ORIGINAL RESEARCH

Synthesis, molecular structure, spectroscopic investigations and computational studies of (E)-1-(4-(4-(diethylamino)-2-hydroxybenzylideneamino)phenyl)ethanone

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Received: 18 December 2014/Accepted: 30 January 2015 © Springer Science+Business Media New York 2015

Abstract The Schiff base compound (E)-1-(4-(diethylamino)-2-hydroxybenzylideneamino)phenyl)ethanone has been synthesized and characterized by IR, UV–Vis, and ¹H and ¹³C NMR techniques. These properties of title compound were also investigated from calculative point of view. UV–Vis spectra of the title compound were recorded in different organic solvents to investigate the dependence of tautomerism on solvent types. Calculated results reveal that its enol form is more stable than its keto form. A detailed analysis of the nature of the hydrogen bonding, using topological parameters, evaluated at bond critical points.

Keywords Schiff base \cdot Spectroscopy \cdot Intramolecular proton transfer \cdot DFT

Electronic supplementary material The online version of this article (doi:10.1007/s11224-015-0571-2) contains supplementary material, which is available to authorized users.

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Introduction

N-salicylidene anilines (anils) are particularly eye-catching since they are synthesized by the condensation of the corresponding aldehydes and amines and exhibit a strong intramolecular H-bonding between the H-atom of the hydroxy group and the N-atom of the imine moiety. Particularly, 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 π -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]. Schiff bases have the wide range of applications spanning the industrial [3, 4], pharmaceutical [5, 6], biological [7, 8], and chemical fields [9–11]. For instance, they are industrially used as dyes and pigments in textile [12] in addition to their application in pharmacology for the synthesis of antibiotics, antiallergic and antitumor substances [13, 14]. Photochromic compounds are important because of their use as optical switches and optical memories, variable electrical current, ion transport through membranes [15].

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. [16]. 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 [17, 18].

A new (E)-1-(4-(4-(diethylamino)-2-hydroxybenzylideneamino)phenyl)ethanone (DHBE) compound was synthesized, and its spectroscopic properties were studied both experimental and theoretical insight. NBO analyses were performed to provide valuable information about various intermolecular interactions. Thus, in the present work, the molecular structure, E_{HOMO} (the highest occupied molecular orbital energy), E_{LUMO} (the lowest unoccupied molecular orbital energy), LUMO-HOMO energy gap (ΔE) , global hardness (η) , softness (S), electronegativity (χ), dipole moment (μ), polarizabilities ($\langle \alpha \rangle$), the anisotropy of the polarizabilities ($<\Delta\alpha>$), and the first-order hyperpolarizabilities ($<\beta>$), Fukui functions, molecular electrostatic potential maps (MEP) and thermodynamic parameters (molecular energy (E), heat capacity $(C_{p,m}^{0})$, entropy (S_m^0) and enthalpy (H_m^0)) are calculated and discussed. Also, intramolecular proton transfer process of DHBE was investigated for ground state in gas phase.

Experimental

Materials and measurements

All reagents and solvents for synthesis and analysis were commercially available and used as received without further purifications. The mid-IR spectrum was obtained in the 4,000–400 cm⁻¹ region with spectral resolution of 2 cm⁻¹ by averaging the results of 16 scans Perkin-Elmer RXI Fourier Transform spectrophotometer using KBr pellet technique (solid phase). The ultraviolet absorption spectra were examined in the range of 250-600 nm using Perkin-Elmer lambda 25 recording spectrophotometer. The NMR spectra were recorded at the ambient temperatures on a Brucker AVANCE DRX 400 MHz using DMSO as solvent. All chemical shifts are reported in δ units down field from TMS. Cyclic voltammetry measurements were performed bv AUTOLAB PGSTAT20 potentiostat-galvanostat (EcoChemie, Netherlands). The electrochemical properties of title compound ($c = 2 \times 10^{-3}$ M) was investigated by cyclic voltammetry with DMSO as the solvent in the presence of 0.1 MBu₄NBF₄ as the supporting electrolyte using Pt working and counter electrodes and Ag/AgCl as the

reference electrodes at an ambient temperatures [19]. Prior to the measurements, the solution was purged with argon to remove residual oxygen.

Synthesis

In this study, we report the synthesis of a new Schiff base. (*E*)-1-(4-(4-(diethylamino)-2-hydroxybenzylideneamino) phenyl)ethanone (Scheme 1). A solution of 4-(diethylamino)salicylaldehyde (1 mmol, 0.193 g) dissolved in ethanol (10 mL) was added to a solution of 4-aminoacetophenone (1 mmol, 0.135 g) in ethanol (10 mL). The resulting yellow solution was stirred at room temperature for 3 h. After completion of the reaction (monitored by TLC analysis), the reaction mixture was allowed to room temperature to afford the fine crystalline powder of N-salicylidene aniline derivative. The product was filtered off, washed with ethanol (5 mL) and dried under vacuum. ¹H NMR (400 MHz, CDCl₃) (δ/ppm): 13.46 (s, 1H, OH), 8.75 (s, 1H, CH = C), 7.98 (d, J = 8.4 Hz, 2H, ArH), 7.40 (d, J = 8.4 Hz, 2H, ArH), 7.35 (d, J = 8.8 Hz, 1H, ArH),6.34 (dd, J = 2.0, 8.8 Hz, 1H, ArH), 6.08 (d, J = 2.0 Hz, 1H, ArH), 3.36-3.42 (m, 4H, CH₂), 2.57 (s, 3H, COCH₃), 1.12 (t, 6.8, 7.2 Hz, 6H, CH₃); ¹³C NMR (100 MHz, CDCl₃) δ: 197.2, 164.2, 163.0, 152.9, 152.5, 135.1, 134.1, 130.3, 121.3, 109.1, 104.7, 97.2, 44.4, 27.1, 13.0.

Computational details

In the present work, the density functional method (DFT) has been employed using Becke's three parameter hybrid exchange functional [20] with the Lee–Yang–Parr correlation functional [21, 22] combined with standard 6-311++G(d,p) basis set and GAUSSIAN 03W program package without any constraint on the geometry [23].

The prediction of vibrational wave numbers and thermodynamical parameters were done at the DFT (B3LYP) level, as it has been well recognized as an efficient theoretical chemistry tool for studying vibrational properties of variety of molecules. Positive values of all the calculated vibrational wave numbers confirmed the geometries to be located at true local minima on the potential energy surface. In this investigation, we observed that the calculated frequencies were slightly greater than the fundamental frequencies. These discrepancies are corrected either by



Scheme 1 Synthesis of (E)-1-(4-(4-(diethylamino)-2-hydroxybenzylideneamino)phenyl)-ethanone (DHBE)

computing anharmonic corrections explicitly [24] or by introducing a scale factor. In the present study, a selective scaling factor of 0.9961 is used for the wave numbers less than 1,700 cm⁻¹ and 0.9556 for greater than 1,700 cm⁻¹ at 6-311++G(d,p) and 0.9963 are used for the wave numbers less than $1,700 \text{ cm}^{-1}$ and 0.9959 for greater than 1,700 cm^{-1} at 6-311++G(2d,p) [25]. The vibrational wave number assignments were carried out by combining the results of the GaussView 4.1.2 program [26] and VEDA4 program [27]. Detailed interpretations of the vibrational spectrum of our compound have been made based on the calculated potential energy distribution (PED).

The nuclear magnetic resonance (NMR) chemical shift calculations were performed using gauge-included atomic orbital (GIAO) method [28] at B3LYP/6-311++G(2d,p) level, and the ¹H and ¹³C chemical shifts were referenced to the corresponding values for TMS, which were calculated at the same levels of theory. The absorption spectra of the tautomers were calculated using time-dependent density functional theory (TD-DFT) method, started from the solution-phase optimized geometries.

Molecular electrostatic potential (MEP) surface is plotted over the optimized geometry to elucidate the reactivity of DHBE molecule. The HOMO and LUMO were calculated by B3LYP/6-311++G(2d,p) method. AIM 2000 software [29] was applied to obtain electron density at the hydrogen bond critical points according to Bader's atoms in molecules (AIM) theory [30] at the B3LYP/6-311++G(d,p) and B3LYP/6-311++G(2d,p) levels. Lorentzian function has been utilized for deconvolution of IR spectrum using the Genplot package.

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 (O_1 – H_1 bond distance) from 0.9 to 1.7 Å with 17 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.

Results and discussion

Molecular geometry optimization

o-hydroxy Schiff bases show prototropic tautomerism via intramolecular proton transfer between the phenolic oxygen and imino nitrogen atoms. The process of proton transfer ends up with two tautomeric forms known as enol and keto structures. These are illustrated for the title compound in Fig. 1. The optimized molecular structure of the title compound with numbering scheme for the atoms is presented in Fig. 2. The selected structural parameters of DHBE are calculated by B3LYP level with 6-311++ G(2d,p) basis set and presented in Table 1. The optimized structure can only be compared with other similar systems for which the crystal structures have been solved [31, 33]. As can be seen from their values in Table 1, the $C_{10}=N_{11}$ double, C₃-C₁₀ single and C₄-O₂₈ ingle bonds point out

