**Investigation of enol-imine/keto-amine tautomerism in (E)-4-[(2-hydroxybenzylidene)amino]phenyl benzenesulphonate by experimental and molecular modelling methods**

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**ABSTRACT**

The Schiff base compound (E)-4-[(2-hydroxybenzylidene)amino]phenyl benzenesulphonate has been synthesised from the reaction of 4-aminophenyl benzenesulphonate and salicylaldehyde, and characterised by spectroscopic and single-crystal X-ray diffraction techniques. Quantum chemical calculations employing density functional theory method with the 6-311\(^{++}\)G(d,p) basis set were performed to study the molecular, spectroscopic and enol-imine/keto-amine tautomerisation mechanism of the title compound. An acceptable correlation between experimental and theoretical findings is obtained. Enol-imine/keto-amine tautomerisation mechanism was investigated in the gas phase and in solution phase using the polarisable continuum model approximation. The energetic and thermodynamic parameters of the enol-imine \(\rightarrow\) keto-amine transfer process show that the single proton exchange is unfavoured in all cases. Contrarily, the reverse reaction seems to be feasible with a very low barrier height and is supported by negative values in enthalpy and free energy changes for all cases.

**1. Introduction**

Salicylaldehydes having the wide application areas are extremely important compounds. They easily give a complex with transition metal ions [1]. Salicylaldehydes and their metal complexes have been used at pharmaceutics, catalysis and optoelectronic materials [2–6]. Recently, there is a great attention to the synthesis of the compounds containing sulphonate esters because these compounds have a good biological activity such as anti-neoplastic and anti-cancer [7]. However, salicylaldehydes containing aryl-sulphonate group are rare in the literature.

On the other hand, the prototropic tautomerism is a subject of great interest in synthetic organic chemistry. The most well-known type is enol-imine/keto-amine tautomerism. Such compounds having enol-imine/keto-amine tautomerism are precious because they are used in the preparation of organic multipurpose molecules [8,9].

Recently, substantial consideration has been dedicated to the synthesis of some Schiff bases based on salicylaldehyde because of showing good thermochromism.
and photochromism properties [10–12]. Previous studies revealed that compounds showing thermochromism are planar, while those showing photochromism are non-planar, and both events associated with H-atom migration from the hydroxyl oxygen atom to the imine nitrogen atom [13–15]. As a result, tautomeric forms derived from 2-hydroxy Schiff bases may be suitable for these events. Usually, o-hydroxy Schiff bases display two possible tautomeric forms, the enol-imine and the keto-amine forms (Scheme 1). Depending on the tautomers, two types of intramolecular hydrogen bonds can exist in Schiff bases: O—H···N [16] in enol-imine and N—H···O [17] in keto-amine tautomers.

In this study, we aimed to investigate the two tautomeric forms, spectroscopic properties and molecular structure of the title compound, and reported the results from both theoretical and experimental points of view. The effect of solvent on the tautomerism was examined by applying the polarisable continuum model (PCM).

2. Materials and methods

2.1. General remarks

All chemicals were purchased from commercial suppliers and used as received. Nuclear magnetic resonance (NMR) spectra were recorded at 297 K on a 600 MHz Bruker Avance III HD or a 300 MHz Bruker Ultra-shield TM NMR spectrometers at 600.13 and 399.88 MHz (1H) and at 150.92 and 100.56 MHz (13C) in CDCl3 with tetramethylsilane (TMS) as the internal standard. Chemical shifts (δ) are given in parts per million. Infrared (IR) spectra were measured with a Perkin Elmer Spectrum One FTIR (fourier transform infrared spectroscopy) system and recorded using a universal ATR (attenuated total reflectance) sampling accessory within the range 550–4000 cm−1. Ultraviolet-visible (UV-Vis) spectra were measured with a Perkin Elmer Lambda 25 system. Melting points were determined in open capillary tubes on a digital Stuart SMP10 melting point apparatus.

2.2. Syntheses

2.2.1. 4-aminophenyl benzenesulphonate (1)

A solution of 4-aminophenol (2.0 g, 18.3 mmol) and NEt3 (3 ml, 21 mmol) in dichloromethane (DCM) (50 ml) was stirred 10 minutes at room temperature. Then a solution of benzenesulphonyl chloride (2.34 ml, 18.3 mmol) in DCM (5 ml) was added dropwise. The reaction mixture was heated under reflux for 8 h. At the end of this time, the solvent was evaporated and the residue was swilled and extracted with 3 × 50 ml DCM. The organic phase was concentrated up to 10 ml and precipitated via drop-wise to hexane (100 ml) and filtered (yield: 67%, 3.0729 g; mp: 94 ºC).

2.2.2. (E)-4-[(2-hydroxybenzylidene)amino]phenyl benzenesulphonate (2)

To a solution of 1 (1.0 g, 4.0 mmol) in EtOH (20 ml) was added salicylaldehyde (0.43 ml, 4.0 mmol) and the mixture was stirred at room temperature for 3 h (Scheme 1). Then the precipitate was obtained by filtration (yield: 61%, 0.8712 g; mp: 143–146 ºC).

2.3. Crystal structure determination

Intensity data of compound 2 were collected on a STOE diffractometer with an IPDS II image plate detector. The

Scheme 1. Formation and tautomerisation of compound 2.
diffraction measurements were performed at room temperature (296 K) using graphite monochromated Mo Kα radiation (λ = 0.71073 Å) by applying the ω-scan method. Data collection and cell refinement were carried out using X-AREA, [18] while data reduction was applied using X-RED32 [18]. The structure was solved by direct methods using SHELXS-2013 [19] and refined with full-matrix least-squares calculations on $F^2$ using SHELXL-2014 [19] implemented in WinGX [20] program suit. All H atoms bonded to C atoms were positioned geometrically and refined as a riding model with C—H = 0.93 Å and $U_{iso}$ (H) = 1.2$U_{eq}$ (C), while the H atom bonded to the O atom was located in a difference Fourier map and refined isotropically [O—H = 0.95(3) Å]. Details of the data collection conditions and the parameters of refinement process are given in Table 1. The general-purpose crystallographic tool PLATON [21] was used for the structure analysis and presentation of the results. The molecular graphics were generated using ORTEP-3 [20].

