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# Theoretical Investigation on Solvent Dependent Shift and Electronic Transition Properties of Certain Schiff Bases

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**Abstract:** Some o-hydroxy Schiff bases and their possible tautomeric structures have been investigated by DFT method (B3LYP/6-311+g(d,p)) and the stable structures have been determined. The UV-Vis spectra of the stable forms of the compounds have been determined and their electronic transition properties, the shifts depending on the solvents and the HOMO-LUMO values have been calculated. The possible molecular electronic properties of the molecules have also determined.

**Keywords:** Solvent effect; Electronic transition; Tautomer, o-hydroxy Schiff base; DFT.

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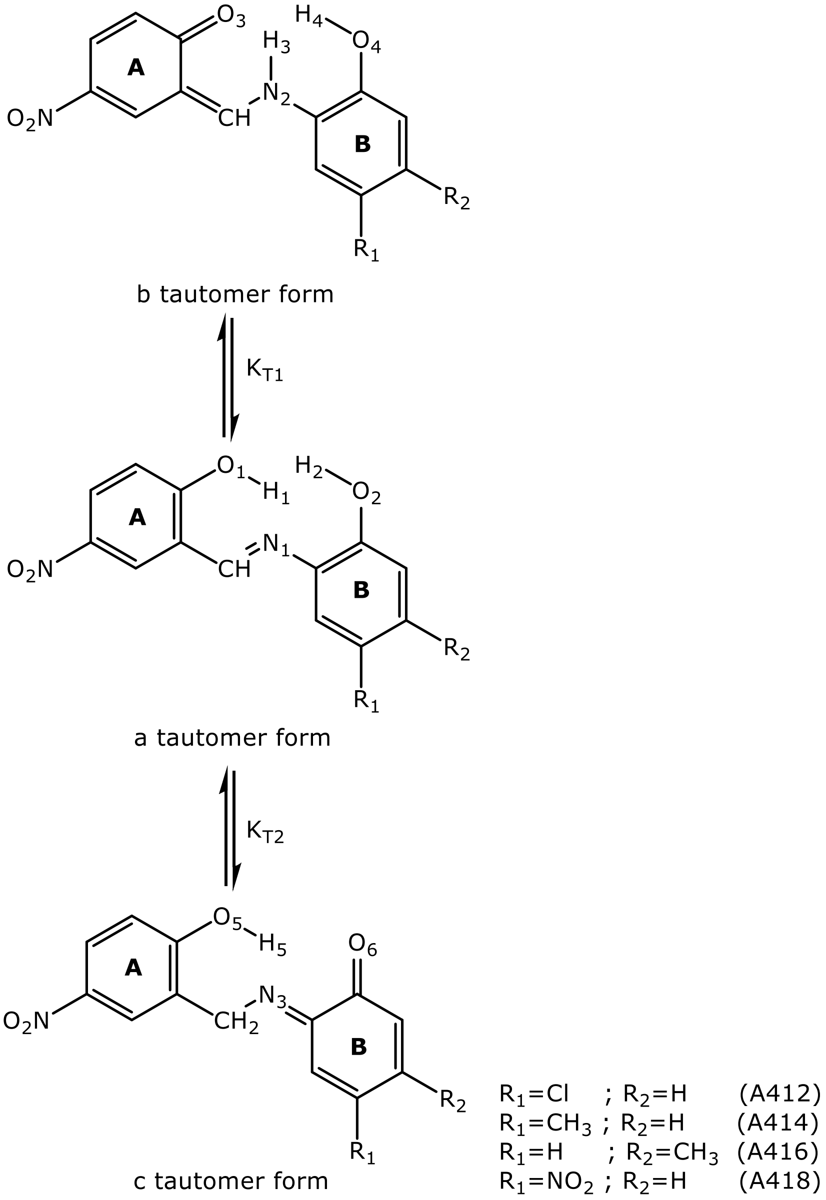
## INTRODUCTION

Schiff bases are a nitrogenous class of organic compounds known as imines or azomethines. Their antibacterial, antifungal, antimalarial, antiinflammatory, antiviral, anticancer, antitumor, anti-tuberculosis and antipyretic properties are attractive for drug design studies (1-7). Their redox and optical properties allow their widespread application for enhancing the sensitivity and selectivity of electrochemical and optical sensors (8, 9). Their complexes with transition metals also allow their usage as catalysts in organic redox and electrochemical reduction reactions (10-12). They have solvatochromic, photochromic and thermochromic properties thanks to their the enol–keto tautomerization and excited state intra-molecular proton transfer (5–9, 13-15). Thus, Schiff bases can be candidates as materials in optoelectronic devices. The π-conjugated Schiff bases have important molecular structures for the development of molecular electronic devices because of their specific electronic structures. Especially, their double bonds cause delocalization of electrons on the molecule and delocalization of electrons via π-bonding gives rise to an increase in the stability of the molecule by lowering its energy. Many Schiff bases including flexible terminal chain exhibits liquid crystalline properties (16-23). Considering the above mentioned applications of the Schiff bases, the investigation of the solvent induced optical properties, HOMO-LUMO and solvatochromic behaviors is needed. Since the solvent is effective for the reorganization of electronic structure of solute, determination of specific interactions (H-bonding donor and H-bonding acceptor interactions) and nonspecific solute–solvent interactions (dipole–dipole and dipole-induced dipole interactions) is crucial to recognize the electronic, chemical and physical properties of the solute molecule in solution phase. In our previous studies, the solvent effect on the electronic absorption bands for certain Schiff bases were investigated for $\pi\rightarrow\pi^*$ and $n\rightarrow\pi^*$ electronic transitions, and specific and non-specific interactions have been analyzed (24-26). In this study, certain theoretical studies have been performed for some o-hydroxy Schiff bases (Figure 1). The compounds and their possible tautomeric structures have been investigated with Gaussian09 program by DFT method (B3LYP/6-311+g(d,p)) (27, 28) in vacuum, chloroform, methyl alcohol, ethyl alcohol, dimethyl sulfoxide, and water phases. The UV-Vis spectra of the stable forms of the compounds have been determined and their electronic transition properties, the shifts depending on the solvents and the HOMO-LUMO values and molecular electrostatic potentials (MEP) have been calculated. The possible molecular electronic properties of the molecules have also determined. To the best of our knowledge, the theoretical study of the Schiff bases have not been encountered in the literature.