Keto form Enol form

Fig. 1 Enol and keto tautomeric forms of title compound







Table 1 Optimized geometrical parameters of DHBE at B3LYP/6-311++G(2d,p) level

Parameters ^a	Cal.		Exp. ^b	Exp. ^c	Exp. ^c Parameters ^a			Exp. ^b	Exp. ^c	
	keto	enol				keto	enol			
Bond lengths					Bond lengths					
$C_1 - C_2$	1.356	1.373	1.367	1.368	N ₁₁ -C ₁₂	1.392	1.3978	1.412	1.418	
$C_1 - C_6$	1.449	1.424	1.420	1.420	C ₁₂ -C ₁₃	1.400	1.4024		1.393	
C ₂ –C ₃	1.425	1.406	1.410	1.404	C ₁₂ -C ₁₄	1.404	1.4039		1.389	
C ₃ -C ₄	1.472	1.422	1.415	1.412	C ₁₃ C ₁₅	1.386	1.3868		1.382	
C ₃ -C ₁₀	1.381	1.431	1.430	1.438	C ₁₄ C ₁₇	1.379	1.3807		1.383	
C ₄ -O ₂₈	1.265	1.342	1.354	1.358	C ₁₅ C ₁₉	1.398	1.3986		1.392	
C ₄ -C ₅	1.422	1.387	1.380	1.383	C ₁₇ C ₁₉	1.401	1.4019		1.390	
C ₅ -C ₆	1.390	1.408	1.408	1.408	RO–H	0.994	1.00	0.950	0.96	
C ₆ -N ₃₀	1.374	1.375	1.369	1.371	RO…N	2.629	2.616	2.578	2.607	
C ₁₀ -N ₁₁	1.338	1.295	1.294	1.289	RH…N	1.735	1.70	1.692	1.744	
Bond angles					Bond angles					
A(3,4,28)	120.8	121.0	120.1	120.3	A(10,11,12)	128.3	121.3	121.7	120.3	
A(3,10,11)	122.3	122.9	121.5	122.1	A(11,12,14)	117.6	118.2	117.5	117.7	
A(5,4,28)	122.1	118.2	118.6	118.2	A(10,11,12)	128.3	121.3	121.7	120.3	
A(28,29,11)	147.49	149.3	153.6	148.0						
Dihedral angles					Dihedral angles	3				
D(3,10,11,12)	-179.5	-176.6	178.4	-179.3	D(10,3,4,28)	-0.4	-0.2	1.8		
D(10,11,12,13)	1.5	36.5	-2.4	33.2	D(2,3,4,28)	179.5	179.2	-179.3		
D(10,11,12,14)	-178.6	-145.9	178.0	-149.1	D(31,30,6,1)	-178.3	179.7	173.5		

^a For atom numbering from Fig. 2

^b Ref. [19]

^c Ref. [20]

that the compound adopts the OH tautomeric form rather than the NH form in the solid state.

The theoretical values for $C_{10}=N_{11}$ (1.295 Å) and $C_{12}=$ N_{11} (1.398 Å) distances indicate the double and single bond character of these bonds, respectively. The bond angle C₃-C₁₀-N₁₁ is 122.9° which is consistent with the sp^2 hybrid character of C₁₀ atom, while the bond angle C₁₀- N_{11} - C_{12} is 121.3° which is consistent with the sp^2 hybrid character of N_{11} atom [33–35]. Ortho position to the imine group of Schiff base occupied with the OH is interesting due to the existence of O-H...N hydrogen bond and possibility of tautomerism between enol-imine and keto-amine form in 2-hydroxy Schiff base [36, 37]. In the structure of Schiff base DHBE, there is an intramolecular O₂₈-H₂₉ $\cdots N_{11}$ hydrogen bond (Fig. 2) as in the Schiff bases derived from salicylaldehyde that always form the O-H...N type of hydrogen bonding, regardless of the nature of the N substituent [38, 39]. It is known that there is a strong correlation between the strength of the H-bond and the delocalization of the system of conjugated double bonds, and the effect is qualitatively interpreted by resonanceassisted hydrogen bond (RAHB) model [40]. The calculated O…N distance (2.616 Å) for the title compound is significantly shorter than 2.656 Å which was reported for O–H…N in the class of RAHB [40]. The dihedral angles between the rings are 36.5° for gas phase optimized OH form and 1.5° 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. According to the value of dihedral angle, the title compound displays photochromic features as mentioned in introduction.

In order to evaluate the strength of this hydrogen bond, the PES of the molecule was explored by scanning the torsional angle (H_{29} – O_{28} – C_4 – C_3) at the B3LYP/6-31G(d,p)level. As can be seen from Fig. S1, the resulting potential energy profile shows one global minimum DHBE, two global maxima and two local minima. The energies of the local minima and the global maxima are 75.8 and 59.3 kJ mol⁻¹ higher than DHBE, respectively. The large barrier-height for rotating about (H_{29} – O_{28} – C_4 – C_3) torsional angle implies a strong hydrogen bonding in this system. The



Fig. 3 Relative energy profile during the proton transfer process

flexibility of the molecule for conversion to different conformers was determined by scanning the torsional angles $(N_{11}-C_{10}-C_3-C_2)$, $(C_{15}-C_{19}-C_{22}-O_{27})$ and $(C_{10}-N_{11}-C_{12}-C_{13})$ as shown in Fig. S1.

The intramolecular proton transfer was investigated in the gas phase for the title compound by performing a PES scan process at the B3LYP/6-311++G(d,p) level in order to determine its effects on the molecular geometry. The process was started from optimized enol geometry by selecting O–H bond as redundant internal coordinate. The graph of the relative energy versus the O–H bond distance is given in Fig. 3. The energy values were calculated relative to the energy of stable enol form. Figure 3 shows two minima representing the stable forms. In the figure, the keto form corresponds to a local minimum, while the global minimum represents the stable enol form. The potential energy needed for the transition from enol form to keto form was calculated as 5.89 kcal mol⁻¹.

The effects of the intramolecular proton transfer on the molecular geometry can be seen better via examining the changes in HOMA index of C_2/C_3 ring and indicative bond lengths for every step in the scan process. Fig. S2 reflects that the changes occurred in the lengths of $C_{10}=N_{11}$ double, C_4-O_{28} and C_3-C_{10} single bonds during the transfer process. Bond lengths of $C_{10}=N_{11}(1.297 \text{ Å})$, $C_3-C_{10}(1.432 \text{ Å})$ and $C_4-O_{28}(1.339 \text{ Å})$ belonging to be stable OH tautomer were found as 1.343, 1.382 and 1.260 Å, 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.

One another way to confirm that the title compound exists in enol form is to calculate the harmonic oscillator model of aromaticity (HOMA) index by using the following equation for the rings [41]:

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

where n is the number of bonds in ring, α normalization constant is equal to 257.7, and R_{opt} is equal to 1.388 Å for C–C bonds. For the purely aromatic compounds, HOMA index is equal to 1, but for non-aromatic compounds it is equal to 0. The HOMA indexes in the range of 0.900–0.990 or 0.500–0.800 show that the rings are aromatic or the nonaromatic, respectively [42]. In the current study, the calculated HOMA index for C₂/C₃ ring is 0.902. This result shows that C₂/C₃ ring in the title compound has aromatic character. The change of HOMA index in terms of scan coordinate is shown in Fig. S2. As expected, the aromaticity level of C₂/C₃ ring decreases with the scan coordinate from 0.9 to 1.7 Å.

Vibrational analysis

The title compound consists of 45 atoms, which have 129 normal modes. Those normal modes of DHBE have been assigned according to the detailed motion of the individual atoms. To the best of our knowledge, there is no detailed quantum chemical study for the molecular structure and vibrational spectra of title compound. For visual comparison, the observed and calculated FT-IR spectra of DHBE at DFT-B3LYP method using 6-311++G(2d,p) basis set are shown in Fig. 4. The observed IR bands and calculated wave numbers (scaled) and assignments are given in Table 2. For clear observation of these bands, the use of band deconvolution techniques in the IR spectrum could be used. A deconvoluted IR spectrum of DHBE was depicted in Fig. S3. It is well known that the DFT and similar methods underestimate interactions like intermolecular hydrogen bonds in gaseous phase (in vacuom). The calculated results by frequency analysis for C=N, O-H and C-O stretching shows significant deviations from experimental values due to intramolecular hydrogen bond between N and O.

Oxygen-hydrogen vibrations

The O–H stretching vibration is very sensitive to inter- and intra-molecular hydrogen bonds and lays in the region 2,000–3,000 cm⁻¹ in FT-IR spectrum. It gives rise to the three vibrations as stretching, in-plane bending and out-ofplane bending vibrations. In 3,000–1,800 cm⁻¹ region, the absorption band was attributed to the v(O–H) stretching vibration which broaden owing to the formation of strong intramolecular hydrogen bonding O–H··N in the structure. Generally, the O–H in-plane bending and out-of-plane bending vibrations of phenols lie in the region 1,400–1,300 cm⁻¹ and 517–710 cm⁻¹, respectively [43]. The remarkable absorption band in the experimental spectrum was in 3,000–1,800 cm⁻¹ regions and can be attributed to the O–H stretching. It is well known that the intramolecular and intermolecular hydrogen bond



Fig. 4 Comparison of observed and calculated IR spectra of DHBE **a** observed; **b** calculated with B3LYP/6-31++G(2d,p)

formations affect the O–H stretching vibration. Due to the formation of strong intramolecular hydrogen bond between the O_{28} and N_{11} atoms, the experimental-based vibrational frequency of O–H stretching was shifted and widened to the 3,000–1,800 cm⁻¹ range. The corresponding theoretical value (3,161 cm⁻¹) is very sharp because the intraand inter-molecular hydrogen bonds formations have not taken into account by the DFT calculations. The band observed at 1,427 cm⁻¹ was assigned to O–H in-plane bending vibration, and the band observed at 866 cm⁻¹ was assigned to O–H out-of-plane bending vibration for the title compound.

Carbon-oxygen vibrations

The C–O stretching vibration in phenols appears as a strong band in $1,300-1,100 \text{ cm}^{-1}$ frequency ranges [43, 44]. According to our deconvolution results, the IR spectrum of DHBE indicates the presence of a medium FT-IR band observed the C–O stretching vibrations at 1,246 cm⁻¹ (see Fig. S4) and at 1,253 cm⁻¹ (B3LYP). The C=O stretching frequency of molecule strongly absorbs in the region 1,850–1,600 cm⁻¹. The absorptions are sensitive for both carbon and oxygen atoms of the carbonyl group. Both

have the same amplitudes while it vibrates. Normally, carbonyl group vibrations occur in the region $1,780-1,680 \text{ cm}^{-1}$ [45]. In the present study, the C=O stretching vibration was assigned at $1,676 \text{ cm}^{-1}$ in FT-IR spectrum with very strong intensity. The dominant in-plane C=O-bending vibration in the case of DHBE was calculated at 614 cm⁻¹ in complete conformity with Rastogi et al. [46]. The band observed for title compound at 590 cm⁻¹ in the IR spectrum, 605 cm⁻¹ (DFT) was assigned as C=O in-plane bending vibration mode.