2.4. Computational procedure

The structures at the local minimum or the transition state (TS) were optimised using the default convergence criteria. The minimum energy or TS nature of the stationary points is verified from frequency analysis. The stable structures exhibited all positive frequencies, whereas the TSs possessed one imaginary frequency. All calculations were performed via the GaussView molecular visualisation program [22] and Gaussian 03W package [23]. The three-parameter hybrid density functional (B3LYP) [24,25] and 6-311++G(d,p) [26,27] basis set were selected for the calculations. A scale factor of 0.9679 [28] was used to correct the calculated vibrational frequencies. The $^1$H and $^{13}$C NMR chemical shifts were calculated within the gauge-independent atomic orbital approach, [29,30] applying the same method and the basis set as used for geometry optimisation. The $^1$H and $^{13}$C NMR chemical shifts were converted to the TMS scale by subtracting the calculated absolute chemical shielding of TMS ($\delta = \Sigma_0 - \Sigma$, where $\delta$ is the chemical shift, $\Sigma$ is the absolute shielding and $\Sigma_0$ is the absolute shielding of TMS), whose values are 31.97 and 184.66 ppm, respectively. The effect of solvent on the theoretical NMR parameters was included using the default model provided by Gaussian 03W. Chloroform was used as a solvent. The electronic absorption spectra were calculated using the time-dependent density functional theory (TD-DFT) method [31,32]. Solvent effects were estimated by means of the PCM method [33–36] at the same level in three kinds of solvents [chloroform (ε = 4.90), methanol (ε = 32.63) and water (ε = 78.39)].

### Table 1. Crystal data and structure refinement parameters for compound 2.

| Parameter                                      | Value                          |
|------------------------------------------------|--------------------------------|
| CCDC deposition no.                            | 759                            |
| Colour/shape                                    | Yellow/plate                   |
| Chemical formula                                | C$_6$H$_{14}$NO$_3$S            |
| Formula weight                                  | 353.38                         |
| Temperature (K)                                 | 90, 99, 437(5), 90              |
| Wavelength (Å)                                  | 0.71073 Mo Kα                  |
| Crystal system                                  | Monoclinic                     |
| Space group                                     | C2/c (No. 15)                  |
| Unit cell parameters                            | 38.146(2), 5.7657(3), 15.2860(8) |
| Volume (Å$^3$)                                   | 3316.5(3)                      |
| Z                                               | 8                              |
| $D_{calc}$ (g/cm$^3$)                           | 1.415                          |
| $\mu$ (mm$^{-1}$)                               | 0.219                          |
| Absorption correction                           | Integration                    |
| $I_{min}$, $I_{max}$                            | 0.77 x 0.35 x 0.05              |
| Crystal size (mm$^3$)                           | 1472                           |
| Diffractometer/measurement method               | STOE IPDS II/ω scan            |
| Index ranges                                    | $-46 \leq h \leq 46, -7 \leq k \leq 7, -18 \leq l \leq 18$ |
| $\theta$ range for data collection (°)          | 18.598                         |
| Reflections collected                           | 3204/1843                      |
| Independent/observed reflections               | 0.091                          |
| $R_{exp}$                                       | Full-matrix least-squares on $F^2$ |
| Refinement method                               | 3204/0/230                     |
| Data/restraints/parameters                      | 1.008                          |
| Goodness-of-fit on $F^2$                        | $R_1 = 0.044$, $wR_2 = 0.054$  |
| Final $R$ indices ($I > 2\sigma(I)$)            | $R_1 = 0.061$, $wR_2 = 0.103$  |
| $\Delta \rho_{max}$, $\Delta \rho_{min}$ (e/Å$^3$) | 0.15, −0.30                   |
favoured over the keto-amine form in compound 2 since the O1—C1 and N1—C7 bond lengths show single and double bond characters. The S1—O3 and S1—O4 distances [1.4128(15) and 1.4228(13) Å] are almost equal and consistent with S=O double bonding, while the S1—O2 distance of 1.6063(16) Å shows single bond character. Furthermore, the sulphur atom has a distorted tetrahedral configuration which is evident from the angles changing from 102.58(9) to 120.75(9)°. All the bond lengths and angles are normal [37] and they are similar to those of the related molecules [38–41]. The Φ\textsubscript{CN} (C6—C7—N1—C8) and Φ\textsubscript{SO} (C14—S1—O2—C11) torsion angles are 177.6(2) and 66.47(16)°, which show that the conformations about the C7—N1 and S1—O2 bonds are (+) antiperiplanar and (+) synclinal, respectively. The dihedral angles between the C1/C6 (ring A), C8/C13 (ring B) and C14/C19 (ring C) planes are found to be 2.73(11)° (A/B), 57.98(12)° (A/C) and 60.02(11)° (B/C).

In the molecular structure of the compound, an intramolecular O1—H1···N1 hydrogen bond (see Figure 1) leads to the formation of six-membered rings with graph-set descriptor S(6) [42]. In the crystal structure, two intermolecular C—H···O interactions [43] are observed. Atom C13 in the molecule at (x, y, z) acts as hydrogen-bond donor, via H13, to atom O1 in the molecule at (−x + 1/2, −y − 1/2, −z + 1), so generating a dimeric unit characterised by an \( R_2^1(8) \) motif. In addition, atom C19 in the molecule at (x, y, z) acts as hydrogen-bond donor, via H19, to atom O3 in the molecule at (−x, −y + 1, −z + 1), so generating another dimeric unit characterised by an \( R_2^1(10) \) motif. Propagation of these two interactions produces a chain of alternating \( R_2^1(8) \) and \( R_2^1(10) \) rings (Figure 2). Finally, two chains are connected to each other by means of \( π—π \) stacking interactions between the rings A and B with a centroid–centroid distance of 3.7652(14) Å. Full details of the hydrogen-bonding geometry are given in Table 2.

