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Spectral, structural and quantum chemical computational and dissociation constant studies of a novel azo-enamine tautomer

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GRAPHICAL ABSTRACT

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HIGHLIGHTS

SEVIE

- A novel azo-enamine dye was synthesized and characterized by analytical and spectroscopic studies.
- X-ray investigation of the dye showed that azo-enamine tautomer is favoured in the solid state.
- Self-isomerisation *via* intramolecular proton transfer was investigated by UV–Vis. spectra and theoretical calculations.
- Acid dissociation constants for the tautomer were determined potentiometrically.

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ABSTRACT

We report here the synthesis of (6Z)-4-[(E)-(4-ethylphenyl)diazenyl]-6-[[(2-hydroxy-5-methylphenyl) amino]methylidene]cyclohexa-2,4-dien-1-one by the condensation reaction between 2-amino-4-methylphenol and 5-<math>[(E)-(4-ethylphenyl)diazenyl]-2-hydroxybenzaldehyde in equimolar ratio in MeOH and characterized by elemental analyses, infrared, electronic, mass, ¹H and ¹³C NMR spectroscopy. Molecular structure of the azo-enamine dye was also determined by single crystal X-ray diffraction technique. X-ray investigation of the dye showed that azo-enamine tautomer is favoured in the solid state. There is an intramolecular hydrogen bonding (N3-H…O1) in the molecule forming a S(6) graph set motif. Additionally, there is an intermolecular O2-H…O1 hydrogen bonding in the structure. The same intermolecular hydrogen bonding contacts are extended between the other symmetry-related molecules in their respective planes to form a 1D hydrogen bond chain. Self-isomerisation *via* intramolecular proton transfer was investigated by UV-Vis. spectra and theoretical calculations. Effects of polarity and temperature on UV-Vis. spectra were examined in detail. Moreover, acid dissociation properties of the polydentate compound was investigated at 25 ± 0.1 °C.

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Wavelength (nm)

Introduction

http://dx.doi.org/10.1016/j.molstruc.2014.06.033 0022-2860/© 2014 Elsevier B.V. All rights reserved. Hugo Schiff described the condensation between an aldehyde and an amine to obtain the compounds, later known as Schiff base [1]. These compounds represent important class of compounds in medical and pharmaceutical field [2] and it has many applications







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in important biological field [3,4], further move it act as corrosion inhibitors [5,6], catalysts [7,8]. Also, a large number of Schiff bases have been investigated for their interesting and important properties, such as their ability to reversibly bind oxygen [9], photochromic properties [10,11] and complexing ability towards some toxic metals [12]. Schiff bases are generally bi- or tri dentate ligands capable of forming very stable complexes with transition metal ions. Recently, there has been a considerable interest in the chemistry of these compounds and their metal complexes due to analytical activities [13,14].

Compounds, such as o-hydroxy Schiff bases, exhibiting selfisomerisation via intramolecular proton transfer are of considerable interest due to their potential usage in higher energy radiation detectors, memory storage devices [15–17]. The presence of enolketo tautomerisms affects their photo-physical and photochemical properties. o-Hydroxy Schiff bases may exist in two tautomeric forms (enol and keto forms) in both solutions and the solid state [18]. Self-isomerisation via proton transfer depends on several factors such as temperature, the substituent structure and solvent polarity etc. [19]. o-Hydroxy Schiff bases containing second hydroxyl group in the aniline ring were reported to exhibit stronger tautomerism due to this second hydroxyl group [20–25]. In recent years, in addition to the experimental studies, quantum chemical computational studies were used to investigate tautomerism and intramolecular proton transfer process in ortho-hydroxy Schiff base compounds [18,21]. Recently, we have reported an azo-ohydroxy Schiff base containing second hydroxyl group. X-ray analysis on this compound revealed that the compound existed in keto-amine form in the solid state [26].

