti conformer to TS is 7.45 kcal/mol, the activation energy from eclipsed conformer to TS is 6.65 kcal/mol (Fig. S3). It is seen that the activation energies for both conformers are relatively low. The activation energy needed for transmission from eclipsed conformer to TS is smaller than that required for anti conformer. In other words, when the title compound is formed in eclipsed conformer, it is easily converted to the anti conformer (thermodynamically stable form) through a reversible reaction. The rate constants for anti and eclipsed conformers are 5.56×10^6 and 1.51×10^7 s^{-1}, respectively, showing that the rotation between two conformers is very fast.

The calculation of Gibbs free energies, entropies and enthalpies were carried out for the temperatures from 100 to 500 K by DFT/B3LYP method with 6-311G(d,p) basis set [22,23]. The results obtained on the basis of vibrational analysis are shown in Table 3. The isomerism of the title compound can also be investigated by using the following equation which gives the change in Gibbs free energy (ΔG) in terms of entropy (ΔS) and enthalpy changes (ΔH) between anti and eclipsed conformers:

$$\Delta G = \Delta H - T\Delta S \tag{4}$$

The reaction is spontaneous for $\Delta G < 0$, disfavored reaction (non-spontaneous) for $\Delta G > 0$ or equilibrium reaction for $\Delta G = 0$. The calculated ΔH and ΔS values are both positive with 0.794 and 0.681 kcal/mol, respectively. It is seen that ΔG of the title compound is positive with 0.591 kcal/mol for the room temperature.

The equilibrium constant from anti conformer to eclipsed conformer can be calculated with following equation [23]:

$$K = e^{-\Delta G/RT} \tag{5}$$

where K is the equilibrium constant from anti conformer to eclipsed conformer. ΔG is the free energy change calculated from anti conformer to eclipsed conformer. The calculated equilibrium constant for isomerism between two conformers is 0.369 in room temperature. This means that two conformers can be converted between them. These results explain why the title compound exists in both anti and eclipsed conformers in the crystal structure.

FT-IR spectrum

FT-IR spectrum of the title compound was given in Fig. 3. The OH group has three vibrations as stretching, in-plane bending and out-of-plane bending vibrations. The OH stretching vibration is very sensitive to inter and intramolecular hydrogen bonding. In 1700–3000 cm^{-1} region, the absorption band is attributed to the υ(O–H) stretching vibration which broaden owing to the formation of strong intramolecular hydrogen bonding O–H···N in the structure. Generally, the OH in-plane bending and out-of-plane bending vibrations of phenols lie in the region 1300–1400 and 517–710 cm^{-1}, respectively [25]. The band observed at 1354 cm^{-1} was assigned to OH in-plane bending vibration and the band observed at 786 cm^{-1} was assigned to OH out-of-plane bending vibration for the title compound. The absorption band located at 1625 cm^{-1} is attributed to υ(C=N) stretching vibration. The aromatic C–H stretching, C–H in-plane bending and C–H out-of-plane bending vibrations appear in 3000–3100, 1100–1500 and 800–1000 cm^{-1} frequency ranges, respectively [25]. The absorption band at 3066 cm^{-1} corresponds to the aromatic CH stretching vibrations of the title compound. In addition, in plane bending and out-of-plane CH vibrations were observed at 1128 and at 823 cm^{-1},

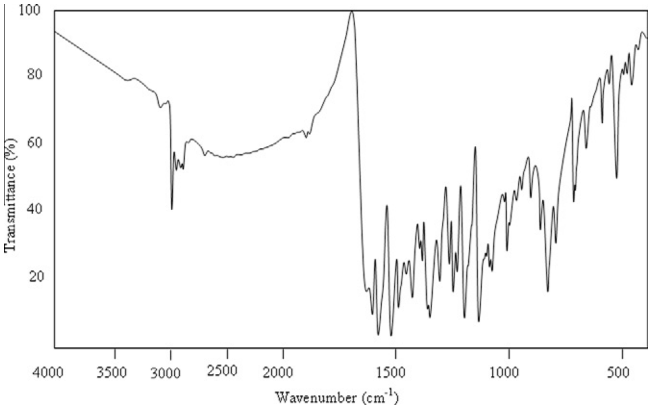

Fig. 3. FT-IR spectrum of the title compound.

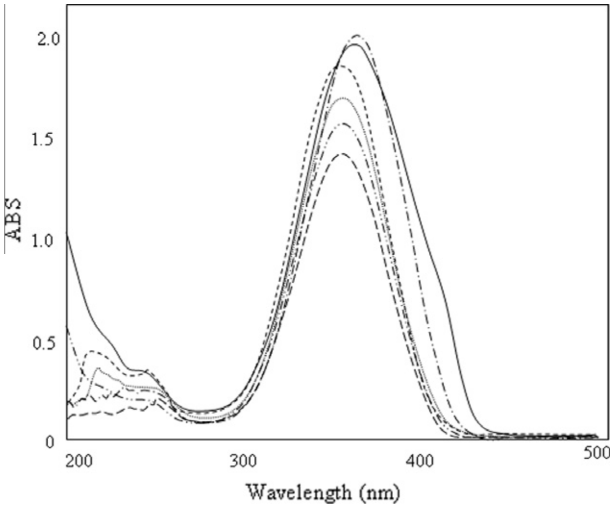

Fig. 4. The solvent effect on UV–Vis spectra of the title compound in (–·–) DMSO, (—) EtOH, (----) THF, (·····) $CHCl_3$, (–··–) CH_3CN, (– – –) benzene.

respectively. The asymmetric and symmetric stretching vibrations of the aliphatic CH_2 and CH_3 group were observed at 2972, 2932, 2896 and 2872 cm^{-1}. The bending vibrations of these groups were observed at 1450, 1423 and 1390 cm^{-1} while rocking modes were observed at 1014 and 707 cm^{-1}. The C–O stretching vibrations in phenols are expected to appear as a strongest band in 1300–1100 cm^{-1} frequency ranges [25]. The absorption band observed at 1191 cm^{-1} for the title compound was assigned to C–O stretching mode of vibration. The absorption bands observed at 1600–1400 cm^{-1} are due to CC stretching vibrations of the aromatic compounds [25]. The CC stretching modes of aromatic rings of the title compound were observed at 1599, 1573, and 1517, 1482 cm^{-1}, which agree well with the literature data.