The theoretical geometric structure of compound 2 is shown in Figure 1(b), while the calculated geometric parameters are listed in Table 3 together with the experimental data. As can be seen in Table 3, there is a good agreement between the experimental and theoretical geometric parameters. The largest difference of bond lengths is about 0.07 Å for the S1—O2 distance.

### Table 2. Hydrogen-bond geometry for compound 2.

| D—H···A     | D—H (Å) | H···A (Å) | D—A (Å) | D·H—A (°) |
|-------------|---------|----------|---------|-----------|
| O1—H1···N1  | 0.95(3) | 1.70(3)  | 2.583(2)| 155(2)    |
| C13—H13···O1\(^1\) | 0.93 | 2.57 | 3.464(3)| 163       |
| C19—H19···O3\(^1\) | 0.93 | 2.64 | 3.264(3)| 125       |

Note: Symmetry codes: \(^1\) x + 1/2, y − 1/2, −z + 1; \(^8\) −x, −y + 1, −z + 1.
while the biggest deviation occurs in the C1—O1—H1 angle by 4.46°. However, conformational discrepancies exist between them. The dihedral angles between the rings A, B and C have been calculated at 40.52° (A/B), 79.61° (A/C) and 54.36° (B/C), while the calculated D—H, H···A, D···A and D—H···A values for the intramolecular interaction in the optimised structure are 0.99 Å, 1.75 Å, 2.64 Å and 147.04°, respectively.

When the experimental and theoretical structures are globally compared by superimposing their molecular skeletons, the obtained root mean square error (RMSE) is 0.458 Å [Figure 1(c)]. Although the experimental

### Table 3. Experimental and optimised structural parameters of the enol-imine/keto-amine tautomers and transition state of compound 2.

| Parameters | X-ray | Enol-imine | TS | Keto-amine |
|------------|-------|------------|----|------------|
| Bond lengths (Å) |       |            |    |            |
| S1—O2      | 1.6603(16) | 1.675      | 1.678 | 1.679 |
| S1—O3      | 1.4228(16) | 1.448      | 1.447 | 1.447 |
| S1—O4      | 1.4228(13) | 1.455      | 1.454 | 1.454 |
| S1—C14     | 1.7444(2)  | 1.790      | 1.790 | 1.790 |
| O1—C1      | 1.357(2)   | 1.341      | 1.292 | 1.261 |
| O1—H1      | 0.95(3)    | 0.992      | —    | —          |
| O2—C11     | 1.413(3)   | 1.397      | 1.395 | 1.394 |
| N1—C7      | 1.276(3)   | 1.289      | 1.313 | 1.332 |
| N1—C8      | 1.408(3)   | 1.407      | 1.404 | 1.405 |
| N1—H1      | —          | —          | —    | 1.045 |
| C6—C7      | 1.437(3)   | 1.449      | 1.415 | 1.395 |
| Bond angles (°) |       |            |    |            |
| O2—S1—O3   | 102.58(9)  | 102.81     | 102.80 | 102.78 |
| O2—S1—O4   | 108.61(9)  | 108.56     | 108.44 | 108.38 |
| O3—S1—O4   | 120.75(9)  | 122.20     | 122.33 | 122.38 |
| O2—S1—C14  | 103.53(9)  | 102.87     | 102.82 | 102.73 |
| O3—S1—C14  | 110.89(10) | 109.65     | 109.63 | 109.68 |
| O4—S1—C14  | 108.93(9)  | 108.92     | 108.95 | 108.98 |
| C1—O1—H1   | 103.2(16)  | 107.66     | —    | —          |
| S1—O2—C11  | 119.04(13) | 121.25     | 121.06 | 120.95 |
| C7—N1—C8   | 124.44(18) | 121.09     | 126.29 | 127.83 |
| C7—N1—H1   | —          | —          | —    | 111.12 |
| C8—N1—H1   | —          | —          | —    | 121.05 |
| O1—C1—C2   | 119.0(2)   | 118.60     | 122.19 | 122.29 |
| O1—C1—C6   | 120.6(2)   | 121.92     | 120.54 | 121.70 |
| N1—C7—C6   | 122.27(19) | 122.59     | 119.68 | 122.66 |
| N1—C8—C9   | 126.1(2)   | 122.84     | 123.05 | 122.88 |
| N1—C8—C13  | 115.48(18) | 118.14     | 117.69 | 117.73 |
| Dihedral angles (°) |       |            |    |            |
| C4—S1—O2—C11 | 66.47(16) | 71.20      | 73.28 | 73.77 |
| C6—C7—N1—C8 | 177.6(2)  | 176.88     | —    | 178.19 |
|               |            |            |     | 178.87 |
As shown in Scheme 1, two tautomeric forms may exist for the title molecule, the enol-imine and keto-amine forms; first with a C7=N1 double bond and the latter with an exocyclic double bond C1=O1. The tautomerisation mechanism for compound 2 has been theoretically investigated at the B3LYP/6-311++G(d,p) level. Some selected structural parameters belonging to the enol-imine, keto-amine and TS geometries of compound 2 are listed in Table 3, while the energies of the enol-imine and keto-amine forms, energy differences and activation energies are given in Table 4.

The two tautomers could be converted to each other via an intramolecular proton transfer reaction. Because of the transfer of a hydrogen atom from atom O1 to atom N1, some changes are observed in the molecular structure. On going from the enol-imine to the keto-amine tautomer, the O1—C1 bond distance is reduced from 1.341 to 1.261 Å, while the N1—C7 distance increases from 1.289 to 1.332 Å. This is consistent with the breaking of the C=N double bond and corresponding formation of a C=O double bond. Furthermore, the distance between atoms C6 and C7 decreases while the C7—N1—C8 and O1—C1—C2 angles expand. The O1⋯H1 and N1⋯H1 distances for TS structure were calculated to be 1.299 and 1.192 Å in the gas phase, 1.278 and 1.209 Å in chloroform, 1.265 and 1.220 Å in methanol, and 1.264 and 1.221 Å in water, respectively.