In continuation of our work on azo Schiff bases [27,28], we report herein the results of our studies on a novelazo-Schiff base tautomer, (6Z)-4-[(*E*)-(4-ethylphenyl)diazenyl]-6-{[(2-hydroxy-5-methylphenyl)amino]methylidene}cyclohexa-2,4-dien-1-one derived from 5-[(*E*)-(4-ethylphenyl)diazenyl]-2-hydroxybenzaldehyde and 2-amino-4-methylphenol. Molecular structure of the tautomer was determined by single crystal X-ray diffraction technique. Self-isomerisation *via* intramolecular proton transfer for the compound was investigated by UV–Vis. spectra and theoretical calculations. Additionally, the dissociation constants of the azo-Schiff base (ligand) were determined potentiometrically at 25 °C, in NaCl (*I* = 0.1 mol dm⁻³) in EtOH–H₂O mixture (1/5, v/v).

Experimental

General

All starting materials were obtained from Aldrich and Fluka, and were used without further purification.

The ¹³C and ¹H NMR spectral measurements were performed on a BrukerAvance 400 (400 MHz). Mass spectrum was recorded on a Thermo Fisher Exactive + Triversa Nanomate mass spectrometer. The electronic spectra in the 200–900 nm range were obtained on a Shimadzu UV-1800 UV–Vis spectrophotometer. IR spectrum was recorded on a Perkin Elmer Paragon 1000 PC using KBr pellet. CHN analysis was performed using a CE-440 Elemental analyser. Melting point was uncorrected and is in degree Celsius. Data collection for X-ray crystallography was completed using a Bruker APEX2 CCD diffractometer and data reduction was performed using Bruker SAINT. SHELXTL was used to solve and refine the structures [29].

Preparation of (6Z)-4-[(E)-(4-ethylphenyl)diazenyl]-6-{[(2-hydroxy-5-methylphenyl)amino]methylidene}cyclohexa-2,4-dien-1-one

The azo Schiff base tautomer (Scheme) was prepared according to the following procedure: A methanolic solution of 5-[(E)-(4-eth-

ylphenyl)diazenyl]-2-hydroxybenzaldehyde (0.255 g, 1 mmol, 25 mL) was added to a methanolic solution of 2-amino-4-methylphenol (0.125 g, 1 mmol, 20 mL) and refluxed for 2 h. After cooling of the solution, the precipitate was separated, filtered, re-crystallization with MeOH, and dried over anhydrous calcium chloride under vacuum.

Yield: 0.290 g (81%), color: red. M.p.: 213–214 °C. Analysis Calc. for C₂₂H₂₁N₃O₂: C, 73.52; H, 5.89; N, 11.69%. Found: C, 73.26; H, 5.50; N, 11.59%. IR (KBr disc, cm⁻¹): 3435 (phenolic O–H), ~3100 (aromatic C–H stretching), 2920 (aliphatic C–H stretching), 1618 (C=O and C–N stretchings), 1518 and 1383 (symmetric and asymmetric stretching vibrations of ethyl group), 1475 (N=N). ESI-MS (*m*/*z* (rel. intensity) assignment): 360 (18%) [M + H]⁺, 382 (100%) [M + Na]⁺. NMR: ¹H (d-DMSO as solvent, δ in ppm), 15.07 (*s*, 1H, NH), 10.41 (*s*, 1H, phenolic OH), 9.25 (*s*, 1H,=CH–N–), 6.80–8.32 (10H, aromatic), 2.64 (*q* (quartet), 2H, Ph–CH₂–C), 2.26 (*s*, 3H, Ph–CH₃), 1.24 (*t*, 3H, Ph–C–CH₃). ¹³C NMR (d-DMSO as solvent, δ in ppm):166.93 (–CH–NH), 114.17–159.87 (C, aromatic), 15.35, 20.21 and 28.01 (C, ethyl (Ph–CH₂–CH₃) and methyl (Ph-CH₃) groups.

X-ray crystallography

A single crystal of dimensions $0.33 \times 0.25 \times 0.08 \text{ mm}^3$ was chosen for the diffraction experiment. Data were collected at $150(2) \text{ K}^\circ$ on a BrukerApexII CCD diffractometer using Mo K α radiation ($\lambda = 0.71073 \text{ Å}$). The structure was solved by direct methods and refined on F^2 using all the reflections [30].