$R_1$=Cl ; $R_2$=H (A412)
$R_1$=$CH_3$ ; $R_2$=H (A414)
$R_1$=H ; $R_2$=$CH_3$ (A416)
$R_1$=$NO_2$ ; $R_2$=H (A418)

**Figure 1.** The o-hydroxy Schiff bases and their tautomeric forms.

## MATERIAL AND METHODS

### Theoretical Calculations

CS ChemBioDraw Ultra 12.0 for Microsoft Windows (29), Gaussian09 (30), GaussView 5.0.9 (31) programs and an Intel(R) Core(TM) i7 X 990, 3.33 GHz, L3 Cache 12 MB, LGA 1366 socket, X58 chipset workstation were used for the theoretical calculations. Stable geometries of all the compounds were determined with "opt=modredundant B3LYP/6-311+g(d,p)" method. Firstly, the stable conformation of each molecule was determined by the basis of –CH=N- group. Then, the geometry of the compound having the most stable conformation was determined by changing the geometries of the substituents on **A** and **B** rings. The theoretical calculations were done by considering the geometries of the determined most stable conformations. The thermodynamic calculations and the electronic absorption spectra were done by "freq B3LYP/6-

311+g(d,p)” and DFT (TD-DFT B3LYP/6-311+g(2d,2p)) scrf=(iefpcm, solvent) methods, respectively. Chloroform, methyl alcohol, ethyl alcohol, dimethyl sulfoxide and water were used for the solvent phase calculations.

## RESULTS AND DISCUSSION

### Energies and Tautomeric Equilibrium

The calculations for the compounds and the tautomeric forms given in Figure 1 have been performed by freq B3LYP/6-311+g(d,p) method in vacuum and different solvent phases. By default, the calculations are done using 1 atm standard state. Since, the number of moles of products and reactants in tautomeric equilibrium are the same for solvent phases, the correction term will be zero and it makes no difference in the calculated energies.

The calculated Sum of Electronic and Thermal Free Energies (SETFE) have been shown in Table 1. The tautomeric equilibrium constants ($K_T$) have been calculated for $a \rightleftharpoons b$ and $a \rightleftharpoons c$ tautomeric forms by using equation 1, 2 and Sum of the Electronic and Thermal Free Energies (Table 2).

$$K_T = G_{(b)} - G_{(a)} \qquad \text{(Eq. 1)}$$

$$K_T = G_{(c)} - G_{(a)} \qquad \text{(Eq. 2)}$$

**Table 1.** The energies* of the Schiff bases derivatives and their tautomeric forms (298 K).

| Compounds | Vacuum kcal/mol | Chloroform kcal/mol | Ethyl alcohol kcal/mol | Methyl alcohol kcal/mol | Dimethyl sulfoxide kcal/mol | Water kcal/mol |
|---|---|---|---|---|---|---|
| **A412a** | -860376.849 | -860391.261 | -860395.296 | -860396.170 | -860395.524 | -860395.741 |
| **A412b** | -860372.345 | -860382.030 | -860384.550 | -860384.696 | -860384.839 | -860384.971 |
| **A412c** | -860345.879 | -860356.987 | -860359.958 | -860360.133 | -860360.305 | -860360.464 |
| **A414a** | -596621.620 | -596629.985 | -596632.108 | -596632.231 | -596632.350 | -596632.461 |
| **A414b** | -596621.968 | -596630.819 | -596633.498 | -596633.654 | -596633.806 | -596633.948 |
| **A414c** | -596593.735 | -596605.075 | -596608.131 | -596608.311 | -596608.487 | -596608.650 |
| **A416a** | -596622.216 | -596632.206 | -596634.262 | -596634.382 | -596634.499 | -596634.608 |
| **A416b** | -596623.465 | -596635.984 | -596639.527 | -596639.749 | -596639.972 | -596640.183 |
| **A416c** | -596593.922 | -596635.984 | -596608.827 | -596609.028 | -596609.226 | -596609.413 |
| **A418a** | -700281.188 | -700292.674 | -700295.642 | -700295.814 | -700295.982 | -700296.137 |
| **A418b** | -700279.377 | -700290.752 | -700294.127 | -700294.323 | -700294.515 | -700294.693 |
| **A418c** | -700245.502 | -700258.719 | -700262.259 | -700262.468 | -700262.673 | -700262.863 |

*SETFE (Sum of Electronic and Thermal Free Energies).

It is observed that the stability order is **A412**; **A418**; **A416** and **A414** molecules (Table 1). It is thought that the electronic effects of $R_1$ and $R_2$ groups, and the substitutuents changing the geometries of the molecules can determine the stability order. The -Cl substituent withdraws inductively electron as and pushes as mesomeric on $R_1$ position for A412 molecule. The net electronic effect is electronic withdrawing effect for the molecule ($\sigma$: substituent constant, $\sigma_m$=0.37; $\sigma_p$=0.23). $-NO_2$ substituent has a withdrawing effect as both inductive and mesomeric for **A418** molecule on $R_2$ position ($\sigma_m$=0.71; $\sigma_p$=0.78). For **A416** ($R_1$=$CH_3$) and **A414** ($R_2$=$CH_3$) compounds, there are inductively electronic withdrawing effect thanks to the $-CH_3$ group ($\sigma_m$=-0.07; $\sigma_p$=-0.17) (32). These effects explain that **A412** and **A418** compounds are more stable than the others, and the stabilities for **A416** and **A414** are close each other. The tautomeric forms of the compounds have been similarly affected with the concerned Schiff base from the electronic effects. a, b and c tautomeric forms having the similar substituent show the same trend like the Schiff bases (Table 2).