Figure 3 shows the potential energy diagram for the enol-imine/keto-amine isomerisation of compound 2. The energy differences between the two tautomers were determined to be −21.62, −13.19, −9.46 and −9.01 kJ mol⁻¹ in going from the gas phase to water, respectively. Considering the ground state energy of the enol-imine and keto-amine tautomers as well as the tautomerisation energies in Table 4 shows that the enol-imine form is

| Method | $\varepsilon$ | Enol-imine | Keto-amine | $\Delta E$ | $E_a(f)$ | $E_a(r)$ | $\Delta H_{298}(f)$ | $\Delta G_{298}(f)$ | $T\Delta S_{298}(f)$ | $\Delta H_{298}(r)$ | $\Delta G_{298}(r)$ | $T\Delta S_{298}(r)$ |
|--------|--------------|------------|-----------|------------|--------|--------|-----------------|-----------------|-----------------|----------------|-----------------|-----------------|
| B3LYP  | 1            | −1487.14106406 | −1487.33282837 | −21.62     | 28.49  | 6.87   | 16.26           | 16.39           | −0.13           | −4.56          | −2.88           | −1.68           |
| PCM    | 4.90         | −1487.15267948 | −1487.14765538 | −13.19     | 22.65  | 9.46   | 10.69           | 11.30           | −0.61           | −2.76          | −0.60           | −2.16           |
| 32.63  | −1487.15736173 | −1487.15376050 | −9.46      | 20.81  | 11.35  | 8.76   | 6.21            | 2.55            | −1.25           | −1.73          | −0.48           |                |
| 78.39  | −1487.15790125 | −1487.15447063 | −9.01      | 20.52  | 11.51  | 8.48   | 6.19            | 2.30            | −1.10           | −1.18          | 0.08            |                |

Note: $\varepsilon$ = dielectric constant, $\Delta E = E_{\text{enol-imine}} - E_{\text{keto-amine}}$, $E_a(f)$ = forward activation energy, $E_a(r)$ = reverse activation energy.
more stable than the keto-amine form in both the gas phase and in solution phase.

Let us define the forward reaction as the proton transfer from the enol-imine to the keto-amine form of the compound, and the reverse is the reaction in the opposite direction. The relative energies of the TS with respect to the enol-imine tautomer were obtained as 28.49, 22.65, 20.81 and 20.52 kJ mol$^{-1}$ in the gas phase, in chloroform, in methanol and in water, respectively. These values show that a considerable energy is necessary for the forward proton transfer to occur. However, the reverse reaction has a very low energy barrier with values of 6.87, 9.46, 11.35 and 11.51 kJ mol$^{-1}$ in going from the gas phase to water, respectively. As a result, this reaction is much easier than the forward proton transfer. It can be easily said that the stronger the dipole moment of the solvent, the higher the barrier to the proton transfer process for the reverse reaction. By contrast, an opposite trend was observed for the forward proton transfer reaction.

The standard enthalpy and free energy changes for the single proton transfer are also listed in Table 4. As can be seen from the table, the forward double proton transfer is endothermic due to positive standard enthalpy and free energy changes in both the gas phase and in solution phase. So, this reaction is a disfavoured process or not a spontaneous process. However, the reverse reaction has a negative value in enthalpy and free energy changes for both the gas phase and in solution phase, so indicating an exothermic process (a favoured process or a spontaneous process).

### 3.3. IR spectroscopy

The FTIR spectra of compounds 1 and 2 are given in Figure S1 in the supplementary material. Harmonic vibrational frequencies of the two compounds were calculated and compared with the experimental ones as shown in Table 5. In general, an acceptable agreement exists between them.

The high frequency region above 3000 cm$^{-1}$ is the characteristic region for the ready identification of C–H, O–H and N–H stretching vibrations. The asymmetric N–H$_2$ stretching vibration appears between 3420 and 3500 cm$^{-1}$, while its symmetric mode is observed in the range 3340–3420 cm$^{-1}$ [44]. In the IR spectra of compound 1, the absorptions at 3435 and 3365 cm$^{-1}$ are assigned to the asymmetric and symmetric N–H$_2$ stretching frequencies that have been calculated at
Table 6. Experimental and theoretical $^1$C and $^1$H NMR chemical shifts $\delta$ (ppm) from TMS for compounds 1 and 2.