All the non-hydrogen atoms were refined using anisotropic atomic displacement parameters and hydrogen atoms bonded to carbon atoms were inserted at calculated positions using a riding model. Hydrogen atoms bonded to oxygen and nitrogen atoms were located from difference maps and refined with temperature factors riding on the carrier atom. Details of the crystal data and refinement are given Table 1. Hydrogen bond parameters are given in Table 2 and bond lengths and angles are given in Table S1.

Computational method

All calculations about tautomers were made with GaussView 5.0.8 and Gaussian 09 IA32W Rev. A.02 programmes [31,32]. In the first step, all tautomers were fully optimized by using B3LYP/ 3-21G in gas phase. B3LYP method is hybrid density functional theory method and it was used in all calculations with 3-21G basis set [33–37]. In the second step, the most stable and reactive tautomer was determined by using total energy, Gibbs free energy, some molecular orbital energies and contour diagrams.

Potentiometric studies

EtOH, NaCl, CuCl₂, NiCl₂ and CoCl₂ were purchased from Merck, potassium hydrogen phthalate (KHP) and borax (Na₂B₄O₇) from Fluka, 0.1 M NaOH and 0.1 M HCl as standard from Aldrich. All reagents were of analytical quality and were used without further purification. For the solutions, CO₂-free double-distilled deionized water was obtained with an aquaMAX[™]-Ultra water purification system (Young Lin Inst.). Its resistivity was 18.2 M Ω cm pH-metric titrations were performed using the Molspin *p*H meter[™] with a Orion 8102BNUWP ROSS ultra-combination pH electrode. The temperature in the double-wall glass titration vessel was constantly controlled using a thermostat (DIGITERM 100, SELECTA) and kept at 25.0 ± 0.1 °C. The cell solution was stirred during the titration at constant. 0.05 m (mol/kg) potassium hydrogen phthalate (KHP) and 0.01 m (mol/kg) borax (Na₂B₄O₇) were prepared for calibration of electrode systems. The electrode was calibrated according to instructions of the Molspin Manuel [38]. The pH

Table 1Crystallographic data for the compound.

Empirical formula	$C_{22}H_{21}N_3O_2$
Formula weight	359.42
Crystal size (mm ³)	$0.57 \times 0.19 \times 0.08$
Crystal color	Red
Crystal system	Monoclinic
Space group	$P2_1/n$
Unit cell a (Å)	9.0973 (12))
b (Å)	8.1678 (11)
<i>c</i> (Å)	24.883 (3)
α (°)	90
β(°)	91.238 (2)°
γ (°)	90
Volume (Å3)	1848.5 (4)
Ζ	4
Abs. coeff. (mm^{-1})	0.084
Refl. collected	18,483
Completeness to θ = 28.02°	99.8 %
Ind. Refl. [R _{int}]	4599 [0.0560]
R1, wR2 $[I > 2\sigma (I)]$	0.0500, 0.1114
R1, wR2 (all data)	0.0985, 0.1310
CCDC number	994,909

Table 2 Hydrogen-bond geometry (Å. °).

,	5 () /			
D—H…A	D—H	H…A	D···A	D—H…A
02—H2…01 ⁱ N3—H3…01	0.94 (2) 0.987 (19)	1.64 (2) 1.718 (19)	2.5831 (17) 2.5625 (19)	177 (2) 141.1 (16)

Symmetry code: (i) -x + 3/2, y + 1/2, -z + 1/2.

electrode was calibrated with buffer solution of *p*H 4.005 (KHP) and *p*H 9.180 (Na₂B₄O₇) at 25.0 (±0.1) °C [39]. Also, the potentiometric cell was calibrated in the H₂O–EtOH mixture solvent before each experiment. An automatic burette was connected to Molspin *p*H-mV-meter. A solution of the compound in EtOH–H₂O mixture (1/5, v/v) (10^{-3} M) and NaOH (0.025 M) were prepared. NaCl (Riedel-de Haën) stock solution (1.0 M) was prepared. All potentiometric *p*H measurements were made on solutions in a 100 mL double-walled glass vessel. The cell was equipped with magnetic stirrer. Atmospheric CO₂ was excluded from the titration cell with a purging steam of purified N₂. The system was maintained at an ionic strength of 0.1 M by NaCl as a supporting electrolyte. In experiment, a solution containing about 0.01 mmol of ligand was placed in the cell. The required amount of NaCl (1.0 M) and HCl (0.1 M) were added.