**Table 2.** Tautomeric equilibrium constants ($K_T$)* for all the compounds (298 K).

| **Vacuum** | | **Chloroform** | | **Ethyl alcohol** | | **Methyl alcohol** | | **Dimethyl sulfoxide** | | **Water** | |
|---|---|---|---|---|---|---|---|---|---|---|---|
| **$K_{T1}$** | | | | | | | | | | | |
| **A412a-A412b** | 4.504 | **A412a-A412b** | 9.231 | **A412a-A412b** | 10.746 | **A412a-A412b** | 11.475 | **A412a-A412b** | 10.685 | **A412a-A412b** | 10.771 |
| **A414a-A414b** | -0.348 | **A414a-A414b** | -0.834 | **A414a-A414b** | -1.389 | **A414a-A414b** | -1.423 | **A414a-A414b** | -1.4568 | **A414a-A414b** | -1.487 |
| **A416a-A416b** | -1.249 | **A416a-A416b** | -3.778 | **A416a-A416b** | -5.265 | **A416a-A416b** | -5.368 | **A416a-A416b** | -5.473 | **A416a-A416b** | -5.575 |
| **A418a-A418b** | 1.811 | **A418a-A418b** | 1.922 | **A418a-A418b** | 1.515 | **A418a-A418b** | 1.491 | **A418a-A418b** | 1.467 | **A418a-A418b** | 1.444 |
| **$K_{T2}$** | | | | | | | | | | | |
| **A412a-A412c** | 30.970 | **A412a-A412c** | 34.274 | **A412a-A412c** | 35.337 | **A412a-A412c** | 36.037 | **A412a-A412c** | 35.219 | **A412a-A412c** | 35.277 |
| **A414a-A414c** | 27.885 | **A414a-A414c** | 24.910 | **A414a-A414c** | 23.978 | **A414a-A414c** | 23.920 | **A414a-A414c** | 23.863 | **A414a-A414c** | 23.811 |
| **A416a-A416c** | 28.294 | **A416a-A416c** | 26.639 | **A416a-A416c** | 25.435 | **A416a-A416c** | 25.354 | **A416a-A416c** | 25.273 | **A416a-A416c** | 25.194 |
| **A418a-A418c** | 35.685 | **A418a-A418c** | 33.955 | **A418a-A418c** | 33.383 | **A418a-A418c** | 33.346 | **A418a-A418c** | 33.309 | **A418a-A418c** | 33.274 |

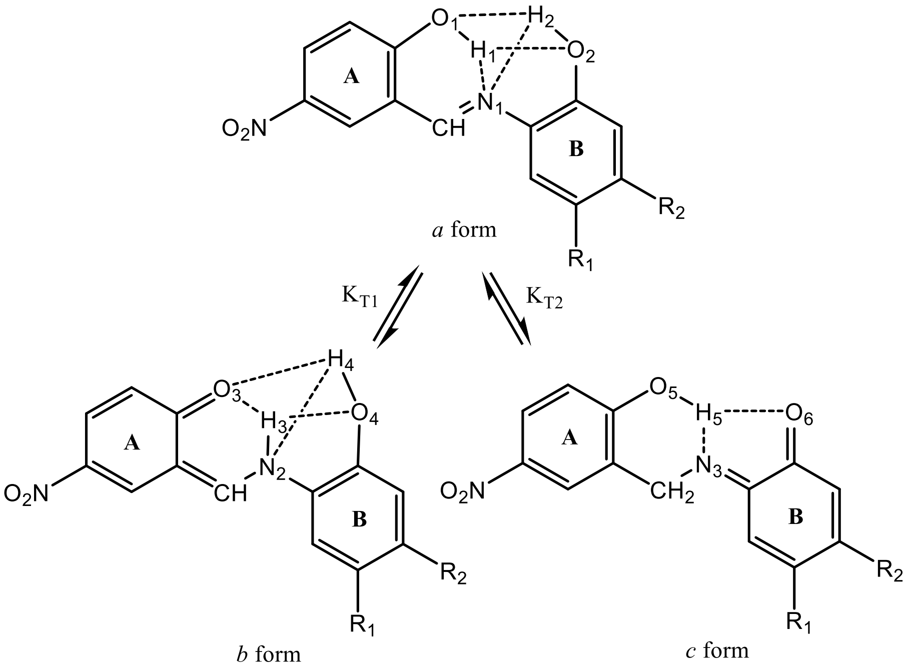
*$K_T = G_{(b,c)} - G_{(a)}$

As seen in Table 2, it is observed that a-b tautomeric equilibrium ($K_{T1}$) is more probable than a-c tautomeric equilibrium ($K_{T2}$). It supports a-b tautomeric equilibrium ($K_{T1}$) is more likely. Although the equilibrium constants belonging to **A412a-A412b** and **A418a-A418b** are different in different solvents, the equilibrium directions are through a tautomeric form, means a tautomeric form is more stable than b form for both molecules. For **A414a-A414b** and **A416a-A416b**, b tautomeric forms are more stable than a forms (Table 2). It is understood that these trends can be sourced from conformations of the molecules.

### The H-bond lengths of the compounds and their tautomeric forms

The other factor affecting the stability of the compounds is intramolecular H-bond in addition to electronic, stability and tautomeric equilibrium effects of the substituent. The intramolecular H-bond lenghts have been given in Table 3.