Carbon-nitrogen vibrations

The C=N stretching mode was observed in the region $1,625 \text{ cm}^{-1}$ [33]. The characteristic band in the FT-IR spectrum of title compound is the appearance of the strong band at $1,627 \text{ cm}^{-1}$, attributed to the C=N stretching vibration frequency. This mode was calculated to be $1,608 \text{ cm}^{-1}$. The C–N stretching modes are difficult, due to possible mixing of vibrations in the $1,600-1,200 \text{ cm}^{-1}$ region [47]. In DHBE, one strong weak FT-IR band at $1,427 \text{ cm}^{-1}$ was assigned to C–N stretching vibration. The C–N in-plane bending vibration is usually occurred at 440 cm⁻¹ [48]. In DHBE, a medium FT-IR band at 453 cm^{-1} was assigned to C–N in-plane bending vibrations.

Phenyl ring vibration

The phenyl ring spectral region chiefly involves the C-H, C-C stretching, and C-C-C as well as H-C-C- bending vibrations. The bands due to the ring C-H stretching vibrations is observed as a collection of weak-to-moderate bands in the region 3,091-3,046 cm⁻¹. The calculated wave number for the CH-stretching modes was found in the range 3,211-3,187 cm⁻¹ and was matched with the experimental FT-IR spectra. The PED for these modes suggested that these are pure modes. The aromatic C-H inplane bending modes of benzene and its derivatives are observed in the region $1,300-1,000 \text{ cm}^{-1}$ [49]. In the case of DHBE, vibrations involving the C-H in-plane bending were found throughout the region 1,338-1,132 cm⁻¹. The C-H wagging (or out of bending vibrations) mode started appearing from 824 cm^{-1} and had contribution up to 590 cm^{-1} and were assigned well in the spectra.

The ring stretching vibrations in each compound readily assigned in the range $1,590-1,000 \text{ cm}^{-1}$ [50]. In DHBE, the FT-IR bands at 1,627, 1,571 and 1,356 cm⁻¹ are assigned to ring stretching vibrations. All the ring stretching modes are expected to appear in the expected range. It shows good agreement between theoretical and experimental C–C stretching vibrations. The C–C–C bending vibrations always occur below 600 cm⁻¹ [51]. Three weak FT-IR bands at 728 and 685 cm⁻¹ are assigned to C–C–C

Table 2 Experimental [FT-IR wave numbers (in cm^{-1})] and theoretical [scaled wave numbers (in cm^{-1})] of DHBE at B3LYP/6-311++G(d,p) and B3LYP/6-311++G(2d,p) level of theory

B3LYI	P/6-311++	G(d,p)		B3LYP/6-311++G(2d,p)								
No.	Freq	I.IR	A _R	Freq	I.IR	A _R	IR(Neat)	Vibrational assignments (PED)				
V ₁₂₉	3083	12	100	3,211	14	146	3,091(w)	ν _s CHI(98)				
v ₁₂₅	3,057	552	231	3,178	7	113	3,046(vw)	v _s CHII(99)				
v ₁₂₂	3,034	8	36	3,161	290	164	2,000-3,000(vbr)	νOH(58), ν _a CHII(40)				
v ₁₂₀	3,002	20	177	3,127	20	175	2,970(m)	v _a CH ₃ (86)				
V ₁₁₉	2,977	66	34	3,100	65	36	2,932(m)	υ _a CH ₃ (amin)(54), υ _a CH ₂ (32)				
v_{116}	2,957	52	198	3,081	49	199	2,910(m)	$v_a CH_3(amin)(85)$				
v ₁₁₂	2,908	74	205	3,031	78	219	2,886(m)	υ _s CH ₂ (97)				
v_{110}	2,899	26	131	3,022	31	328	2,724(vw)	$vC_{10}-H_{45}(47), v_sCH_3(amin)(37)$				
V ₁₀₉	2,899	58	315	3,021	56	133	2,700(w)	$vC_{10}-H_{45}(92)$				
							1,932(w)	Overtone/combination				
							1,896(w)	Overtone/combination				
							1,752(vw)	Overtone/combination				
V ₁₀₆	1,659	275	416	1,722	258	387	1,676(65)	vC=O(86)				
V ₁₀₃	1,544	1,449	9,625	1,608	1,398	9,024	1,627(81)	vC=N(16), vPhII(14), vPhII(12)				
V100	1.479	643	927	1.543	622	951	1.571(84.br)	$vPhI(16), \delta sCH_2(16), vC_6-N_{30}(10)$				
Vos	1.456	15	9	1.520	14	21	1.521(34)	δ_{a} CH ₃ (amin)(30), δ_{s} CH ₂ (29)				
V97	1.442	32	203	1.504	36	264	1.509(34)	$\delta_{\rm s}$ CH ₂ (33), $\delta_{\rm s}$ CH ₃ (amin)(27)				
Voz	1.420	113	754	1.481	106	756	1.479(37.sh)	δ_{3} CH ₃ (amin)(16)				
V80	1.390	152	234	1,449	139	202	1.427(55.br)	$\delta OH(15), vC_6 - N_{30}(10)$				
Ven	1.323	203	123	1.381	169	101	1.381(15.sh)	δ_{2} CH ₂ (76)				
V80	1.314	74	642	1.366	56	592	1.356(61)	vPhII(41)				
V70	1,280	41	49	1,336	52	58	1.338(31)	$\delta CHI(34)$, $\tau CH_2(22)$, $\nu C=O(12)$				
V76	1,257	42	7	1,314	24	5	1,308(13.sh)	τCH ₂ (27)				
V74	1,222	425	249	1,275	316	166	1,266(29)	$v_{-}C_{10}=C_{22}=CH_{2}(29)$				
V72	1 214	259	376	1 268	320	466	1,257(40)	δCHI(39)				
V73	1 202	28	44	1,253	29	36	1,226(35)	vC = O(23)				
V72	1,202	208	1 014	1,255	185	909	1,240(33) 1,232(40)	$v C = C = N = C(19)$ $v C_{20} = N_{20} = C_{21}(13)$				
V/1	1 1 2 0	200	1,014	1 188	309	1 727	1,200(46)	δCHII(53)				
V69	1,105	306	1,571	1,100	347	133	1,200(45) 1 170(45 sh)	$oCH_2(11)$ vPhI(10)				
V67	1,105	500	8	1,133	יד-נ ד	5	1,170(49,51)	$\delta CHI(65) \rightarrow PbII(14)$				
V66	1,000	23	1	1,135	23	1	1,132(40) 1,117(30)	$oCH_{a}(amin)(25)$, $V_{Cat}=N_{ac}=C_{ac}(21)$				
V65	1,005	25	12	1,110	25	13	1,117(30) 1,072(41)	ρ CH ₂ (amin)(22), v_a C ₃₁ = v_{30} =C ₃₈ (21)				
V62	007	1	12	1,079	1	15	1,0/2(41) 1,0/0(w.sh)	$\rho CH_{3}(annn)(22), VC=CH_{3}(annn)(22)$				
V61	050	1	4	1,045	21	204	1,040(w,sh)	$\gamma C = H_{13}(00), \gamma C = O(25)$				
V58	939	102	128	052	105	122	055(34)	$\gamma C_{10} H_{45}(05), \gamma C H_{10}(10)$				
V54	914	102	120	933	105	123	933(34) 808(0 hr)	$\Lambda(12)$ γ				
V51	825	10	0	908	17	0	898(9,01)	$\Delta(15), vC = C11_3(amm)(12)$				
V49	700	43	9	000 921	19	79	800(22)	yOII(43)				
V46	799	17	05	700	10	10	824(03) 780(22)	γCHI(48)				
V43	755	0	2	784	13	3	789(32)	γ CHI(31)				
V ₄₂	152	8	2 15	784	11	1	759(9,br)	γ CHI(23), ρ CH ₂ (11), ρ CH ₃ (amin)(13)				
V39	090	5	15	/30	0	6/	/28(W)					
V38	664	55	4	693	34 7	4	080(20)	OUUU(10)				
V37	633	6	2	662	-7	2	000(13)	$\gamma pn1(51), 1 (29)$				
V35	580	39	14	605	37	14	590(45)	$oC=O(26), vC_{22}-CH_3(12)$				
V ₃₃	563	1	3	589	8	3	554(8,sh)	$\Delta(12)$, $\delta phl(11)$				
v_{30}	496	4	35	518	5	36	510(13)	γph11(16)				

Table 2 continued

B3LYP/6-311++G(d,p)				B3LYP/	B3LYP/6-311++G(2d,p)					
No.	Freq	I.IR	A _R	Freq	I.IR	A _R	IR(Neat)	Vibrational assignments (PED)		
V ₂₉	479	3	5	501	3	5	480(w)	δPhII(22)		
v_{26}	426	9	1	445	8	1	453(13)	δC_{22} -CH ₃ (18), Δ (13), δC_{34} -C ₃₁ -N ₃₀ (11)		

in-plane bending vibrations of DHBE. The bands that are assigned to CCC out-of-plane bending vibrations are observed at 655 and 510 cm^{-1} in DHBE.