Finally, doubly distilled deionised water was added to the cell to a total volume of 50 mL and titration was started. The *p*H data points were collected after each addition of 0.03 cm³ of the standardised NaOH solution. The HYPERQUAD computer program was used for the calculation of the acid dissociation constants [40].

Results and discussion

Synthesis and solubility

The azo-Schiff base ligand was prepared by the condensation between one equivalent of 2-amino-4-methylphenol with one equivalent of 5-[(*E*)-(4-ethylphenyl)diazenyl]-2-hydroxybenzaldehyde in MeOH as shown in Scheme 1. The compound is stable at room temperature and insoluble in water and *n*-hexane and it is soluble in common organic solvents such as DMSO, DMF, EtOH, MeOH, CH₃CN, CH₃Cl and CH₂Cl₂. Elemental analysis data are given in the experimental section and are in well agreement with the theoretical values. The data are in good agreement with single crystal X-ray determination.

Spectroscopy

The ¹H and ¹³C NMR spectra were recorded in d₆-DMSO and data are given in the experimental part. The ¹H NMR spectrum of the title ligand displays a tripletat δ 1.24 ppm and a quartet at δ 2.69 ppm corresponding to ethyl group protons (Ph--CH₂--CH₃) (Fig. 1). A singlet at δ 2.26 ppm was assigned to the protons of methyl group. Two broad signals at δ 10.25 and 15.07 ppm could be assigned to the protons of enamine (C--NH--C) and phenol (Ph--OH), respectively. A singlet at δ 9.23 ppm was assigned to the protons were seen in the range of 6.80-8.32 ppm.

In the ¹³C NMR spectrum of the compound aliphatic carbon shifts were observed at 15.35, 20.21 and 28.01 ppm assigned to ethyl and methy groups. The signal at δ 166.93 ppm could be assigned to the carbon (–CH–NH). All other aromatic carbon shifts were observed in the range of δ 114.17–159.87 ppm (Fig. S1). The NMR data showed that azo-enamine tautomer is maintained in DMSO and agreed with values reported in literature [26].

The ESI mass spectrum of the synthesized azo-azomethine tautomer was performed in MeOH and is shown in Fig. S2. Two signals at m/z 382 (100%) and 360 (18%) were assigned to molecular ion signals [M + Na]⁺ and [M + H]⁺, respectively.

The IR spectrum of the dye shows several bands in 4000–400 cm⁻¹ region. The bands of the dye are also listed in experimental section. The functional groups of the dye have been identified from the infrared spectrum. The band at 1618 cm⁻¹ was assigned to C12=O1 and C15–N3 stretchings (Fig. S3). The azo v(N=N) stretching band of the compound is observed in the spectrum at 1475 cm⁻¹. A broad peak at 3435 cm⁻¹ was assigned to phenolic (O–H) stretching. The peaks observed at 1518 and 1383 cm⁻¹ are attributed to symmetric and asymmetric stretching vibrations of ethyl group. The aromatic and aliphatic C–H stretchings in the compound were observed at ~3100 cm⁻¹ (aromatic C–H stretching).