**Table 3.** H-bond lengths (Å) for the compounds and tautomeric forms in vacuum phase at 298 K.



| Compounds | a form | | | | b form | | | | c form | |
|---|---|---|---|---|---|---|---|---|---|---|
| | H1-N1 | H1-O2 | H2-N1 | H2-O1 | H3-O3 | H3-O4 | H4-O3 | H4-N2 | H5-N3 | H5-O6 |
| **A412** | 1.721 | 3.088 | 2.285 | 3.033 | 1.433 | 2.507 | 2.363 | 2.523 | 1.804 | 2.760 |
| **A414** | 1.707 | 3.067 | 2.291 | 3.011 | 1.614 | 2.597 | 2.724 | 2.453 | 1.775 | 2.731 |
| **A416** | 1.709 | 3.060 | 2.283 | 3.004 | 1.481 | 2.513 | 2.425 | 2.517 | 1.785 | 2.737 |
| **A418** | 2.265 | 3.042 | 1.733 | 3.102 | 1.586 | 2.578 | 2.633 | 2.438 | 1.837 | 2.801 |

As seen from Table 3, when the H-bond for the Schiff bases and their tautomeric forms are compared, the shortest (the strongest) bond is between **H1-N1** atoms for **A412, A414** and **A416** molecules for a tautomeric forms. The shortest one for **A416** a form is between **H2-N1** atoms**.** For b tautomeric forms, the shortest H-bond is between **H3-O3** atoms and. The H-bond is the shortest between **H5-N3** atoms for c tautomeric forms. It can also be thought that the intramolecular H-bond and all the tautomeric forms (a, b and c) affect the stabilities of the molecules. Any molecule changes geometry and becomes more stable thanks to the strength intramolecular H-bond (short H-bond). Thus, the energy of the molecule is lower (Table 1).

### The Dipole moments of the compounds and their tautomeric forms

The charge distrubutions (polarization) of the molecules are different from each other because of the different electronic effects and geometries depending on substituents. The calculated dipole moments of the Schiff bases and their tautomeric forms have been given in Table 4.

**Table 4.** The dipole moments (Debye) of the Schiff bases and the tautomeric forms in vacuum phase at 298 K.

| Compounds | a form | b form | c form |
|---|---|---|---|
| **A412** | 3.332 | 4.804 | 7.972 |
| **A414** | 4.595 | 7.097 | 10.271 |
| **A416** | 4.910 | 11.120 | 10.198 |
| **A418** | 4.961 | 4.855 | 6.275 |

As seen in Table 4, all the molecules have high dipole moments. The dipole moments of the compounds on a form are the lowest among all the tautomeric forms. This means that the charge on the tautomeric forms does not polarize too much. The charges on b and c forms polarize differently. Thus, the molecules having the higher dipole moment can dissolve easily in the solvents having the more strength H-bond and/or the more strength dipole-dipole attraction and similar dipole moment.

### HOMO-LUMO energy and MEP of the compounds

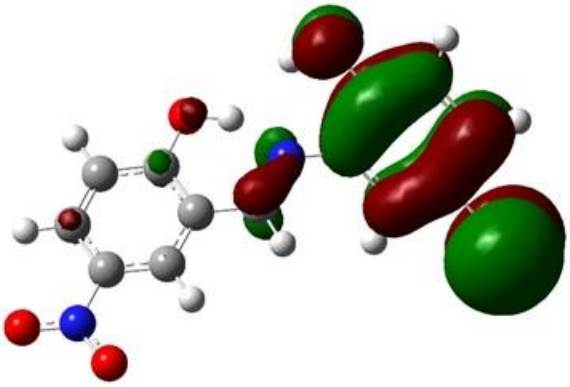
The HOMO, LUMO and the gap energies ($E_{GAP}$) have been calculated for a form in vacuum (B3LYP/6-311+g(d,p)). The HOMO, LUMO, and $E_{GAP}$ values, calculated from Equation 3, are given in Table 5. The corresponding HOMO-LUMO plots are shown in Figure 2.

$$E_{GAP} = LUMO - HOMO \quad (3)$$

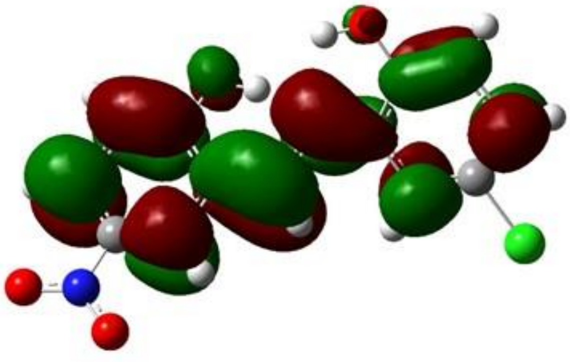
**Table 5.** The typical HOMO-LUMO energy of the compounds in vacuum phase.

| Compounds | HOMO (eV) | LUMO (eV) | $E_{GAP}$ (eV) |
|---|---|---|---|
| **A412a** | -8.033 | -5.902 | 2.131 |
| **A414a** | -8.593 | -5.902 | 2.691 |
| **A416a** | -8.610 | -5.886 | 2.724 |
| **A418a** | -8.547 | -6.055 | 2.493 |

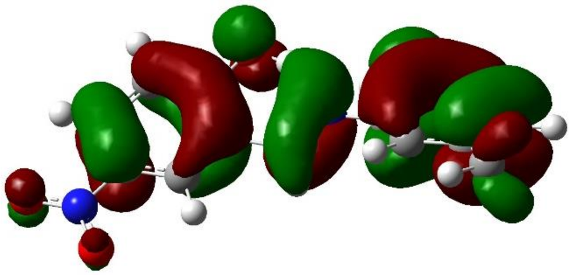
As seen in Table 5, the calculated $E_{GAP}$ are between 2.1 and 2.7 eV. The values show that the molecules have conductive properties (17, 32).