Methylene group vibrations

For the assignments of CH₂ group frequencies, basically six fundamentals can be associated with each CH₂ group, which was expected to be depolarized [52]. The asymmetrical CH₂ stretching vibrations are generally observed above $3,000 \text{ cm}^{-1}$, while the symmetric stretch will appear between 3,000 and 2,900 cm^{-1} region [53]. In this study, the asymmetric and symmetric stretching vibrations are observed at 2,932 and 2,886 cm⁻¹, respectively, in FT-IR. For n-alkyl benzenes, the assignments of the C-C stretching mode at about 1,464 and 1,290 cm^{-1} are quite problematic, since these bands are frequently masked by the CH₂ scissoring and wagging vibrations, respectively [54, 55]. For DHBE, the CH₂ scissoring mode has been assigned at 1,521 and 1,509 cm^{-1} in FT-IR. The band at 1,170 cm⁻¹ in FT-IR was assigned to CH₂ rocking in-plane vibration. The CH₂ twisting out of plane bending vibrations was observed at 1,338 and 1,308 cm^{-1} in FT-IR spectrum.

Methyl group vibrations

The CH stretching in CH₃ occurs at lower frequencies than those of the aromatic ring $(3,000-2,800 \text{ cm}^{-1})$ [56]. In the present work, CH₃ asymmetric stretching is found at 2,970, 2,931 and 2,910 cm⁻¹ in FT-IR spectrum. In many molecules, the symmetric deformation appears with an intensity varying from medium to strong and expected in the range $1,380 \pm 25 \text{ cm}^{-1}$ [57]. According to our deconvolution results, the IR spectrum of DHBE indicated that the presence of one band observed the $\delta_s CH_3$ frequencies at $1,381 \text{ cm}^{-1}$ (see Fig. S4) and at 1381 cm⁻¹ (B3LYP). For the title compound, the scissoring modes of the CH₃ group are calculated to be 1,520, 1,504, 1,481 cm^{-1} (B3LYP) and $1,521, 1,509, 1,479 \text{ cm}^{-1}$ (IR). The rocking vibrations of CH₃ group are generally observed in the region $1,070-1,010 \text{ cm}^{-1}$ [58]. The band at 1,117, 1,072 and $1,040 \text{ cm}^{-1}$ in the IR spectrum and at 1,110, 1,079 and 1,043 cm⁻¹ (B3LYP) is assigned as ρ CH₃ mode for the DHBE. The twisting modes were not observed in the FT-IR

because they appear at very low frequency. The band at 145 cm⁻¹ (B3LYP) is assigned as the twisting mode τ CH₃.

The calculated values of v (C–CH₃) were 953 and 908 cm⁻¹. The experimental observed values in the FT-IR spectrum at 955 and 898 cm⁻¹ confirm the assignment on a comparison with the calculated values.

It can be seen from Fig. S4 (which shows the theoretical FT-IR spectra along with the experimental spectra for DHBE) that there is an excellent correlation between the theoretical and experimental FT-IR spectra. As can be seen from Fig. S4, experimental fundamentals have a good correlation with B3LYP. The correlation graph follows the linear equation, y = 73.967 + 0.9235x; where 'y' is the calculated wave number, 'x' is the experimental wave number (cm⁻¹). The value of correlation coefficient ($R^2 = 0.9965$) shows that there is good agreement between experimental and calculated results.

NBO analysis

The natural bond orbital (NBO) calculations were performed using NBO 3.1 program [59] as implemented in the Gaussian03 package at the DFT/B3LYP level to understand various second-order interactions between the filled orbitals of one subsystem and vacant orbitals of another subsystem. Delocalization of electron density between occupied Lewis-type (bond or lone pair) NBO orbital and formally unoccupied (anti-bond or Rydberg) non-Lewis NBO orbital corresponds to a stabilizing donor-acceptor interaction. NBO analysis has been performed on the molecule at the DFT (B3LYP)/6-311++G(2d,p) level to elucidate the intra-molecular, rehybridization and delocalization of electron density within the molecule. The interactions result in a loss of occupancy from the localized NBO of the idealized Lewis structure into an empty non-Lewis orbital. For each donor (i) and acceptor (j), the stabilization energy $E^{(2)}$ associated with the delocalization $i \rightarrow j$ is determined as

$$E^{2} = \Delta E_{ij} = q_{i} \frac{(F_{ij})^{2}}{(E_{j} - E_{i})^{2}}$$
(2)

where q_i is the donor orbital occupancy, E_i and E_j are diagonal elements and F_{ij} is the off-diagonal NBO Fock matrix element. In NBO analysis, large E^2 value shows the

Solvent	Donor	Acceptor	E^2 (kcal mol ⁻¹)	0–H (Å)	N…H (Å)	N…O (Å)
Gas phase	LP(1)N ₁₁	BD*(1)O ₂₈ -H ₂₉	20.45	0.9956	1.7350	2.6344
Hexane	LP(1)N ₁₁	BD*(1)O ₂₈ -H ₂₉	21.34	0.9974	1.7264	2.6293
CH_2Cl_2	LP(1)N ₁₁	BD*(1)O ₂₈ -H ₂₉	22.99	1.0002	1.7091	2.61834
EtOH	LP(1)N ₁₁	BD*(1)O ₂₈ -H ₂₉	23.35	1.0008	1.7058	2.6165
CH ₃ CN	LP(1)N ₁₁	BD*(1)O ₂₈ -H ₂₉	23.41	1.0010	1.7052	2.6079

Table 3 Second-order perturbation theory analysis of the Fock matrix in NBO basis and intramolecular hydrogen bond lengths in different solvents

intensive interaction between electron donors and electron acceptors and greater the extent of conjugation of the whole system; the possible intensive interactions are given in NBO Table 3.

NBO analysis of the title compound was performed by applying same level of theory in the enol form in different solvents and gas phase. The interactions between donor N₁₁ lone pair and acceptor O28-H29 bond for the title compound in various solvents and gas phase are shown in Table 3. NBO analysis for the title compound shows that there is a strong interaction $nN_{11} \rightarrow \sigma^*O_{28}$ -H₂₉. This interaction increases with the increase in polarity of the solvent, and as a result, O₂₈-H₂₉ bond weakens and lengthens. The delocalization energy of the title compound increases with the increase in polarity of the solvent. The increasing of delocalization energy of the title compound indicates that it is more stable in the polar solvent. In addition, N...O distance shortens with the increase in polarity of the solvent. The increase in $nN_{11} \rightarrow$ σ^*O_{28} -H₂₉ delocalization with the increase in polarity of the solvent strengthens the intramolecular hydrogen bond and weakens and elongates the O-H sigma bond.

NMR spectral studies

The ¹H NMR spectrum of the title compound was recorded in DMSO (Fig. 5). Normally, the proton chemical shift of organic molecules varies greatly with the electronic environment of the proton. Hydrogen attached or nearby electron-withdrawing atom or group can decrease the shielding and move the resonance of attached proton toward a higher frequency, whereas electron-donating atom or group increases the shielding and moves the resonance toward lower frequency [60]. The resonance of hydroxyl proton is at 12.46 ppm which is typical for intramolecular hydrogen bonding (O-H...N) proton. The resonance of imino proton is at 8.75 ppm. The absorption of ring protons is in the range of 6-8 ppm, which corresponds to aromatic character. In ¹H NMR spectrum of the title compound, the absorption peaks of aromatic ring protons are between 6.07 and 7.99 ppm (Fig. 5). These results are in accordance with the literature values [31, 44]. This result reveals that the title compound adopts enol form in solution.

In the ¹³C NMR spectrum of the title compound recorded in DMSO (Fig. 6), the imino carbon (C_{10}) peak was observed at 163.015 ppm, and the phenolic carbon (C₄) peak appeared at 164.180 ppm. The ¹³C NMR spectrum of the title compound shows peaks at 197.22 ppm (C_{22}) , 152.904 ppm (C_{12}) and 152.537 ppm (C_6) . The C_3 , C₅, C₁, C₂ and C₁₉ carbons of aromatic ring are at 109.102, 97.169, 104.714, 135.123 134.092 ppm, respectively. The C13, C14 and C15, C17 carbons of aromatic ring are at 121.331 and 130.257 ppm, respectively. The $CH_2(C_{31})$ and CH₃(C₃₄) peaks of ethyl group are seen at 44.444 and 13.002 ppm, respectively (Fig. 6). The results agree well with the reported values [31, 44]. The computed ¹³C and ¹H NMR chemical shifts at the B3LYP/6-311++G(2d,p) level of theory along with experimental data are given in Table 4. As can be seen, the results obtained by using all DFT methods are in reasonable agreement with experimental values.