UV–Vis absorption spectra

The UV–Vis spectra of the title compound in various organic solvents (EtOH, DMSO, THF, CH_3CN, benzene and $CHCl_3$) were recorded within 200–500 nm range (Fig. 4). The absorption bands at 356 nm (in THF, CH_3CN, benzene and $CHCl_3$) and 364 nm (in DMSO) are attributed to $\pi \rightarrow \pi^*$ transition. However, a new absorption band at 410 nm was observed in the spectrum of the title compound in EtOH (Fig. 4), which was not observed in case of DMSO, THF, CH_3CN, benzene and $CHCl_3$.

HOMO and LUMO called Frontier molecular orbitals (FMO) are the most important ones in terms of their roles in reactions between molecules and in electronic spectra of a molecule [26]. The frontier molecular orbitals for both conformers are shown in Fig. S4 for gas phase. HOMO and LUMO of both conformers are similar. Therefore, it is expected that absorption bands of two conformers have same values. To prove this conclusion, the first 10 spin-allowed singlet-singlet excitations for both conformers were calculated by TD-DFT approach. TD-DFT calculations started from optimized geometry were performed for gas phase to calculate excitation energies so that we can see if two conformers show two absorption bands in the spectrum. The percentage contributions of molecular orbitals to formation of the bands were obtained by using SWizard Program [27]. Considering TD-DFT calculations it can be said that the excitation energy value at 355.09 nm arises from HOMO → LUMO (81%) transitions for both conformers since HOMO and LUMO of two conformers are same.

The previous computational and experimental studies show that the new absorption band above 400 nm belongs to the keto form of *o*-Hydroxy Schiff bases [8,28]. While the compound prefers enol form in the solid state, it exists in both enol and keto form in EtOH. The keto form is important in the solution and stabilized by the polar solvents through solute and solvent interactions. Fig. S5 shows the possible structures of compounds in the solution.

N,N-diethylamino group is an electron-donating group. Before keto form occurs, zwitter ionic form arises. The electron-donating N,N-diethylamino group stabilizes zwitter ionic form and eases the formation of keto form with resonance. If it depended on the electron-donating N,N-diethylamino group, keto form would be observed in all solvents. This shows that the solvent is also effective in the formation of keto form in addition to the electron-donating N,N-diethylamino group. In addition, the formation of keto form cannot be explained only by the polarity of solvent. If it depended on the polarity of solvent, keto form would be observed in DMSO. The fact that keto structure did not formed in DMSO shows that the solvent polarity is not effective on the proton transfer and instead it depends on the H-donor-acceptor property of solvent. The title compound adopts both enol and keto forms in EtOH which is a polar and protic solvent. Previous computational studies also proved that protic solvents decrease activation energy and ease proton transfer [17,29].

Conclusion

The conformational isomerism in (*E*)-2-[(4-bromophenylimino) methyl]-5-(diethylamino)phenol compound was experimentally investigated by X-ray diffraction, FT-IR and UV–Vis spectroscopic techniques, and computationally by DFT method. In the crystal structure, the compound has two conformers (anti and eclipsed) related to the ethyl groups. The two conformers are connected to each other by non-covalent C–H···Br and C–H···π interactions. The combination of these interactions generate fused $R_2^2(10)$ and $R_2^4(20)$ synthons which form a tape structure in the crystal packing. The X-ray diffraction and FT-IR analyses also reveal the existence of enol form in the solid state. From thermochemical point of view, the computational investigation of isomerism includes three studies: The rate constants for transmission from anti or eclipsed conformations to transition state were calculated using Eyring equation. The results show that the transmission rate to TS of eclipsed conformer is more than that of anti conformer. Applying Arrhenius equation for the activation energies needed for isomerism, it is found that the eclipsed conformer of the title compound is easily converted to the anti conformer (thermodynamically stable form) through a reversible reaction. The calculated equilibrium constant for isomerism between two conformers is 0.369 in room temperature, supporting the previous conclusion related to the conversion of two conformers. The dependence of tautomerism on solvent types was studied on the basis of UV–Vis spectra recorded in different organic solvents. The results showed that the compound exists in enol form in DMSO, THF, CH_3CN, benzene and $CHCl_3$ while both enol and keto forms are observed in EtOH.

Appendix A. Supplementary data

Crystallographic data for the structure in this paper have been deposited with the Cambridge Crystallographic Data Centre as the supplementary publication no. CCDC 801848. Copies of the data can be obtained, free of charge, on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (fax: +44-1223-336033 or e-mail: deposit@ccdc.cam.ac.uk). The crystal packing (Fig. S1), correlation graphic (Fig. S2), energy profile (Fig. S3), molecular orbital surfaces (Fig. S4) and the possible structures of the title compound (Fig. S5) are also provided.

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