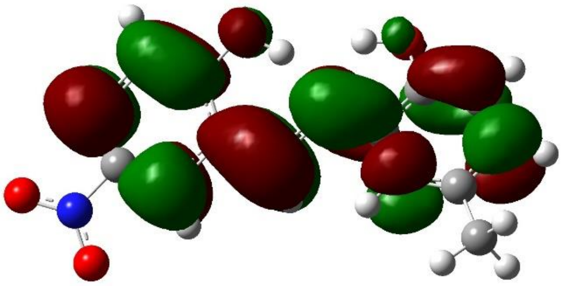
**A412a-HOMO**



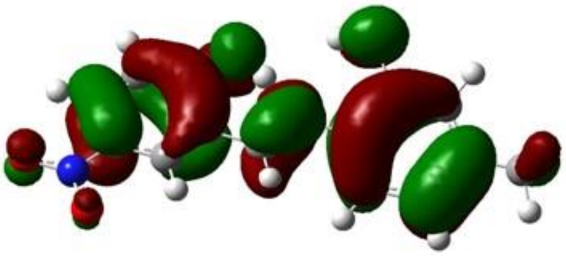
**A412a-LUMO**



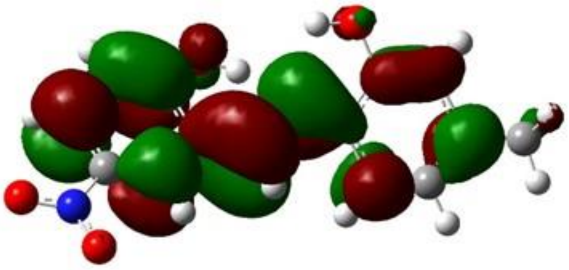
**A414a-HOMO**



**A414a-LUMO**



**A416a-g-homo**



**A416a-g-lumo**

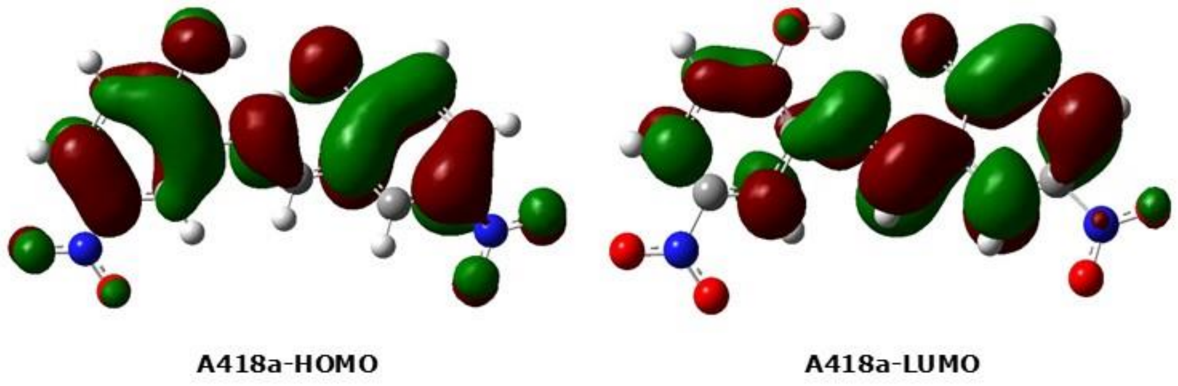


**Figure 2.** The typical HOMO and LUMO shapes of the a form in vacuum phase.

It can be seen that the HOMO and LUMO electrons condense on the aromatic ring in general for **A414a-A18a**. The electrons condense on the ring where –Cl substituent presents in HOMO shape and on the both aromatic rings in LUMO shape for **A412a**.

The calculated molecular electrostatic potential map (MEP) have been given in Figure 3.