X-ray structure

Molecular structure of the azo-enamine tautomer is shown in Fig. 2. The compound crystallizes in monoclinic crystal system, $P2_1/n$ space group with unit cell parameters a = 9.0973(12), $b = 8.1678(11), c = 24.883(3) \text{ Å}, \beta = 91.238(2)^\circ, V = 1848.5(4) \text{ Å}^3$ and Z = 4. All bond lengths and angles are within the normal ranges. All bond lengths and angles in the phenyl rings have normal Csp2-Csp2 values and are in the expected ranges (Table S1). X-ray investigation of the compound showed that azo-enamine tautomer is favoured in the solid state. The C12–O1 bond length of 1.290(2) Å indicates a double bond character, whereas the C15-N3 bond length of 1.307(2) Å is longer than a double bond (C=N) character and the C11-C15 bond length of 1.405(2) Å is longer than a double bond (C=C) character. Aromatic rings (C9–C14) and (C15–C20) adopt the trans configuration with regard to the azo double bond (-N2=N3-) with a distance of 1.2656(19) Å the torsion angle C6–N1–N2–C9 of 179.69(14) Å which is in good agreement with published values [27]. In order to confirm the existence of azo-enamine tautomer in the solid state, the harmonic oscillator model of aromaticity (HOMA) indexes for rings are calculated using the following equation [18,42].

$$HOMA = 1 - \left[\frac{\alpha}{n}\sum_{i=1}^{n}(Ri - Ropt)2\right]$$

n is the number of bonds in ring, α is the constant 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



Scheme 1. Synthesis of (6*Z*)-4-[(*E*)-(4-ethylphenyl)diazenyl]-6-{[(2-hydroxy-5-methylphenyl)amino]methylidene}cyclohexa-2,4-dien-1-one dye and its possible tautomers. (i) HCl/NaNO₂, salicylaldehyde, 0–5 °C and (ii) 2-amino-4-methylphenol, MeOH, reflux.



Fig. 1. ¹H NMR spectrum of azo-enamine compound.



Fig. 2. Molecular structure of the azo-enamine tautomer with atom numbering thermal ellipsoid 50% probability, intra-molecular hydrogen bonding is shown as dash lines.

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 non-aromatic, respectively [18,42]. HOMA indexes for the rings of C3–C8, C9–C14 and C16–C21 were found to be 0.9993, 0.5959 and 0.9996, respectively. These results revealed that the rings C3–C8 and C16–C21 show aromatic character however C9–C14 ring deviates from aromaticity.

There is an intramolecular hydrogen bonding (N3–H···O1) in the molecule forming a S(6) graph set motif. Additionally, there is an intermolecular O2–H···O1 hydrogen bonding in the structure (symmetry code: -x + 3/2, y + 1/2, -z + 1/2). The same intermolecular hydrogen bonding contacts are extended between the other symmetry-related molecules in their respective planes to form a 1D hydrogen bond chain (Fig. 3).

In the structure, the azo benzene ring slightly twisted with respect to the central benzene ring. The mean planes of C3-C8 and C16–C21 are at 3.13 $(10)^{\circ}$ and 4.15 $(10)^{\circ}$ to the central (C9-C14) ring, respectively. This is possibly a consequence of the intermolecular interactions in the lattice. The molecules show two sets of interactions with neighbouring dimeric units. First, C3-C12 section of the molecules is stacked with the same section of an adjacent molecule under symmetry operation of 1-x, 1-y, -z (C3/C8–C9/C14 centroid–centroid distance is 3.599 Å). Second, the central benzene ring (C9-C14) is stacked with 4-methylphenol unit of a neighbouring compound under symmetry operation of x, -1 + y, z (C9/C14–C16/C21 centroid-centroid distance is 3.531 Å) (Fig. 4). Hydrogen bonded chains are linked by π - π interactions and crystal packing of the compound is determined by intermolecular hydrogen bonding and π - π interactions. The packing plot of the compound is shown in Fig. 4.

Optimized structures

Optimized structures of tautomers (1–3) were represented in Fig. S4. Experimental and calculated bond lengths and angles of tautomer (2) were given in Table S1.

As can be seen from Table S1, compared with experimental datum and calculated bond lengths/angles of tautomer (2), it can be seen that B3LYP/3-21G level is the appropriate level. The differences average between experimental and calculated bond lengths of tautomer (2) is 0.012 Å and the differences average between experimental and calculated bond angles is 2.4°. These results show that there is a good agreement with experimental and optimized structure of tautomer (2).