| Atom | Experimental | Calculated | Experimental | Calculated |
|------|--------------|------------|--------------|------------|
| C1   | –            | –          | 161.32       | 171.87     |
| C2   | –            | –          | 117.51       | 123.35     |
| C3   | –            | –          | 134.60       | 141.85     |
| C4   | –            | –          | 119.47       | 125.19     |
| C5   | –            | –          | 133.78       | 140.50     |
| C6   | –            | –          | 122.51       | 126.33     |
| C7   | –            | –          | 163.71       | 172.26     |
| C8   | 135.43       | 155.01     | 128.74       | 124.23     |
| C9   | 115.37       | 119.15     | 119.21       | 130.86     |
| C10  | 123.20       | 130.89     | 147.63       | 158.16     |
| C11  | 141.57       | 149.86     | 119.21       | 132.36     |
| C12  | 123.20       | 133.12     | 128.74       | 133.47     |
| C13  | 115.37       | 119.99     | 148.26       | 148.13     |
| C14  | 145.45       | 147.75     | 123.60       | 134.83     |
| C15  | 128.59       | 135.42     | 132.75       | 135.56     |
| C16  | 134.04       | 135.56     | 129.47       | 142.05     |
| C17  | 129.03       | 141.65     | 132.75       | 137.09     |
| C18  | 134.04       | 136.74     | 123.60       | 134.94     |
| C19  | 128.59       | 134.76     | –            | –          |
| H1 (O) | –            | –          | -12.89 (s)   | 12.73      |
| H1 (N) | 3.68 (br. s) | 3.59a      | –            | –          |
| H2   | –            | –          | 7.36–7.40 (m) | 7.18      |
| H3   | –            | –          | 6.97–7.06 (m) | 7.67      |
| H4   | –            | –          | 6.94 (td, $J_1 = 7.51$ Hz, $J_2 = 7.51$ Hz) | 7.16 |
| H5   | –            | –          | 7.36–7.40 (m) | 7.58      |
| H7   | –            | –          | 8.55 (s)     | 8.76       |
| H9   | 6.51 (d, $J = 8.80$ Hz) | 6.49 | 6.97–7.06 (m) | 7.10      |
| H10  | 6.72 (d, $J = 8.80$ Hz) | 6.35 | 7.17 (d, $J = 8.97$ Hz) | 6.75      |
| H12  | 6.72 (d, $J = 8.80$ Hz) | 7.58 | 7.17 (d, $J = 8.97$ Hz) | 7.99      |
| H13  | 6.51 (d, $J = 8.80$ Hz) | 6.90 | 6.97–7.06 (m) | 7.69      |
| H15  | 7.81 (d, $J = 8.44$ Hz) | 7.38 | 7.86 (dd, $J_1 = 8.19$ Hz, $J_2 = 1.17$ Hz) | 7.48      |
| H16  | 7.50 (t, $J = 7.89$ Hz) | 7.55 | 7.54 (t, $J = 7.80$ Hz) | 7.56      |
| H17  | 7.64 (t, $J = 7.52$ Hz) | 7.88 | 7.68 (t, $J = 7.61$ Hz) | 7.93      |
| H18  | 7.50 (t, $J = 7.89$ Hz) | 7.86 | 7.54 (t, $J = 7.80$ Hz) | 7.89      |
| H19  | 7.81 (d, $J = 8.44$ Hz) | 8.27 | 7.86 (dd, $J_1 = 8.19$ Hz, $J_2 = 1.17$ Hz) | 8.32      |

Note: The atom numbering according to Figure 1(a) used in the assignment of chemical shifts.

Average.

3551 and 3457 cm$^{-1}$, respectively. The N–H$_2$ scissoring deformation modes are expected in the region 1650–1590 cm$^{-1}$ with strong to very strong IR intensity [44,45]. We assigned the band at 1634 cm$^{-1}$ due to the pure N–H$_2$ scissoring, which is in coincidence with theoretical value of 1611 cm$^{-1}$. The N–H$_2$ twisting mode recorded at 1039 cm$^{-1}$ is in good agreement with theoretical result of 1043 cm$^{-1}$.

The O–H group gives rise to three vibrations as stretching, in-plane bending and out-of-plane bending vibrations. The non-hydrogen-bonded or a free hydroxyl group absorbs strongly in the 3550–3700 cm$^{-1}$ region [46]. Intramolecular hydrogen bonding would reduce the O–H stretching band to the 3550–3200 cm$^{-1}$ region [47]. We could not observe the O–H stretching vibration in the FTIR spectra of compound 2 due to the broadband width between 3200 and 3000 cm$^{-1}$ that superimposes C–H stretching bands. However, this band is calculated at 3136 cm$^{-1}$ in the theoretical spectra. The O–H in-plane bending occurs between 1440 and 1395 cm$^{-1}$ and out-of-plane bending occurs between 960 and 875 cm$^{-1}$ [48]. The in-plane and out-of-plane vibrations of the O–H group as pure mode are observed at 1374 and 835 cm$^{-1}$ that have been calculated at 1403 and 815 cm$^{-1}$, respectively.

The aromatic C–H stretching, C–H in-plane bending and C–H out-of-plane bending vibrations appear in 2900–3150, 1100–1500 and 750–1000 cm$^{-1}$ frequency ranges, respectively [49]. The C–H aromatic stretching modes were observed at 3109 and 3073 cm$^{-1}$ for compound 1 and at 3095 and 3060 cm$^{-1}$ for compound 2 experimentally and were calculated at 3103 and 3062 cm$^{-1}$ for compound 1 and at 3096 and 3090 cm$^{-1}$ for compound 2, respectively. In addition, the imine C–H stretching mode of compound 2 was observed at 2938 cm$^{-1}$ while this band appeared at 2939 cm$^{-1}$ in the theoretical spectra.

The main difference in the FTIR spectra of compound 2 is the loss of the peaks assigned to the N–H$_2$ group and a new peak formed due to C=N group. The
characteristic region of 1500–1700 cm$^{-1}$ can be used to identify the proton transfer of Schiff bases. Azomethine (C=N) bond stretching vibrations of compound 2 were observed at 1612 cm$^{-1}$ as a pure mode and at 1568 cm$^{-1}$ as a mixed mode experimentally, while these were calculated at 1611 and 1556 cm$^{-1}$ for B3LYP. The bands at 1582 and 1480 cm$^{-1}$ in the FTIR spectra of compound 1 and the band at 1590 cm$^{-1}$ in the FTIR spectra of compound 2, which can be attributed to the ring C=C stretching vibrations, were calculated at 1593, 1486 and 1579 cm$^{-1}$ for B3LYP, respectively. The C$_{ar}$—O stretching vibration of compound 2 was observed at 1451 cm$^{-1}$ that has been appeared at 1442 cm$^{-1}$ theoretically, which also confirms the presence of phenol group in compound 2.

The symmetric and asymmetric S=O$_2$ stretching vibrations occur in the region 1125–1150 and 1295–1330 cm$^{-1}$, respectively [44]. We calculated the asymmetric and symmetric S=O$_2$ stretching vibrations at 1292 and 1104 cm$^{-1}$ for compound 1 and at 1295 and 1104 cm$^{-1}$ for compound 2 as pure modes, while these bonds were obtained at 1329, 1170, 1302 and 1149 cm$^{-1}$ in their FTIR spectra, respectively. The other experimental and theoretical vibrational frequencies can be seen in Table 5.