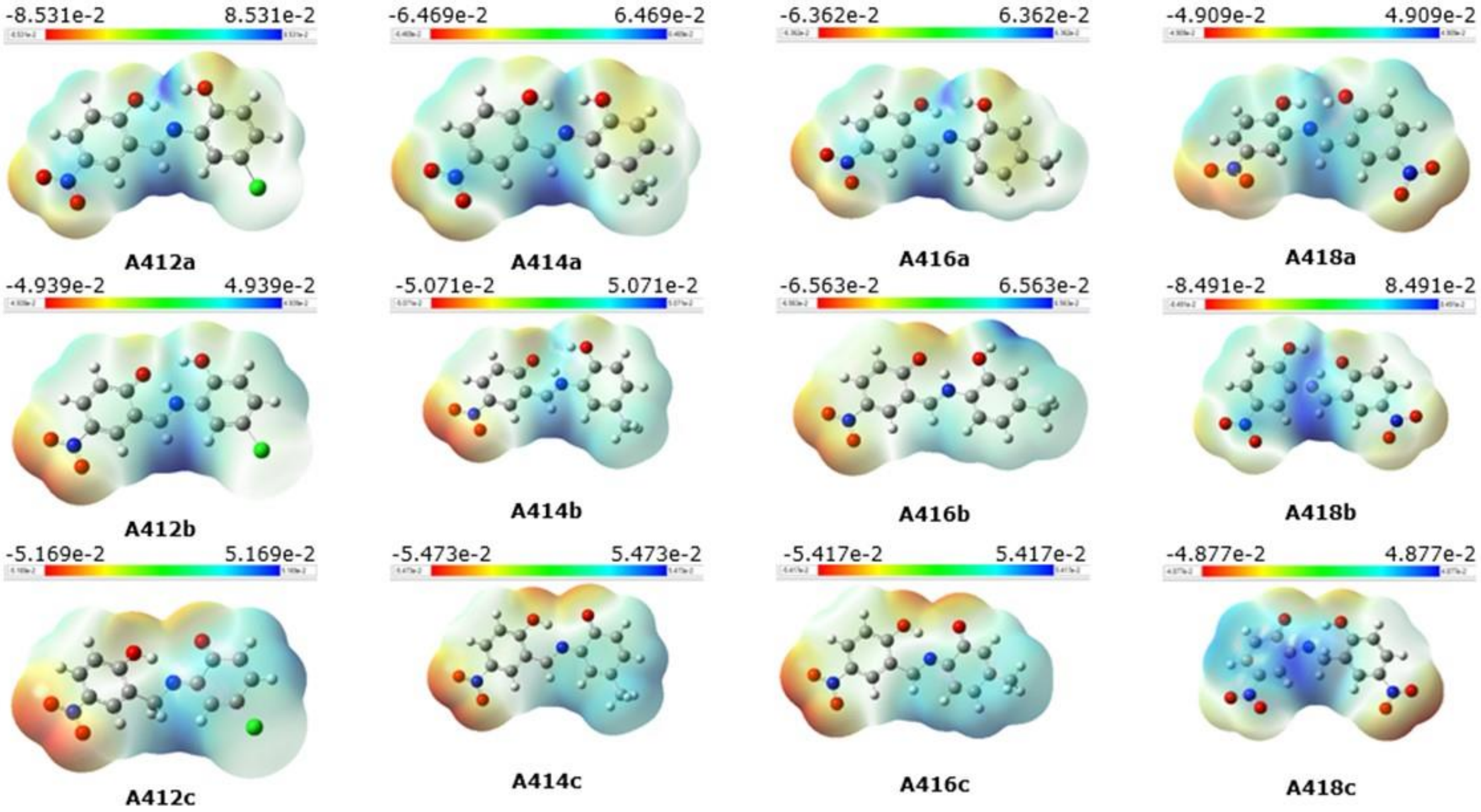


**Figure 3.** B3LYP /6-311+g(d,p) calculated molecular electrostatic potentials (MEP)*.
*Red and blue colors represent electron efficient and deficient centers, respectively.

Molecular electrostatic potential (MEP) mapped onto a molecular surface can provide further insights into the nature of intermolecular interactions. This utilizes the calculated MEP surfaces around the molecule, where the potential maxima and minima correspond to hydrogen bond donor and acceptor sites, respectively. It means MEP is a descriptor for determining negative and positive regions of a molecule (33). In Figure 3, red and blue colors show positively and negatively charged centers on the MEP, respectively. The blue and red zones represent nucleophilic and electrophilic reaction center, respectively. It is seen that the electron-withdrawing substituents (-$NO_2$, C=O and -OH) on aromatic rings present on the red zone and the nitrogen atom present on the blue zone (Figure 3).

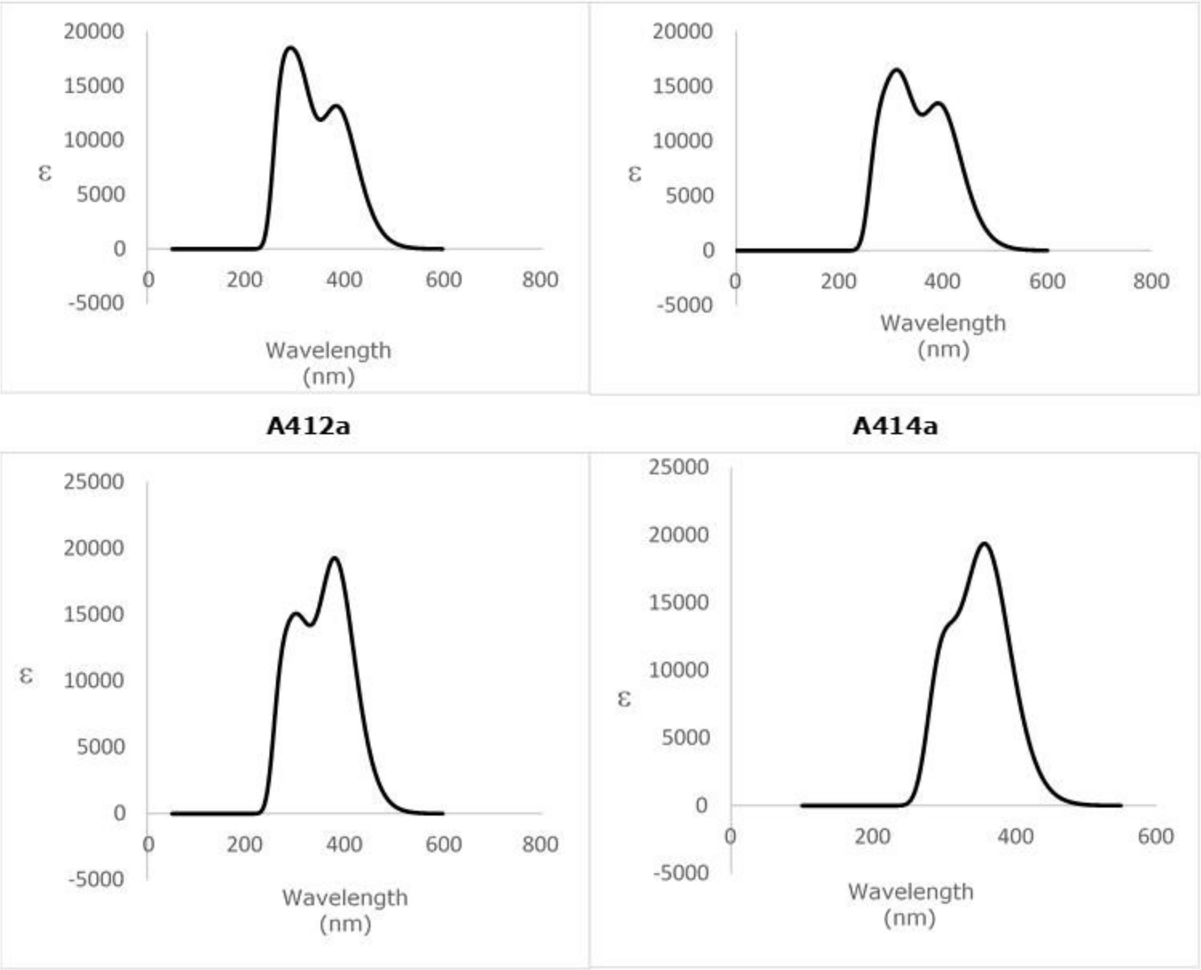
## The excitation energies of the compounds

The excitation energies of the *a* forms of the compounds were calculated in vacuum and five solvents (chloroform, ethyl alcohol, methyl alcohol, dimethyl sulfoxide, and water). The calculated electronic transition spectra of the compounds are given in Figure 4 and the related $\lambda_{max}$ values are tabulated in Table 6.