Molecular electrostatic potential (MEP) surface

In order to investigate the chemical reactivity of the molecule, molecular electrostatic potential (MEP) surface is plotted over the optimized electronic structure of DHBE using density functional B3LYP level with 6-311++G(2d,p) basis set. MEP is related to the electronic density and is a very useful descriptor in understanding sites for electrophilic and nucleophilic reactions as well as hydrogen bonding interactions [61]. Figure 7 shows the computationally observed MEP surface map in association with the fitting point charges to the electrostatic potential *V*(r) for title compound. MEP values were calculated as described previously, using the equation [62].

$$v(r) = \sum_{A} \frac{Z_A}{|\vec{R} - \vec{r}|} - \int \frac{p(\vec{r})dr'}{|\vec{r}' - \vec{r}|}$$
(3)

where p(r) is the electron density function of the molecule, Z_A is the charge of nucleus A located at \overrightarrow{R} , and r' is the dummy integration variable. The negative (red) regions of MEP were related to electrophilic reactivity and the positive (blue) regions to nucleophilic reactivity. These sites give information about the region where the compound can



have intermolecular interaction. In Fig. 7, this molecule has several possible sites for the electrophilic attacks over the oxygen atoms: O_{27} and O_{28} . The maximum negative electrostatic potential value for these electrophilic sites calculated at B3LYP/6-311++G(2d,p) is about -22.041 and -22.036 a.u. The fitting point charges to those

electrostatic potentials are $-0.238(O_{27})$ and $-0.3(O_{28})$. Also a maximum positive region is localized on the hydrogen atoms, indicating a possible site for nucleophilic attack. The MEP map shows that the negative potential sites are on electronegative atoms as well as the positive potential sites are around the hydrogen atoms. However, a

Table 4 Experimental and theoretical, ¹H and ¹³C NMR isotropic chemical shifts (with respect to TMS) of DHBE with DFT (B3LYP 6-311++G(2d,p)) method

Assignment	B3LYP	Exp.	Assignment	B3LYP	Exp.
H _{35,36,37,42,43,44}	1.97	1.12	C _{34,41}	16.27	13.00
H _{24,25,26}	2.67	2.54	C ₂₃	30.50	27.07
H _{32,33,39,40}	3.67	3.39	C _{31,38}	53.01	44.44
H ₉	6.44	6.08	C ₅	102.04	97.17
H ₇	6.51	6.34	C ₁	109.79	104.71
H ₈	7.53	7.35	C ₃	116.23	109.10
H _{16,18}	7.63	7.40	C _{13,14}	123.42	121.33
H _{20,21}	8.44	7.98	C _{15,17}	135.31	130.26
H ₄₅	8.69	8.75	C ₁₉	140.24	134.09
H ₂₉	12.86	12.46	C ₂	142.20	135.12
			C ₆	159.67	152.54
			C ₁₂	164.68	152.90
			C ₁₀	169.67	163.02
			C_4	172.66	164.18
			C ₂₂	207.00	197.22

maximum positive region is localized on the C_{10} -H₄₅ bond, indicating a possible site for nucleophilic attack.

The MEP is best suited for identifying sites for intraand inter-molecular interactions [63]. For the MEP surface in the studied molecule, the weak negative regions associated with the N₁₁ atom and also the weak positive region by the nearby H₂₉ atom are indicative of intramolecular (N₁₁...H₂₉–O₂₈) hydrogen bonding.

UV-Vis spectra analysis

The energy gap between HOMO and LUMO is a critical parameter in determining molecular electrical transport properties [64]. The conjugated molecules are characterized by a highest occupied molecular orbital–lowest unoccupied molecular orbital (HOMO–LUMO) separation, which is the result of a significant degree of intra-molecular charge

transfer (ICT) from the end-capping electron-donor groups to the efficient electron-acceptor groups through π -conjugated path. Therefore, an ED transfer occurs from the more aromatic part of the π -conjugated system in the electrondonor side to its electron-withdrawing part. HOMO and HOMO–1 is second highest and lowest unoccupied molecular orbitals LUMO and LUMO + 1 as shown in Fig. 8. The energy gap of HOMO–LUMO explains the eventual charge-transfer interaction within the molecule, and the frontier orbital gap in case of DHBE is found to be 3.5108 eV obtained at TD-DFT method using 6-311++G(2d,p) basis set. This large energy gap implies that the structure of the title Schiff base ligand is very stable [65].

In addition, the first 10 spin-allowed singlet–singlet excitations for both enol and keto forms were calculated by TD-DFT approach. TD-DFT calculations were started from optimized geometry using the same level of theory and performed for gas phase to calculate excitation energies. For both enol and keto forms of the title compound, wavelength (λ), oscillator strength (f) and major contributions of calculated transitions are given in Table 5. The absorption peaking at 384–417 nm arises excitation from HOMO to LUMO transition in solution for enol form.

The UV–Vis spectra of the title compound in various organic solvents (hexane, dichloromethane, ethanol and acetonitrile) were recorded within 250–600 nm range (Fig. 9). The characteristic UV–Vis absorption bands of the molecule in hexane, dichloromethane, ethanol and acetonitrile are comparatively given in Table 5. The absorption bands at 384(in hexane), 401 (in dichloromethane), 417 (in ethanol) and 417 nm (in acetonitrile) are attributed $\pi \rightarrow \pi^*$. However, new absorption band peaking at 443 nm was observed in the spectrum of the title compound in EtOH (Fig. 9), which was not present in the case of other solvents. Referring to the computational and experimental studies, new absorption bands above 400 nm can be attributed to the keto form of *o*-hydroxy Schiff bases [31–33]. It can be said that the absorption band peaking at

Fig. 7 Molecular electrostatic potential map (MEP) of DHBE. (For interpretation of the references to color in this figure, the reader is referred to the web version of the article)





Table 5 Wavelength, oscillator strength, major contributions of calculated transitions in gas phase and various solvents for keto and enol forms

	Exp.	Calculat	ed		Calculated				
		Enol for	m		Keto form				
	λ (nm)	λ (nm) f		Major contribution		f	Major contribution		
Gas phase	_	383	1.068	$H \rightarrow L(99 \%)$	394	1.284	$H-1 \to L(91 \%)$		
	_	308	0.181	H-2 \rightarrow L(53 %), H \rightarrow L + 1(38 %)	309	0.029	$H-1 \rightarrow L + 1(82 \%)$		
					444	0.014	$H \to L + 1(91 \%)$		
Hexane	384	401	1.194	$\mathrm{H} \rightarrow \mathrm{L}(99~\%)$	412	1.446	$\text{H-1} \rightarrow \text{L(96 \%)}$		
	273	311	0.241	H-2 \rightarrow L + 1(46 %), H \rightarrow L + 1(47 %)	309	0.037	$H-1 \rightarrow L + 1(84 \%)$		
					444	0.021	$H \to L + 1(95 \%)$		
CH ₂ Cl ₂	401	411	1.147	$\mathrm{H} \rightarrow \mathrm{L}(99~\%)$	416	1.473	$H \rightarrow L(93 \%)$		
	278	314	0.325	H-2 \rightarrow L(37 %), H \rightarrow L + 1(58 %)	313	0.011	H-1 \rightarrow L + 1(77 %), H \rightarrow L + 1(15 %)		
					435	0.010	$H-1 \rightarrow L(93 \%)$		
EtOH	417	411	1.114	$\mathrm{H} \rightarrow \mathrm{L}(99~\%)$	415	1.456	$H \rightarrow L(93 \%)$		
	280	314	0.343	H-2 \rightarrow L(35 %), H \rightarrow L + 1(59 %)	311	0.047	H-1 → L + 1(34 %), H → L + 1(28 %)		
	<u>443</u>				432	0.009	$H-1 \rightarrow L(93 \%)$		
CH ₃ CN	419	411	1.105	$\mathrm{H} \rightarrow \mathrm{L}(99~\%)$	414	1.450	$\mathrm{H} \rightarrow \mathrm{L}(92~\%)$		
	296	315	0.347	H-2 \rightarrow L(35 %), H \rightarrow L + 1(59 %)	311	0.043	H-1 \rightarrow L + 1(75 %), H \rightarrow L + 1(22 %)		
					432	0.009	H-1 \rightarrow L(92 %)		

compositions of the frontier molecular orbital for DHBE

Fig. 8 Atomic orbital



Fig. 9 UV-Vis absorption spectra of DHBE in different solvents

384–417 nm arises from enol form and the absorption band peaking at 443 nm arises from keto form in the solution.

The title compound exists in enol form in the solid state, while both enol and keto forms are shown in EtOH. The keto form is important in the solution and stabilized by the polar solvents through solute and solvent interactions. The *N*,*N*-diethylamino group is an electron-donating group. The zwitter ionic form arises before the formation of keto form. The electron-donating N,N-diethylamino group stabilizes zwitter ionic form and eases the formation of keto form with resonance. However, not only the electron-donating group but also the solvent is effective in the formation of keto form. If the formation of keto form depended on the electron-donating group, the keto form would have observed in all solvents. In addition, the formation of keto form cannot be related to the polarity of solvent. Such a relation would require the formation of keto form in acetonitrile unlike observed results. Therefore, the proton transfer is affected by H-donor-acceptor property of solvent instead of solvent polarity. EtOH is a polar and protic solvent. This property causes both enol and keto forms to be stable in solvent. The hydrogen bond formation between the compound and solvent plays an important role in the stabilization of the keto form.

Electrochemical properties

The IP is defined as the minimum energy necessary to bring an electron from the material into a vacuum. In other words, ionization potentials (IPs) are the energy difference between neutral molecules and the corresponding cationic systems. The electron affinity (EA) is defined as the first unoccupied energy level that injected electrons coming from a vacuum into the material would occupy. In other words, EA is the energy difference between neutral molecules and the corresponding anionic systems. IP and EA are usually used to assess the energy barrier for the injection of holes and electrons [66]. Obviously, lower reorganization energy is necessary to achieve a high charge-transfer rate.

Enol form has an IP of 6.9457 eV (Table 6), which is bigger than that of keto form (6.1925 eV), indicating the hole-transporting ability of keto better than that of enol. On the other hand, the electron-transporting ability of keto an EA of 1.9495 eV should be better than that of enol with an EA of 0.8143 eV.

Cyclic voltammogram of supporting electrolyte is also shown in Fig. 10. The oxidation and reduction peaks associated with the HOMO and LUMO levels, respectively. In the part of the paper which deals with experimental results, one should discuss EA and IP values rather than HOMO and LUMO levels since the molecular orbital energies are not observables but originate from quantum chemical approximations. Using cyclic voltammetry, the IP was estimated from the onset of the first oxidation peak, whereas EA from the onset of the first reduction peak. The oxidation and reduction peaks associated with the HOMO and LUMO levels, respectively. The HOMO energy level, E_H , was estimated from bellow equation [67]: $E_{\text{HOMO}} = E^{\text{ox}} + 4.4 \text{ V}$. The LUMO energy level, E_L , was obtained by adding the energy of the HOMO–LUMO gap, ΔE_{HI} , to E_H value, while the energy gap ΔE_{HL} was determined from the difference between oxidation and reduction potentials. It is generally indicative of a HOMO/ LUMO absorption transition to bear a significant chargetransfer character. The higher HOMO/LUMO energy levels than those corresponding estimations from the experimental data may be related to various effects from conformation and solvents, which have not been taken into account here.