The stability and reactivity of tautomers

Total energy (*E*), Gibbs free energy (G°) were calculated to predict the stability of tautomers at B3LYP/3-21G level in gas phase and given in Table S2. Total energy (E_{Total}) comprises electronic energy (E_{elec}), zero-point energy (ZPE), vibrational energy (E_{vib}), rotational energy (E_{rot}), translational energy (E_{transl}) and represented in Eq. (1) and Gibbs free energy (*G*) includes entalphy (*H*), entropy (*S*) and it represented in Eq. (2).

$$E_{\text{Total}} = E_{\text{elec}} + ZPE + E_{\text{vib}} + E_{\text{rot}} + E_{\text{transl}} \tag{1}$$

$$G = H - TS \tag{2}$$

 E_{Total} and *G* can be used to explain the stability. The tautomer with the lowest energy has the most stability. The stability ranking of tautomers should be:

$$(2) > (1) > (3)$$
(according to the *E*_{Total})

(2) > (1) > (3)(according to the*G*)

Taken into account *E* and *G*, the most stable tautomer is tautomer (2). But the stabilities of tautomers (2) and (1) are close to each other.

Contour diagram of HOMO and LUMO can be used to predict the reactive region of tautomers. Contour diagrams of frontier molecular orbitals of tautomers were represented in Fig. 5.

HOMO of tautomers (1) and (2) is mainly delocalized on all atoms of molecules while LUMO is localized on oxygen, nitrogen and middle benzene ring. If mentioned tautomers are taken into account as tridentate ligands, electrons are given from HOMO, HOMO–1 and HOMO–2 of tautomers. The energies of LUMO, HOMO, HOMO–1 and HOMO–2 were given in Table S3.

The tendency of donating electron increases with increasing of orbital energies. The total energies of HOMO, HOMO-1 and HOMO-2 are important to determine the most reactive tautomer.



Fig. 3. 1D hydrogen bonded chain within the structure.



Fig. 4. Packing diagram of the azo-enamine dye viewing down a axis showing π - π stacking interactions between hydrogen bonded molecules.

According to Table 2, total energies of tautomers (2) and (3) are close to each other, yet tautomer (3) is very unstable. Based on this comparison, the most reactive tautomer was found as tautomer (2). Electron density surface of tautomer (2) was given in Fig. 6. The highest electron density surface is on the oxygen atom numbered with O1.

Electronic absorption spectra

Electronic spectroscopy is very useful tool for studying tautomerism in Schiff bases involving ahydroxyl group in *ortho* position to the azomethine group. *o*-Hydroxy Schiff bases may exist in two tautomeric forms (enol and keto forms) in solid state and solvent media [18].

To examine the behavior of the title compound in solution, electronic spectra in four organic solvents with different polarity (CHCl₃, MeOH, DMSO and DMF) were performed in the wavelength range 200–800 nm at room temperature. UV–Vis. spectra of the title compound are shown in Fig. 7.

In all four solvents, maximum absorptions observed in the range of 320–410 nm were assigned to the $\pi \rightarrow \pi^*$ transitions of the aromatic rings and active functional groups (azo and



Fig. 6. Electron density surface of tautomer (2).

azomethine groups). Absorption intensity of the $\pi \to \pi^*$ transitions increased with increasing the solvent polarity (hyperchromic effect). The $\pi \to \pi^*$ transitions in DMF and DMSO shifted to higher



Fig. 5. Contour diagrams of frontier molecular orbitals for tautomers (1-3).



Fig. 7. UV-Vis. spectra of the compound (10^{-5} M) in various solvent.

wavelengths (batochromic effect) with higher absorption intensities than in CHCl₃. Additionally, new absorption bands at 465, 465 and 470 nm were observed in MeOH, DMF and DMSO, respectively. The intensity of these new bands increased with decreasing the solvent polarity (hyperchromic effect). The earlier computational and experimental studies on *o*-hydroxy Schiff bases indicate that presence of a new band above 400 nm is indicative of the existence of keto-enamine tautomer in solution [21]. No new band due to keto-amine tautomer was observed in CHCl₃.