**Table 6.** The excitation energies of the *a* forms of the compounds in vacuum and different solvents (298 K)

| Solvent/Vacuum | Excitation energies (nm) | | | | | |
|---|---|---|---|---|---|---|
| | $\lambda_1$ | $\lambda_2$ | $\lambda_3$ | $\lambda_1$ | $\lambda_2$ | $\lambda_3$ |
| | **A412a** | | | **A414a** | | |
| **Vacuum** | 392.07 | | 269.56 | 396.74 | | 229.09 |
| **Chloroform** | 387.01 | 312.54 | | 399.43 | 317.40 | 282.25 |
| **Ethyl alcohol** | 382.81 | 315.98 | 270.15 | 396.25 | 328.23 | 270.85 |
| **Methyl alcohol** | 382.20 | 315.99 | 270.03 | 395.67 | 320.14 | 286.07 |
| **Dimethyl sulfoxide** | 383.15 | 275.06 | 227.42 | 396.76 | 328.42 | 271.04 |
| **Water** | 381.92 | 316.47 | 270.07 | 395.50 | 327.88 | |
| | **A416a** | | | **A418a** | | |
| **Vacuum** | 385.61 | 300.28 | | 364.75 | 396.20 | |
| **Chloroform** | 389.77 | 318.53 | 271.21 | 353.62 | | |
| **Ethyl alcohol** | 386.76 | 321.27 | 271.18 | 353.48 | | |
| **Methyl alcohol** | 386.12 | 321.12 | 271.09 | 353.10 | | |
| **Dimethyl sulfoxide** | 387.43 | 322.26 | 271.34 | 354.08 | | |
| **Water** | 386.01 | 321.55 | 271.12 | 353.13 | | |

The common observed peak was $\lambda_1$ peak for the all compounds. $\lambda_1$, $\lambda_2$ and $\lambda_3$ represent n-$\pi^*$ transition on nitrogen atoms, n-$\pi^*$ transition on oxygen atoms, and $\pi$-$\pi^*$ transition on imine and aromatic rings, respectively. However, it is observed that certain peaks are not seen because the other peaks cover the peaks. This can be sourced from solvent-solute interaction. The electronic transition spectra of the peaks given in Table 6 have been given in Figure 4.



**A412a** **A414a**

**A416a** **A418a**

**Figure 4.** The typical theoretical UV-Vis electronic transition spectra for the **a** tautomeric forms of the compounds in vacuum phase (298 K).

To determine whether the electronic excitations of the compounds show a shift depending on the solvent, Equation 4 was used. The vacuum wavelength as a comparison wavelength was used in Equation 4. The calculated shift values depending on the solvent ($\Delta\lambda$, nm) have been given in Table 7.

$$\text{Shift, depending on the solvent } (\Delta\lambda, \text{nm}) = \lambda_{\text{vacuum}} - \lambda_{\text{solvent}} \qquad (4)$$

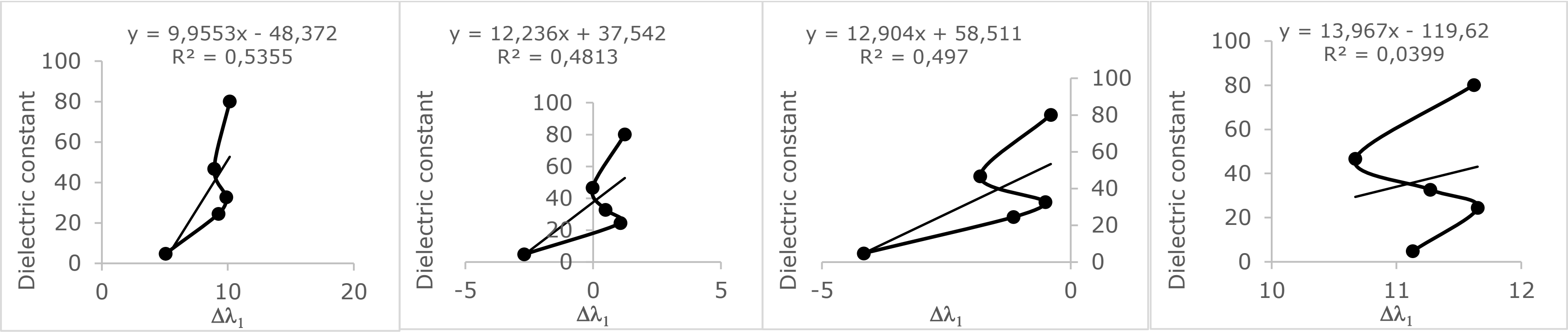
**Table 7.** The UV-Vis shifts depending on the solvent for tautomers of the molecules in different solvents.

| **Solvent** | **$\Delta\lambda_1$*** | **$\Delta\lambda_2$*** | **$\Delta\lambda_3$*** | **Dielectric Constants (at 25 °C)**** |
|---|---|---|---|---|
| **A412a** | | | | |
| **Chloroform** | 5.06 | | | 4.8 |
| **Ethyl alcohol** | 9.26 | | -0.59 | 25.0 |
| **Methyl alcohol** | 9.87 | | -0.47 | 33.0 |
| **Dimethyl sulfoxide** | 8.92 | | 42.14 | 47.0 |
| **Water** | 10.15 | | -0.51 | 79.0 |
| **A414a** | | | | |
| **Chloroform** | -2.69 | | -53.16 | 4.8 |
| **Ethyl alcohol** | 0.49 | | -41.76 | 25.0 |
| **Methyl alcohol** | 1.07 | | -56.98 | 33.0 |
| **Dimethyl sulfoxide** | -0.02 | | -41.95 | 47.0 |
| **Water** | 1.24 | | | 79.0 |
| **A416a** | | | | |
| **Chloroform** | -4.16 | -18.25 | | 4.8 |
| **Ethyl alcohol** | -1.15 | -20.99 | | 25.0 |
| **Methyl alcohol** | -0.51 | -20.84 | | 33.0 |
| **Dimethyl sulfoxide** | -1.82 | -21.98 | | 47.0 |
| **Water** | -0.40 | -21.27 | | 79.0 |
| **A418a** | | | | |
| **Chloroform** | 11.13 | | | 4.8 |
| **Ethyl alcohol** | 11.27 | | | 25.0 |
| **Methyl alcohol** | 11.65 | | | 33.0 |
| **Dimethyl sulfoxide** | 10.67 | | | 47.0 |
| **Water** | 11.62 | | | 79.0 |