Table 6	Electrochemical	properties	of the title	compound	
Table 6	Electrochemical	properties	of the title	compound	

Comp	$E_{\rm HOMO}/E_{\rm LUMO}^{\rm a}$	IP^{a}	EA ^a	IP/EA ^a	E ^{ox} onset ^b (V)	$E_{\rm HOMO}/E_{\rm LUMO}^{\rm c}$
Enol	-5.5600/-2.0892	6.9457	0.8143	6.9457/0.8143	1.049	5.449/1.938
Keto	-5.6261/-2.3594	6.1925	1.9495	6.1925/1.9495		

^a DFT/B3LYP calculated values

^b Oxidation potential in DMSO (2 \times 10⁻³ mol L⁻¹) containing 0.1 mol L⁻¹ Bu₄NBF₄ with a scan rate of 100 mV s⁻¹

^c E_{HOMO} was calculated by $E^{\text{ox}} + 4.4 \text{ V}$, and $E_{\text{LUMO}} = E_{\text{HOMO}} - \Delta E_{HL}$ [55]



Fig. 10 Cyclic voltammogram of 2×10^{-3} M title compound. Scan rate 100 mV s⁻¹, electrolyte 0.1 M Bu₄NBF₄ in DMSO

Nonlinear optical properties

NLO is at the forefront of current research because of its importance in providing the key functions of frequency shifting, optical modulation, optical switching, optical logic, and optical memory for the emerging technologies in areas such as telecommunications, signal processing, and optical connectors [68]. Organic molecules that exhibit extended π conjugation, in particular, show enhanced second-order NLO properties [69]. The total static dipole moment (μ), the linear polarizability (α), anisotropy polarizability($\Delta \alpha$) and the first hyperpolarizability (β) using the *x*, *y*, *z* components are defined as [40]:

$$\mu = \left(\mu_x^2 + \mu_y^2 + \mu_z^2\right)^{\frac{1}{2}}$$
(4)

$$\alpha_{tot} = \frac{1}{3} \left(\alpha_{xx} + \alpha_{yy} + \alpha_{zz} \right)$$
(5)

$$\Delta \alpha = \frac{1}{\sqrt{2}} \left[\left(\alpha_{xx} - \alpha_{yy} \right)^2 + \left(\alpha_{yy} - \alpha_{zz} \right)^2 + \left(\alpha_{zz} - \alpha_{xx} \right)^2 + 6 \alpha_{xz}^2 \right. \\ \left. + 6 \alpha_{xy}^2 + 6 \alpha_{yz}^2 \right]^{\frac{1}{2}}$$
(6)

$$\langle \beta \rangle = \left[\left(\beta_{xxx} + \beta_{yyy} + \beta_{zzz} \right)^2 + \left(\beta_{yyy} + \beta_{yzz} + \beta_{yxx} \right)^2 + \left(\beta_{zzz} + \beta_{zxx} + \beta_{zyy} \right)^2 \right]^{\frac{1}{2}}$$

$$(7)$$

It is well known that the higher values of dipole moment, molecular polarizability and hyperpolarizability are important for more active NLO properties. The numerical values of above-mentioned parameters were listed in Table S1. The calculated dipole moment is equal to 8.276 and 8.240 Debye (D) in DHBE which is nearer to the value for urea ($\mu = 1.3732$ D). The calculated polarizability α_{ij} have nonzero and zero values and are dominated by the diagonal components. Total polarizability (α_{tot}) calculated as -20.257×10^{-24} and -20.211×10^{-24} esu for title molecule. The calculated first hyperpolarizability values ($<\beta$ >) of the title compound are 44.404 $\times 10^{-30}$ and 43.950 $\times 10^{-30}$ esu, which comparable with the reported values of similar derivatives [31, 32] and which are greater



Fig. 11 Correlation graph of thermodynamic properties and temperatures by B3LYP/6-311++G(2d,p) for DHBE molecule

than that of the standard NLO material urea $(0.13 \times 10^{-30}$ esu) [70]. These results indicate that title compound is a good candidate of nonlinear optical material.

Thermodynamic functions

The standard thermodynamic functions, namely the heat capacity $(C_{p,m}^{0})$, entropy (S_{m}^{0}) , enthalpy (H_{m}^{0}) and molecular energy (*E*) were calculated at B3LYP/6-311++G(2d,p) level for varying temperatures from 100 to 700 K. The results obtained on the basis of vibrational analysis are shown in Table S2. The results reveal that an increase in temperature causes an increase in heat capacities, entropies, enthalpies and molecular energy due to increasing intensities of molecular vibrations [71].

The corresponding quadratic equations obtained by B3LYP/6-311++G(2d,p)are as follows, and the related figure was shown in Fig. 11.

For DHBE by B3LYP/6-311++G(2d,p),

$$C_{p,m}^{0} = .4424 + 0.2997T - 1 \times 10^{-4}T^{2} \quad (R^{2} = 0.9991)$$

$$S_{m}^{0} = 63.343 + 0.2968T - 5 \times 10^{-5}T^{2} \quad (R^{2} = 1)$$

$$H_{m}^{0} = 1.8223 + 0.0829T - 2 \times 10^{-4}T^{2} \quad (R^{2} = 1)$$

$$E = 234.84 + 0.011T - 1 \times 10^{-5}T^{2} \quad (R^{2} = 0.9999)$$
(8)

They can be used to compute the other thermodynamic energies according to relationship of thermodynamic functions and estimate directions of chemical reactions according to the second law of thermodynamics in thermochemical field. Notice that all thermodynamic calculations were done in gas phase, and they could not be used in solution.

The values of some thermodynamic parameters (such as zero-point vibrational energy (ZPVE), thermal energy, specific heat capacity, rotational constants, rotational **Fig. 12** Atomic charge distribution of Enol and Keto forms (Color figure online)



Table 7 Calculated energy values of DHBE by B3LYP/6-311++G(2d,p) basis set

	Gas (NH)	Gas (OH)	Hexane (OH)	Dichloromethane (OH)	Ethanol (OH)	Acetonitrile (OH)
E_{total} (hartree)	-997.52473	-997.53046	-997.53535	-997.54259	-997.54460	-997.54467
$E_{\rm HOMO}~({\rm eV})$	-5.621	-5.600	-5.655	-5.715	-5.785	-5.833
$E_{\text{HOMO-1}}$ (eV)	-5.715	-6.727	-6.424	-6.492	-6.519	-6.519
$E_{\rm LUMO}~({\rm eV})$	-0.087	-2.489	-2.511	-2.541	-2.582	-2.604
$E_{\text{LUMO}+1}$ (eV)	-0.047	-0.389	-1.121	-1.196	-1.221	-1.221
E _{HOMO-LUMO} gap (eV)	-5.534	-3.111	-3.144	-3.174	-3.203	-3.229
Chemical potential (μ)	2.854	4.045	4.083	4.128	4.184	4.219
Global hardness (η)	2.767	1.555	1.572	1.587	1.602	1.615
Global softness (S)	0.361	0.643	0.636	0.630	0.624	0.619
Electronegativity (χ)	-2.854	-4.045	-4.083	-4.128	-4.184	-4.219
Electrophilicity indices (ω)	1.472	5.259	5.302	5.369	5.464	5.511

temperature and entropy) of title compound are listed in Table S3. The variation in ZPVE seems to be significant. The ZPVE is higher by the B3LYP/6-311++G(2d,p) level than by the B3LYP/6-311++G(d,p) level.

Charge distribution

The natural atomic charge has an important role in the application of quantum mechanical calculation for the molecular system. The natural atomic charge of enol and keto forms calculated by B3LYP/6-311++G(2d,p) method is shown in Fig. 12. The charge distributions over the atoms suggest the formation of donor and acceptor pairs involving the charge transfer in the molecule. The charge distribution of DHBE shows that the carbon atom attached with hydrogen atoms is negative, whereas the remaining carbon atoms are positively charged. The oxygen and nitrogen atoms have more negative charges, whereas all the hydrogen atoms have positive charges. Resulting in the positive charges on the C₄, C₆, C₁₀, C₁₂, C₂₂, H₂₉, H₂₄, H₂₅, H₂₆ and H₂₁ shows the direction of delocalization. The oxygen and nitrogen atoms in the molecule bear negative charges; the phenyl ring carbon atoms with substituent (i.e.,

 C_4 , C_6 and C_{12}), the carbonyl carbon C_{22} and bridging C_{10} atom bear positively charges, while the remaining carbon atoms of the phenyl rings bear negative charges.

Reactive descriptors of DHBE

Global reactivity parameters

The NH and OH tautomers of the title compound are given in Fig. 1. To investigate the tautomeric stability, optimization calculations at B3LYP/6-311++G(2d,p) level were performed for the NH and OH forms of the title compound. The energies of frontier molecular orbitals $(E_{\text{HOMO}}, E_{\text{LUMO}})$, energy band gap $(E_{\text{HOMO}}, E_{\text{LUMO}})$, electronic chemical potential (μ), electronegativity (χ), global hardness (η), global softness (S) and electrophilicity indices (ω) [72] of DHBE have been listed in Table 7. On the basis of E_{HOMO} and E_{LUMO} , these are calculated by using the below equations.

$$\mu = \frac{1}{2} (E_{\text{HOMO}} + E_{\text{LUMO}}) \tag{9}$$

$$\chi = -\mu = -\frac{1}{2}(E_{\text{HOMO}} + E_{\text{LUMO}}) \tag{10}$$

$$\eta = \frac{1}{2} (E_{\text{HOMO}} - E_{\text{LUMO}}) \tag{11}$$

$$S = \frac{1}{2\eta} \tag{12}$$

$$\omega = \frac{\mu^2}{2\eta} \tag{13}$$

The chemical hardness is quite useful to explain the chemical stability. The molecules having a large HOMO-LUMO energy gap will be more stable and less reactive than soft molecules having small HOMO-LUMO energy gap [73]. From Table 7, the total energy of the OH form is lower than the NH form, while chemical hardness of the OH form is greater than the NH one, which indicates that the OH form of the title compound is more stable than its NH form in the gas phase. In additional, in order to evaluate the solvent effect to the herein above-mentioned properties of the title compound, we carried out calculations in four kinds of solvent (hexane, dichloromethane, ethanol and acetonitrile) with the B3LYP/6-311++G(2d,p) level using the PCM model, and the results are given in Table 7. From Table 7, we can conclude that the total molecular energies obtained by PCM method decrease with the increasing polarity of the solvent, while the hardness will increase with the increase in the polarity of the solvent. The energy gap (ΔE) between the highest occupied molecular orbital (HOMO) and the lowest lying unoccupied molecular orbital (LUMO) increase in enol form when an increase occurs in the polarity of the solvent. According to these results, the stability of the title compound increases in going from the gas phase to the solution phase.