The above conclusions are in accord with the similar Schiff base compounds [50,51]. Consequently, the characteristic vibration bands, such as phenol O—H, azomethine C=N and C$_{ar}$—O, belonging to only the enol-imine tautomeric form of compound 2 as shown in Scheme 1 are observed in the FTIR spectra, and these clearly indicate that compound 2 has the enol-imine form in the solid state.

### 3.4. NMR spectroscopy

The characterisation of compounds 1 and 2 was further enhanced by the use of $^1$H and $^{13}$C NMR spectroscopy. The NMR spectra of the compounds are shown in Figures S2 and S3 in the supplementary material, respectively. Theoretical $^1$H and $^{13}$C NMR chemical shift values of the compounds have been computed using the same method and the basis set for the optimised geometry. The results of these calculations are tabulated in Table 6 together with the experimental values. Since experimental $^1$H chemical shift values were not available for individual hydrogen atoms of NH$_2$ group in compound 1, the average of the calculated values for these hydrogen atoms has been given.

All NMR data are consistent with the structural formula of compounds. In the $^1$H NMR spectra of compound 1, a broad peak at 3.68 ppm may be assigned to the -NH$_2$ protons, which has been calculated at 3.59 ppm. The -H$_9$–13 and -H$_{10}$–12 protons belonging to aminobenzene backbone were monitored as doublets at 6.51 and 6.72 ppm, respectively. On the other hand, the -H$_{15}$–19, -H$_{16}$–18 and -H$_{17}$ protons belonging to sulphonyl-benzene...
Table 7. Experimental and electronic absorptionspectra values for compound 2.

|                  | Experimental | Calculated |
|------------------|--------------|------------|
|                  | Wavelength (nm) | Abs     | Wavelength (nm) | Oscillator strength |
| Dichloromethane  |               |          |               |                   |
| 369              | 0.794        |          | 346           | 0.627             |
| 310              | 0.892        |          | 314           | 0.172             |
| 254              | 0.939        |          | 270           | 0.203             |
| Dimethysulphoxide|               |          |               |                   |
| 375              | 0.855        |          | 345           | 0.632             |
| 319              | 0.897        |          | 313           | 0.167             |
| 282              | 0.832        |          | 270           | 0.204             |
| Methanol         |               |          |               |                   |
| 441              | 0.027        |          | —             |                   |
| 370              | 0.756        |          | 344           | 0.611             |
| 308              | 0.845        |          | 313           | 0.165             |
| 253              | 0.907        |          | 270           | 0.214             |
| Toluene          |               |          |               |                   |
| 375              | 0.869        |          | 349           | 0.624             |
| 311              | 0.984        |          | 315           | 0.185             |
| 268              | 0.515        |          | 271           | 0.192             |

backbone were observed as doublet and triplet at 7.81, 7.50 and 7.64 ppm, respectively.

The main difference in the $^1$H NMR spectra of compound 2 is the loss of the peaks assigned to the -NH$_2$ group, and new peaks formed due to salicyaldimine group. In the $^1$H NMR spectra of compound 2, the chemical shift observed at 8.55 ppm as a singlet is assigned to the azomethine (-CH=N-) proton. This signal has been calculated as 8.76 ppm for B3LYP. On the other hand, the phenolic -OH proton gives a signal at 12.89 ppm that has been appeared at 12.73 ppm in the theoretical spectra. In addition, the peaks belonging to -H$_{15-19}$ protons shifted to higher field after Schiff base reaction. The remaining protons of compound 2 were observed between 6.94 and 7.86 ppm.

The total count of carbon peaks for compounds 1 and 2 matched well with the composition of the compounds. In the $^{13}$C NMR spectra of compound 1, the carbon peaks belonging to sulphonyl-benzene backbone were observed at 128.59, 129.03, 134.04 and 145.45 ppm, while the carbon peaks belonging to aminobenzene backbone were monitored at 115.37, 123.20, 135.43 and 141.57 ppm. The main difference in the $^{13}$C NMR spectra of compound 2 is due to salicyaldimine group. In the $^{13}$C NMR spectra of compound 2, a group of signals were observed in the region 148.26–123.60 ppm and these correspond to the carbon atoms of the ring in the sulphonyl-benzene backbone. The hydroxyl carbon atom gives a signal at the higher ppm value (161.32 ppm) than the other ring carbon atoms (between 117.51 and 134.60 ppm), while the azomethine carbon appears at 163.71 ppm. These signals have been calculated as 171.87 and 172.26 ppm, respectively. The carbon peaks belonging to aminobenzene backbone were observed in the range 119.21–147.63 ppm.

3.5. Electronic absorption spectra

Tautomeric species of 2-hydroxyaldimine compounds may often characterised by UV-Vis spectroscopy. Many papers show that if there are enol-imine tautomers, an absorption peak belonging to the $\pi \rightarrow \pi^*$ transition of -CH=N- group might be appeared in the range between 300 and 400 nm. On the other hand, if you have a keto-amine tautomer, the absorption peak belonging to the $n \rightarrow \pi^*$ transition of -C=O group is above 400 nm [52,53].

The UV-Vis spectra of compound 2 in dichloromethane, dimethylsulphoxide, methanol and toluene solvents were recorded within the 200–800 nm range, and a representative normalised spectrum is shown in Figure 4. In the UV-Vis spectra of 2, there generally are two main transition bands for all solvents except for methanol. The first (200–320 nm) is attributed to the $\pi \rightarrow \pi^*$ transition of the aromatic rings. The second band in the range of 320 and 400 nm is attributed to the $\pi \rightarrow \pi^*$ transition of the -C=N- group. For methanolic solution, there is a small absorption region between 410 and 470 nm. As a result, enol-imine tautomeric form in all solvents is dominated. However, compound 2 in methanol has a small amount of keto-amine tautomeric form.