The electronic absorption spectra of the azo-azomethine compound at different volume ratios of the applied pair solvents DMF/H₂O and DMSO/H₂O were also measured. The absorption curves of the dye in DMF/H₂O and DMSO/H₂O mixtures are shown in Fig. S5. In DMF/H₂O, the absorption bands shifted to lower wavelengths (hypsochromic effect) but with higher absorption intensities (hyperchromic effect). No particular differences were observed in UV–Vis absorption spectra of the compound in DMF/ H₂O (1:1 and 1:2 v/v ratios) solutions. However, in DMSO/H₂O, as amount of water increased, the absorption bands shifted to lower wavelengths (hypsochromic effect) with lower absorption intensities (hyporchromic effect) (Fig. S5).

The UV–Vis. spectra of the compound in DMF and DMSO solvents were performed at 20–80 °C range (Fig. S6). In DMF, considerable increase both the absorption wavelengths and intensities were observed when temperature increased from 20 to 40 °C. However, no particular differences were observed after 40 °C. Interestingly, in DMSO, as the temperature increased, the intensity of the band due to the $\pi \rightarrow \pi^*$ transitions shifted lower values but intensity of the band due to azo-enamine tautomer increased. Again, no particular change was observed after 40 °C.

Non-linear optic properties

Non-linear optical properties (NLO) is current research field because of its importance in providing the key functions of frequency shifting, optical modulation, optical switching, optical logic and optical memory. The non-linear optical properties of molecules increase with conjugation of π electrons on molecule or adding donor/acceptor groups to molecule. Quantum chemical calculations can be used to describe the relationship between the electronic structures of molecules and their non-linear optical properties. Non-linear optical properties of tautomer (2) which has delocalized π electrons was studied by B3LYP/3-21G level.

The total static dipole moment (μ), the average linear polarizability (α) and first hyperpolarizability (β) can be calculated by using the Eqs. (1), (2), (1)–(3), respectively and given in Table S4 [43]:

$$\mu = \sqrt{\mu_x^2 + \mu_y^2 + \mu_z^2} \tag{1}$$

$$\alpha = \frac{1}{3}(\alpha_{xx} + \alpha_{yy} + \alpha_{zz}) \tag{2}$$

$$\beta = \left[\left(\beta_{xxx} + \beta_{xyy} + \beta_{xzz} \right)^2 + \left(\beta_{yyy} + \beta_{xxy} + \beta_{yzz} \right)^2 + \left(\beta_{zzz} + \beta_{xzz} + \beta_{yzz} \right)^2 \right]^{1/2}$$
(3)

The calculated polarizability and hyperpolarizability for tautomer (**2**) are 48.7674 Å³ and 6.00×10^{-26} cm⁵/esu. These values are greater those of urea (α = 3.8312 Å³ and β = 0.37289 × 10⁻³⁰ cm⁵/esu), respectively. Therefore, tautomer (**2**) can be used as a non-linear optical material.

Acid dissociation constants

Acid dissociation constants were potentiometrically calculated from a series of several independent measurements. The ligand species, which occurred in solution under experimental conditions, are LH_{3}^{++} , LH_{4}^{++} , LH_{3}^{++} , LH_{2} , LH^{-} and L^{2-} . If LH_{3}^{++} denotes the fully protonated form of the ligand, its acid dissociation equilibriums are as follows:

$LH_5^{3+} + H_2O \Longrightarrow LH_4^{2+} + H_3O^+$ $K_{a1} = [LH_4^{2+}][H_3O^+]/[LH_5^{3+}]$	(4)
$LH_4^{2+} + H_2O \rightleftharpoons LH_3^+ + H_3O^+$ $K_{a2} = [LH_3^+][H_3O^+]/[LH_4^{2+}]$	(5)
$LH_3^+ + H_2O \rightleftharpoons LH_2 + H_3O^+ K_{a3} = [LH_2][H_3O^+]/[LH_3^+]$	(6)
$LH_2 + H_2O \rightleftharpoons LH^- + H_3O^+$ $K_{a4} = [LH^-][H_3O^+]/[LH_2]$	(7)

$$LH^{-} + H_2 O \rightleftharpoons L^{2-} + H_3 O^{+}$$
 $K_{a5} = [L^{2-}][H_3 O^{+}]/[LH^{-}]$ (8)

Hence, titration curves and distribution diagrams illustrated in Fig. 8. Five dissociation constants were determined for the ligand as 3.45 (pK_{a1}), 4.78 (pK_{a2}), 6.75 (pK_{a3}), 9.27(pK_{a4}) and 9.96 (pK_{a5})



Fig. 8. (a) Titration curves of the ligand; (b) Species distribution curves for ligand ($25.0 \pm 0.1 \circ C$, *I*: 0.1 mol dm⁻³ by NaCl).

Table 3

Acid dissociation constants of the compound in EtOH–H₂O mix. (1/5, v/v) (25.0 \pm 0.1 °C, *I* = 0.1 mol dm⁻³ by NaCl, 0.05 mmol HCl).

Species	$\log \beta^{a}$	pK _a Values
LH ₄	28.80 ± 0.05	3.58 ± 0.02
LH ₃	25.22 ± 0.03	6.30 ± 0.01
LH ₂	18.92 ± 0.03	9,23 ± 0.03
LH	9.69 ± 0.03	9.69 ± 0.03

^a Log β is overall dissociation constants.

and the autoprotolysis constants (p K_w) calculated as 13.99 ± 0.01for EtOH–H₂O mixture (1/5, v/v). According to recent published paper by Atabey et al. which they have worked on a number of Schiff Base derivatives, the p K_a values of —OH groups are reported between 9 and 11. Besides, in the same paper, the p K_a values of azomethine nitrogen atom reported between 4 and 6 in EtOH–H₂O mixture (1/5, v/v) [44]. Therefore, it can be said that while, p K_{a4} and p K_{a5} values are related to hydroxyl groups in the ligand, p K_{a2} value is related to azomethine nitrogen atom in this study. Moreover, it may be thought that p K_{a1} and p K_{a3} values were related to the nitrogens atoms of the azo chromophore (—N=N—). All calculated acid dissociation constants of the ligand are given in Table 3.

Conclusion

A novel azo-azomethine derivative was prepared via a Schiff base condensation reaction and characterised by UV-Vis, IR, ¹H, ¹³C NMR, mass spectrometry and elemental analyses. Molecular structure of the compound was determined by single crystal Xray diffraction technique. X-ray data showed that the compound favors azo-enamine tautomer in the solid state. The hydroxyl group in the aniline ring involves in intermolecular hydrogen bonding with C=O group of a neighbouring molecule. The same intermolecular hydrogen bonding contacts are extended between the other symmetry-related molecules in their respective planes to form a 1D hydrogen bond chain. The π - π interactions were observed between hydrogen bonding chains in the structure. In the electronic spectra of the compound, maximum absorptions observed in the range of 320-410 nm were assigned to the $\pi \rightarrow \pi^*$ transitions of the aromatic rings and active functional groups (azo and azomethine groups). Absorption intensity of the $\pi \rightarrow \pi^*$ transitions increased with increasing the solvent polarity (hyperchromic effect). Dissociation constants of the ligand were calculated as 3.45, 4.78, 6.759.27 and 9.96.

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Appendix A. Supplementary material

CCDC 994909 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge *via* www.ccdc.cam.ac.uk/data_request/cif, by e-mailing data_request@ccdc.cam.ac.uk, or by contacting The Cambridge Crystallographic Data Centre 12 Union Road Cambridge CB2 1EZ, UK Fax: +44(0)1223-336033. Supplementary data associated with this article can be found, in the online version, at http://dx.doi.org/ 10.1016/j.molstruc.2014.06.033.

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