The usefulness of this new reactivity quantity has recently demonstrated in understanding the toxicity of various pollutants in terms of their reactivity and site selectivity [74]. The computed electrophilicity index of DHBE describes the biological activity of drug–receptor interaction.

Local reactivity descriptors

The most relevant local descriptor of reactivity is the Fukui function, the derivative of the electronic chemical potential with respect to the external potential due to the compensating nuclear charges in the system. For a system of N electrons, independent calculations are to be made for corresponding N + 1, N - 1 and N are total electrons present in anion, cation and neutral state of molecules, respectively. Natural population analysis yields gross charges q_k (N + 1), $q_k(N - 1)$, $q_k(N)$, and for all atoms k. In a finite difference approximation, the condensed Fukui functions are given by the equations:

For nucleophilic attack $f_k^+ = q_k(N+1) - q_k(N)$ (14) For electrophilic attack $f_k^- = q_k(N) - q_k(N-1)$ (15)

For free radical attack $f_k^0 = \frac{1}{2} [q_k(N+1) - q_k(N-1)]$ (16)

The condensed-to-atom quantity, ω_k^{α} corresponding to local electrophilicity index, $\omega(\mathbf{r})$, was obtained as described previously [21]

$$\omega_k^{\alpha} = \omega f_k^{\alpha} \tag{17}$$

where $\alpha = +, -$ and 0 refer to nucleophilic, electrophilic and free radical reactions, respectively. Fukui functions, local softness and local electrophilicity indices for selected atomic sites in DHBE have been listed in Table S4. The reactivity orders for the nucleophilic attack; the reactivity of C₄ in the substitution was found to have a loss in DHB Eat 6-311++G(d,p) level. The nucleophilic reactivity order was $C_4 > C_{23}$ at 6-311++G(d,p) basis set on DHBE. Note it was observed a major reactivity for this kind of attack in comparison with the electrophilic attack. On the other hand, the reactivity order for the electrophilic case was $N_{30} > C_3 > N_{11} > C_1 > C_{19} >$ $C_5 > C_{27} > C_{13} > C_{14} > O_{28}$ at 6-311++G(d,p) basis sets on DHBE. If one compares the three kinds of attacks, it is possible to observe that the electrophilic attack shows a more reactivity in comparison with the free radical and nucleophilic case.

Topological parameters

One of the most useful implements to characterize atomic and molecular interactions, particularly hydrogen bonding, is the topological analysis using 'atoms in molecules' (AIM) theory [42]. According to AIM theory, any chemical bond including hydrogen bonding is characterized by the existence of bond critical points (BCPs). After the bond critical points have been localized, several properties can be calculated at their position in space. Among these, ρ_{BCP} or the charge density at the bond critical point is of chief importance. Laplacian of the charge density at the bond critical point, $\nabla^2 \rho_{\rm BCP}$, and the ellipticity are the two derived quantities. The latter provides a measure of the magnitude to which charge is favorably accumulated in given plane. It has been observed that for closed-shell interactions, as found in ionic bonds, hydrogen bonds and van der Waals molecules, $\nabla^2 \rho_{\rm BCP}$ should be positive (in the range 0.015–0.15 a.u.) and ρ low (0.002–0.040 a.u.). The values mentioned here are according to Koch and Popelier criteria [75] based on AIM theory. Molecular graph of the dimer is shown in Fig. 13. As indicated, in addition to usual bonds, the molecular graphs indicate a BP

Fig. 13 Molecular graphs of DHBE, red points indicate the bond critical points (BCPs) between bonded atoms



Table 8Topologicalparameters for hydrogen bondedinteractions

^a B3LYP/6-311++G(d,p) ^b B3LYP/6-311++G(2d,p)

Parameters	O–H···N(BCP)					
	d,p ^a	2d,p ^b				
Electron density	0.0498 a.u.	0.0495 a.u.				
Laplacian of electron density	0.0278 a.u.	0.0276 a.u.				
Lagrangian kinetic energy G(r)	0.0368 a.u.	0.0360 a.u.				
Hamiltonian kinetic energy $K(\mathbf{r})$	-0.0091 a.u.	-0.0084 a.u.				
Potential energy density $V(\mathbf{r})$	-0.0459 a.u.	-0.0445 a.u.				
H-bond energy	$14.4011 \text{ kcal mol}^{-1}$	$13.9619 \text{ kcal mol}^{-1}$				

and a BCP between nitrogen and hydrogen, which confirms that there is an intramolecular hydrogen bond (H-bond) in these molecules. Interestingly, each BCP contains a wealth of chemical information that properly describes the nature of the corresponding chemical bond. The values of electron density, ρ_{BCP} , Laplacian of electron density, $\nabla^2 \rho_{BCP}$, kinetic energy density, G_{BCP} , potential energy density, V_{BCP} , and electronic energy density, at the BCP are the parameters that are usually used to characterize a chemical bond. These values for the BCP of the H-bonds in the compound of the current work have been listed in Table 8. The value of ρ BCP of this compound is slightly larger than that of normal hydrogen bonds. This suggests that these interactions should be stronger than normal H-bonds, in view of the fact that there is a linear correlation between $\rho_{\rm BCP}$ and H-bond energy [76]. The energy of N···H–O hydrogen bond can be calculated using the relationship $E_{\rm HB} = V(r_{\rm BCP})/2$ described by Espinosa et al. [77]. In case of DHBE, $E_{\rm HB}$ has been calculated to be 14.4011 kcal/mol by B3LYP/6-311++G(d,p) and 13.9619 kcal/mol B3LYP/ 6-311++G(2d,p) methods.

The ratio $G/\rho_{\rm BCP}$ may be used to define the character of the interaction, where G is kinetic energy density and is always positive. This ratio may be larger than 1.0 for closed shell (hydrogen bonding, ionic bonds and van der Waals interaction) [42]. The ratio $G/\rho_{\rm BCP}$ in the present study is 0.739, which is close to 1.0 for the hydrogen bonding. Similar results (with $G/\rho_{\rm BCP}$ value slightly lower than 1.0) have been stated for extraordinarily strong hydrogen bonding in other compounds [78].

In contrast to this largely electrostatic and rather directional interaction, evidence also suggests that a closed-shell stabilizing interaction can occur between hydrogen atoms that are electrically neutral, close to electrical neutrality, or bearing identical or similar charges. The identity or similarity of these charges is due to molecular symmetry or similarity of the electronic environment, respectively, of the two hydrogen atoms involved in this bonding. Cioslowski and Mixon [79] reported atomic interaction lines connecting hydrogen atoms separated by short distances $(d_{\rm H} \cdots_{\rm H} \le 2.18 \text{ Å})$ in several polycyclicaromatic hydrocarbons (PAHs). Cioslowski and Mixon paper is credited for being the first to report the existence of this interaction in angular PAHs and for obtaining functional dependencies between $d_{H\cdots H}$ and several properties determined directly at the BCP or derived from them. Since the H-H is locally stabilizing, and since these paths are present in equilibrium geometries where there are no net forces on the nuclei, they will be referred to as 'bond paths.'

Figure 13 shows the existence of hydrogen-hydrogen (H…H) bonds. For the C-H…H-C contacts analyzed here, the values of electron density for H…H links lie within the range of 0.005 -0.015 a.u. and Laplacian are 0.004-0.014 a.u. for B3LYP/6-311++G(2d,p) calculations. The H-bond energy for title compound amounts to 0.78-2.85 kcal/mol. Hence, if one assumes that the

CH…HC interactions analyzed here may be classified as H-bonds, they are weak H-bonds.

Conclusions

In this study, we have synthesized a new Schiff base compound, (E)-1-(4-(4-(diethylamino)-2-hydroxybenzylideneamino)phenyl)ethanone, and characterized by spectroscopic and structural techniques as well as the theoretical methods. FT-IR, NMR and UV-Vis methods confirm the OH form of the title compound. The PES scanned process in gas phase shows that the potential barrier is 5.89 kcal mol^{-1} 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 C_2/C_3 ring and lengths of the indicative bonds. UV-Vis spectra of the title compound were recorded in different organic solvents in order to investigate the dependence of tautomerism on solvent types. The results show that the title compound exists in both keto and enol forms in EtOH, while it has enol form in hexane, CH₂Cl₂ and CH₃CN. The computational studies on the nonlinear optical properties of the title compound show that the title compound can be used as a good nonlinear optical material. The HOMO-LUMO energy gap and implications of the electronic properties are discussed. In addition, thermodynamic properties were obtained in the range of 100-800 K. Fukui functions, local softness and electrophilicity indices for atomic sites in DHBE have been calculated.

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

Acknowledgments Authors are grateful to the Damghan University for financial support.