Electronic absorption spectra of compound 2 were calculated by the TD-DFT method based on the B3LYP/6-311++G(d,p) level optimised structure in the same solvents using the PCM model. The calculated results are listed in Table 7 along with the experimental absorption spectra data. The theoretical absorption bands predicted in the ranges 270–271, 313–315 and 344–349 nm are in agreement with the recorded spectral data.
4. Conclusions

In this article, 4-aminophenyl benzenesulphonate (1) was obtained from the reaction of 4-aminophenol and benzenesulphonyl chloride in the presence of triethylamine with good yields. Then, (E)-4-[(2-hydroxybenzylidene)amino]phenyl benzenesulphonate (2) was synthesised via Schiff base reaction between compound 1 and salicylaldehyde. The two compounds were stable both in air and moisture and soluble most organic solvents such as DCM, MeOH, DMSO and THF. Different spectroscopic techniques (IR, $^1$H NMR, $^{13}$C NMR and UV-Vis) were used to characterise the compounds. Solid state structure of compound 2 was confirmed by single-crystal X-ray diffraction technique. The corresponding theoretical studies have also been performed employing B3LYP method with the 6–311++G(d,p) basis set, in which solvent effects are analysed through the use of a PCM. Structural, spectroscopic and quantum chemical investigations on compound 2 emphasise that the compound exists in the enol-imine form mainly stabilising by the intramolecular O—H···N hydrogen bond. When the experimental and theoretical spectral data are compared, an acceptable correlation is found between them. The energy difference in the enol-imine and keto-amine tautomers is predicted within the range ca 9–22 kJ mol$^{-1}$. The barrier height for the proton transfer from the enol-imine to keto-amine is found to be ca 20–29 kJ mol$^{-1}$. The barrier height for the proton transfer from the enol-imine to keto-amine is found to be ca 20–29 kJ mol$^{-1}$. The barrier height for the proton transfer from the enol-imine to keto-amine is found to be ca 20–29 kJ mol$^{-1}$. The barrier height for the proton transfer from the enol-imine to keto-amine is found to be ca 20–29 kJ mol$^{-1}$ indicating an unfavoured process with large positive standard enthalpy and free energy changes both in the gas phase and in solution phase. However, very low energy barrier is obtained for the reverse reaction, within the range ca 7–12 kJ mol$^{-1}$. These low barrier energies as well as negative values in enthalpy and free energy changes make the reverse reaction favoured both in the gas phase and in solution phase.