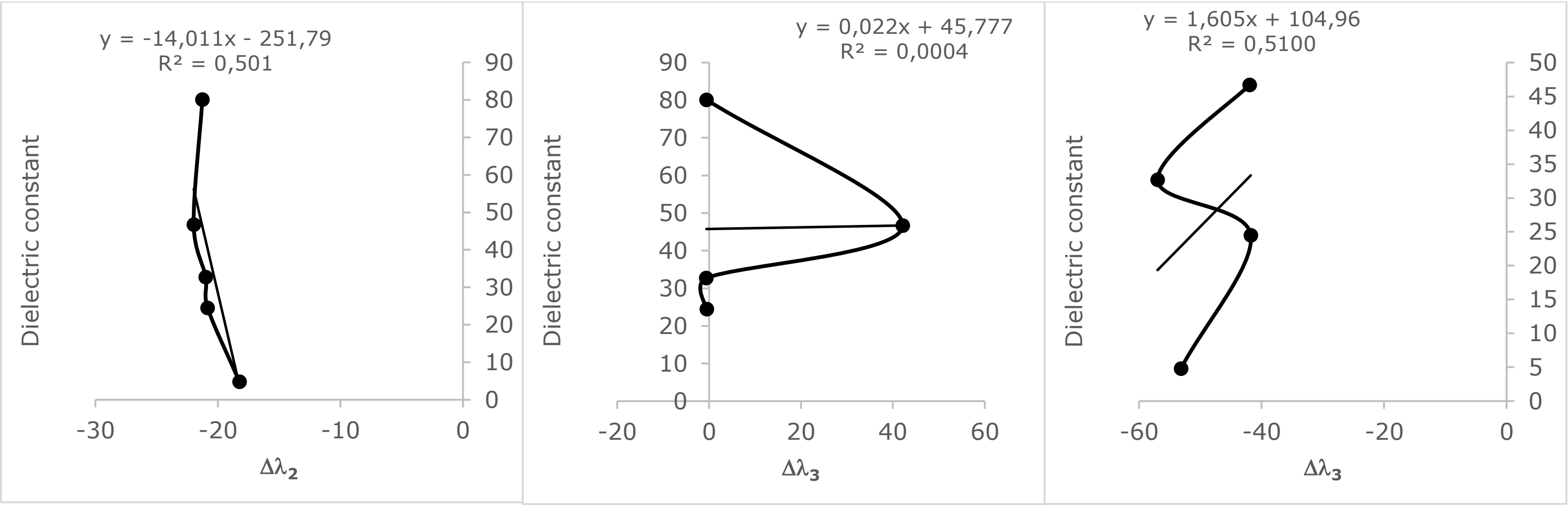
*Shift depending on the solvent ($\lambda$, nm) = $\lambda_{vacuum}$- $\lambda_{solvent}$, ** (34, 35)

The maximum electronic shift ($\Delta\lambda_1$) has been observed for **A418a** and **A412a**. The minimum electronic shift was observed for **A414a** and **A416a**. These can be sourced from **A418a** and **A412a** have strong solvent-solute interaction, on the contrary **A414a** and **A416a** have weak solvent-solute interaction. The shift, $\Delta\lambda_2$, was observed in only **A416a.** All of the compounds have $\Delta\lambda_1$ value. It can be thought that the excitation belonging to the $\lambda_1$ is related with the strong solvent-solute interaction. The maximum electronic shift ($\Delta\lambda_3$) and minimum electronic shift ($\Delta\lambda_3$) were observed for **A414a** and **A412a**, respectively.

The changes versus the shift depending on the solvent ($\Delta\lambda$, nm) and dielectric constant have been given in Figure 5.



**A412a** **A414a** **A416a** **A418a**



**A416a** **A412a** **A418a**

**Figure 5.** The changes versus the shift depending on the solvent (Δλ, nm) and dielectric constant.

A meaningful correlation was not observed between the shift depending on the solvent and dielectric constant (Figure 5).

## CONCLUSION

Some o-hydroxy Schiff bases and their possible tautomeric structures have been investigated with Gaussian09 program by DFT method (B3LYP/6-311+g(d,p)) in vacuum, chloroform, methyl alcohol, ethyl alcohol, dimethyl sulfoxide, and water phases. It is observed that the stability order is **A412**; **A418**; **A416** and **A414** molecules. a-b tautomeric equilibrium ($K_{T1}$) is more probable than *a-c* tautomeric equilibrium ($K_{T2}$). The shortest (the strongest) H-bond is between **H1** and **N1** atoms for **A412**, **A414** and **A416** molecules for *a* tautomeric forms. The shortest one for **A416** a form is between **H2** and **N1** atoms**.** For b tautomeric forms, the shortest H-bond is between **H3** and **O3** atoms. The H-bond is the shortest between **H5** and **N3** atoms for c tautomeric forms. All the molecules have high dipole moments. The dipole moments of the compounds on a form are the lowest among all the tautomeric forms. The calculated $E_{GAP}$ are between 2.1 and 2.7 eV for all of the molecules. The values show that the molecules have conductive properties. The electron-withdrawing substituents (-$NO_2$ and oxygen (C=O and -OH)) present on aromatic ring on the red zone of MEP and the nitrogen atom presents on the blue zone onto MEP. The common observed peak was $\lambda_1$ peak for the all compounds. The maximum electronic shift ($\Delta\lambda_1$) has been observed for **A418a** and **A412a**. The minimum electronic shift was observed for **A414a** and **A416a**. A meaningful correlation was not observed between the shift depending on the solvent and dielectric constant.

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