References

- 1. Cohen MD, Schmidt GMJ, Flavian S (1964) J Chem Soc 2041–2051
- Koll A, Janski J, Karpfen A, Wolschann P (2010) J Mol Struct 976:19–29
- Papić S, Koprivanac N, Grabarić Z, Parac-Osterman Đ (1994) Dyes Pigments 25:229–240
- McAuliffe A, Parish RV, Abu-El-Wafa SM, Issa RM (1986) Inorg Chim Acta 115:91–94
- 5. Zolezzi S, Spodine E, Decinti A (2002) Polyhedron 21:55-59
- Ambike V, Adsule S, Ahmed F, Wang Z, Afrasiabi Z, Sinn E, Sarkar F, Padhye S (2007) J Inorg Biochem 101:1517–1524
- Jones RD, Summerville DA, Basolo F (1979) Chem Rev 79:139–179
- 8. Foundation H (1981) J Am Chem Soc 2:4073-4081
- 9. Ismail TMA (2005) J Coord Chem 58:141–151

- Crouse KA, Chew K-B, Tarafder MTH, Kasbollah A, Ali AM, Yamin BM, Fun H-K (2004) Polyhedron 23:161–168
- 11. Chandra S, Gupta LK (2005) Transit Met Chem 30:630-635
- Taggi AE, Hafez AM, Wack H, Young B, Ferraris D, Lectka T (2002) J Am Chem Soc 124:6626–6635
- 13. Layer RW (1963) Chem Rev 63:489-510
- Atkinson RS, Barton D, Ollis WD (1979) Comprehensive organic chemistry. Pergamon, Oxford
- Dürr H, Bouas-Laurent H (2003) Photochromism: molecules and systems: molecules and systems. Gulf Professional Publishing, Houston
- Gill PMW, Johnson BG, Pople JA, Frisch MJ (1992) Chem Phys Lett 197:499–505
- Chattopadhyay B, Basu S, Chakraborty P, Choudhuri SK, Mukherjee AK, Mukherjee M (2009) J Mol Struct 932:90–96
- Kluba M, Lipkowski P, Filarowski A (2008) Chem Phys Lett 463:426–430
- 19. Eschwege KGV, Swarts JC (2010) Polyhedron 29:1727-1733
- 20. Becke AD (1993) J Chem Phys 98:5648-5652
- 21. Lee C, Yang W, Parr RG (1988) Phys Rev B 37:785-789
- Miehlich B, Savin A, Stoll H, Preuss H (1989) Chem Phys Lett 157:200–206
- 23. Frisch MJ, Trucks GW, Schlegel HB, Scuseria GE, Robb MA, Cheeseman JR, Montgomery Jr JA, Vreven T, Kudin KN, Burant JC, Millam JM, Iyengar SS, Tomasi J, Barone V, Mennucci B, Cossi M, Scalmani G, Rega N, Petersson GA, Nakatsuji H, Hada M, Ehara M, Toyota K, Fukuda R, Hasegawa J, Ishida M, Nakajima T, Honda Y, Kitao O, Nakai H, Klene M, Li X, Knox JE, Hratchian HP, Cross JB, Adamo C, Jaramillo J, Gomperts R, Stratmann RE, Yazvev O, Austin AJ, Cammi R, Pomelli C, Ochterski JW, Ayala PY, Morokuma K, Voth GA, Salvador P, Dannenberg JJ, Zakrzewski VG, Dapprich S, Daniels AD, Strain MC, Farkas O, Malick DK, Rabuck AD, Raghavachari K, Foresman JB, Ortiz JV, Cui Q, Baboul AG, Clifford S, Cioslowski J. Stefanov BB, Liu G. Liashenko A. Piskorz P. Komaromi I, Martin RL, Fox DJ, Keith T, Al-Laham MA, Peng CY, Nanayakkara A, Challacombe M, Gill PMW, Johnson B, Chen W, Wong MW, Gonzalez C, Pople JA (2004) Gaussian 03, Revision C.02. Gaussian, Wallingford
- 24. Scott AP, Radom L (1996) J Phys Chem 3654:16502-16513
- 25. Karabacak M, Cinar M, Kurt M (2009) Spectrochim Acta A 74:1197–1203
- 26. Millam J, Al-Nielsen A, Al-Holder A., Al-Hiscocks J (2004) Gaussview 4.1.2. Gaussian, Inc. Wallingford, CT
- 27. Jamróz H (2013) Spectrochim Acta A 114:220-230
- 28. Wolinski K, Hinton JF, Pulay P (1990) J Am Chem Soc 112:8251–8260
- 29. Biegler Konig FW, Schonbohm J, Bayles D (2001) J Comput Chem 22:545–559
- 30. Bader RFW (1990) Atoms in molecules. Wiley Online Library
- Albayrak Ç, Kaştaş G, Odabaşoğlu M, Frank R (2011) Spectrochim Acta A 81:72–78
- 32. Albayrak Ç, Frank R (2010) J Mol Struct 984:214-220
- Khalaji AD, Grivani G, Seyyedi M, Fejfarova K, Dusek M (2013) Polyhedron 49:19–23
- Morshedi M, Amirnasr M, Slawin AMZ, Woollins JD, Khalaji AD (2009) Polyhedron 28:167–171
- Morshedi M, Amirnasr M, Triki S, Khalaji AD (2009) Inorg Chim Acta 362:1637–1640
- Ünver H, Yildiz M, Dülger B, Özgen Ö, Kendi E, Durlu TN (2005) J Mol Struct 737:159–164
- Unver H, Yildiz M, Ozay H, Durlu TN (2009) Spectrochim Acta A 74:1095–1099
- 38. Elmali A, Elerman Y (1998) J Mol Struct 442:31-37
- 39. Elmali A, Elerman Y (1998) J Mol Struct 443:123-130

- 40. Gilli G, Bellucci F, Ferretti V, Bertolasi V (1989) J Am Chem Soc 111:1023–1028
- 41. Krygowski TM, Cyrański MK (2001) Chem Rev 101:1385-1419
- Filarowski A, Kochel A, Kluba M, Kamounah FS (2008) J Phys Org Chem 21:939–944
- Subramanian MK, Anbarasan PM, Manimegalai S (2009) J Raman Spectrosc 40:1657–1663
- Silverstein R, Webster F (2006) Spectrometric identification of organic compounds. Wiley, NY
- 45. Mohan J (2001) Organic spectroscopy, principle and applications. New Age International (P) Limited Publishers, New Delhi
- 46. Rastogi VK, Palafox MA, Lang K, Singhal SK, Soni RK, Sharma R (2006) Indian J Pure Appl Phys 44:653–660
- 47. Woolley MS, Otero JC, Marcos JI, Lo I (1998) J Mol Struct 470:241–246
- Krishnakuma Y, Xavier RJ (2003) Indian J Pure Appl Phys 41:597–601
- Arjunan V, Sakiladevi S, Rani T, Mythili CV, Mohan S (2012) Spectrochim Acta A 88:220–231
- 50. Parimala K, Balachandran V (2011) Spectrochim Acta A 81:711–723
- 51. Gunasekaran S, Sailatha E (2009) Indian J Pure Appl Phys 47:259–264
- Okamoto H, Inaba R, Yoshihara K, Tasumi M (1993) Chem Phys Lett 202:161–166
- 53. Paulraj EI, Muthu S (2013) Spectrochim Acta A 106:310–320
- 54. Wiberg KB, Shrake A (1973) Spectrochim Acta A 29:583-594
- 55. Sundaraganesan N, Anand B, Meganathan C, Joshua BD, Saleem H (2008) Spectrochim Acta A 69:198–204
- Dollish FR, Fateley WG, Bentley FF (1974) Characteristic Raman frequencies of organic compounds. Wiley Interscience, New York
- 57. Silverstein RM, Bassler GC, Morrill TC (1981) Spectroscopic identification of organic compounds, 4th edn. Wiley, New York
- 58. Pasterny K (2002) J Mol Struct 616:17-32

- 59. Glendening ED, Reed AE, Carpenter JE, Weinhold F (1988) NBO, version 3.1. There is No Corresp. Rec. This Ref
- Subramanian N, Sundaraganesan N, Jayabharathi J (2010) Spectrochim Acta A 76:259–269
- 61. Scrocco E, Tomasi J (1978) Adv Quantum Chem 11:115-193
- 62. Politzer P, Murray JS (2002) Theor Chem Acc 108:134–142
- 63. Politzer P, Concha MC, Murray JS (2000) Int J Quantum Chem 80:184–192
- 64. Fukui K (1982) Science 218:747-754
- 65. Tezer M, Kanbul S (2009) Procedia Soc Behav Sci 1:390-394
- 66. Li X, Liu X, Wu Z, Zhang H (2008) J Phys Chem A 112:11190–11197
- Wang HY, Chen LF, Zhu XL, Wang C, Wan Y, Wu H (2014) Spectrochim Acta A 121:35–39
- Bernstein J, Davis RE, Shimoni L, Chang N (1995) Angew Chemie Int Ed Engl 34:1555–1573
- 69. Bondi A (1964) J Phys Chem 68:441-451
- Adant C, De Chimie S, De Recherche C, York N (1995) Int J Quantum Chem 507:497–507
- 71. Alcolea Palafox M (2000) Int J Quantum Chem 77:661-684
- Padmanabhan J, Subramanian R, Subramanian V, Chattaraj PK (2007) J Phys Chem A 111:1358–1361
- Özbek N, Kavak G, Özcan Y, İde S, Karacan N (2009) J Mol Struct 919:154–159
- Subramanian V, Chattaraj PK (2003) Internet Electron J Mol Des 2:798–813
- 75. Koch U, Popelier PLA (1995) J Phys Chem 99:9747-9754
- 76. Pakiari AH, Eskandari K (2006) J Mol Struct (Theochem) 759:51-60
- 77. Espinosa E, Molins E, Lecomte C (1998) Chem Phys Lett 285:170–173
- Hibbs DE, Overgaard J, Piltz RO (2003) Org Biomol Chem 1:1191–1198
- 79. Cioslowski J, Mixon ST (1992) Can J Chem 70:443-449