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Disclosure statement

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References

[1] J.A. Bertrand, J.L. Breece and P.G. Eller, Inorg. Chem. 13, 125 (1974).
[2] P.Chellan, N. Shunmoogam-Gounden, D.T. Hendrick, J. Gut, P.J. Rosenthal, C. Lategan, P.J. Smith, K. Chibale and G.S. Smith, Eur. J. Inorg. Chem. 22, 3520 (2010).
[3] K. Manna, T. Zhang, M. Carboni, C.W. Abney and W. Lin, J. Am. Chem. Soc. 136, 13182 (2014).
[4] S. Dayan, N.K. Ozpozan, N. Özdemir and O. Dayan, J. Organomet. Chem. 770, 21 (2014).
[5] K. Dhanunjayarao, V. Mukundam, M. Ramesh and K. Venkatasubbiah, Eur. J. Inorg. Chem. 3, 539 (2014).
[6] H. Dinçalp, S. Yavuz, Ö. Hakl, C. Zafer, C. Özsoy, I. Durucausu and S. İçli, J. Photoch. Photobio. A 210, 8 (2010).
[7] B.V. Kendre, M.G. Landge, S.R. Maujan and S.R. Bhusare, Chem. Biol. Interface 1, 116 (2011).
[8] A. Jiménez-Sánchez, N. Farfán and R. Santillan, J. Phys. Chem C 119, 13814 (2015).
[9] M. Monajjemi, L. Mahdavian, F. Mollaamin and B. Honarparsar, Fuller. Nanotub. Car. N. 18, 45 (2010).
[10] M.D. Cohen, G.M.J. Schmidt and S. Flavian, J. Chem. Soc. 2041 (1964).
[11] J. Bregman, L. Leiserowitz and K. Osaki, J. Chem. Soc. 2086 (1964).
[12] E. Hadjoudis, M. Vittarakis and I. Moustakali-Mavridis, Mol. Cryst. Liq. Cryst. 137, 1 (1986).
[13] I. Moustakali-Mavridis, E. Hadjoudis and A. Mavridis, Acta Crystallogr. B34, 3709 (1978).
[14] E. Hadjoudis, M. Vittarakis and I. Moustakali-Mavridis, Tetrahedron 43, 1345 (1987).
[15] D. Higelin and H. Sixl, Chem. Phys. 77, 391 (1983).
[16] H. Tanak, J. Phys. Chem. A 115, 13865 (2011).
[17] H. Ünver, M. Kabak, D.M. Zengin and T.N. Durlu, J. Chem. Crystallogr. 31, 203 (2001).
[18] Stoe & Cie, X-AREA Version 1.18 and X-RED32 Version 1.04 (Stoe & Cie, Darmstadt, 2002).
[19] G.M. Sheldrick, Acta Crystallogr. A64, 112 (2008).
[20] L.J. Farrugia, J. Appl. Crystallogr. 45, 849 (2012).
[21] A.L. Spek, Acta Crystallogr. D65, 148 (2009).
[22] R. Dennington II, T. Keith and J. Millam, GaussView, Version 4.1.2 (Semichem, Inc., Shawnee Mission, KS, 2007).
[23] M.J. Frisch, G.W. Trucks, H.B. Schlegel, G.E. Scuseria, M.A. Robb, J.R. Cheeseman, J.A. Montgomery Jr., T. Vreven, K.N. Kudin, J.C. Burant, J.M. Millam, S.S. Iyenagar, J. Tomasi, V. Barone, B. Mennucci, M. Cossi, G. Scalmani, N. Rega, G.A. Petersson, H. Nakatsuji, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, M. Klene, X. Li, J.E. Knox, H.P. Hratchian, J.B. Cross, V. Bakken, C. Adamo, J. Jaramillo, R. Gomperts, R.E. Stratmann, O. Yazyev, A.J. Austin, R. Cammi, C. Pomelli, J.W. Ochterski, P.Y. Ayala, K. Morokuma, G.A. Voth, P. Salvador, J.J. Dannenberg, V.G. Zakrzewski, S. Dapprich, A.D. Daniels, M.C. Strain, O. Farkas, D.K. Malick, A.D. Rabuck, K. Raghavachari, J.B. Foresman, J.V. Ortiz, J. Cui, A.G. Baboul, S. Clifford, J. Cioslowski, B.B. Stefanov, G. Liu, A. Liashenko, P. Piskor, I. Komaromi, H. Nakajima, M. Klene, X. Li, J.E. Knox, H.P. Hratchian, J.B. Cross, V. Bakken, C. Adamo, J. Jaramillo, R. Gomperts, R.E. Stratmann, O. Yazyev, A.J. Austin, R. Cammi, C. Pomelli, J.W. Ochterski, P.Y. Ayala, K. Morokuma, G.A. Voth, P. Salvador, J.J. Dannenberg, V.G. Zakrzewski, S. Dapprich, A.D. Daniels, M.C. Strain, O. Farkas, D.K. Malick, A.D. Rabuck, K. Raghavachari, J.B. Foresman, J.V. Ortiz, J. Cui, A.G. Baboul, S. Clifford, J. Cioslowski, B.B. Stefanov, G. Liu, A. Liashenko, P. Piskor, I. Komaromi, R.L. Martin, D.J. Fox, T. Keith, M.A. Al-Laham, C.Y. Peng, A. Nanayakkara, M. Challacombe, P.M.W. Gill, B. Johnson, W. Chen, M.W. Wong, C. Gonzalez and J.A. Pople, Gaussian 03W, Revision E.01 (Gaussian, Inc., Wallingford, CT, 2004).
[24] A.D. Becke, J. Chem. Phys. 98, 5648 (1993).
[25] C. Lee, W. Yang and R.G. Parr, Phys. Rev. B 37, 785 (1988).
[26] R. Krishnan, J.S. Binkley, R. Seeger and J.A. Pople, J. Chem. Phys. 72, 650 (1980).
[27] M.J. Frisch, J.A. Pople and J.S. Binkley, J. Chem. Phys. 80, 3265 (1984).
[28] M.P. Andersson and P. Uvdal, J. Phys. Chem. A 109, 2937 (2005).
[29] R. Ditchfield, J. Chem. Phys. 56, 5688 (1972).
[30] K. Wolinski, J.F. Hinton and P. Pulay, J. Am. Chem. Soc. 112, 8251 (1990).
[31] R. Bauernschmitt and R. Ahlrichs, Chem. Phys. Lett. 256, 454 (1996).
[32] R.E. Stratmann, G.E. Scuseria and M.J. Frisch, J. Chem. Phys. 109, 8218 (1998).
[33] S. Miertuš, E. Scrocco and J. Tomasi, Chem. Phys. 55, 117 (1981).
[34] V. Barone and M. Cossi, J. Phys. Chem. A 102, 1995 (1998).
[35] M. Cossi, N. Rega, G. Scalmani and V. Barone, J. Comput. Chem. 24, 669 (2003).
[36] J. Tomasi, B. Mennucci and R. Cammi, Chem. Rev. 105, 2999 (2005).
[37] F.H. Allen, O. Kennard, D.G. Watson, L. Brammer, A.G. Orpen and R. Taylor, J. Chem. Soc. Perkin Trans. 2, S1 (1987).
[38] D. Kand, P.S. Mandal, T. Saha and P. Talukdar, RSC Advances 4, 59579 (2014).
[39] Y.-N. Shen, L. Lin, H.-Y. Qiu, W.-Y. Zou, Y. Qian and H.-L. Zhu, RSC Advances 5, 23767 (2015).
[40] I. Kaabi, L. Sibous, T. Douadi and S. Chafaa, J. Mol. Struct. 1084, 216 (2015).
[41] K.M. Hutchins, S. Dutta, B.P. Loren and L.R. MacGillivray, Chem. Mater. 26, 3042 (2014).
[42] J. Bernstein, R.E. Davis, L. Shimoni and N.-L. Chang, Angew. Chem. Int. Ed. Engl. 34, 1555 (1995).
[43] G.R. Desiraju and T. Steiner, The Weak Hydrogen Bond in Structural Chemistry and Biology (Oxford University Press, New York, 1999).
[44] L.J. Bellamy, The Infrared Spectra of Complex Molecules (Chapman and Hall, London, 1980), Vol. 2.
[45] S. Maney, W.L. Peticolas and R.S. Tobias, Spectrochim. Acta A 35, 315 (1979).
[46] A. Teimouri, A.N. Cheraghimi, K. Taban and H.A. Dabbagh, Spectrochim. Acta A 72, 369 (2009).
[47] H.A. Dabbagh, A. Teimouri, A.N. Cheraghimi and M. Shahraki, Spectrochim. Acta A 69, 449 (2008).
[48] R.M. Silverstein, G.C. Bassler and T.C. Morill, Spectroscopic Identification of Organic Compounds (Wiley, New York, 1991).
[49] R.M. Silverstein, F.X. Webster and D.J. Kiemle, Spectroscopic Identification of Organic Compounds (Wiley, New York, 2005).
[50] H. Ünver, M. Yıldız, H. Özay and T.N. Durlu, Spectrochim. Acta A 74, 1095 (2009).
[51] Ç. Albayrak, G. Kastaş, M. Odabaşoğlu and R. Frank, Spectrochim. Acta A 81, 72 (2011).
[52] G.O. Dudek and E.P. Dudek, J. Am. Chem. Soc. 88, 2407 (1966).
[53] M. Gavranic, B. Kaitner and E. Meštrovic, J. Chem. Crystallogr. 26, 23 (1996).