Theoretical Study on the Stability, Acidity Constants and Molecular Electronic Properties of Certain o-Hydroxy Schiff Bases and their Tautomers

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Abstract: In the present work, certain novel o-hydroxy Schiff bases and possible tautomer forms, which were previously synthesized by our group and their structures elucidated, have been calculated by DFT/6-311g(2d,2p) in both vacuum and polar solvents and the most stable tautomeric forms have been determined. The acidity constants of the Schiff bases have been calculated with PM6 method by MOPAC2016. HOMO-LUMO values of the studied Schiff bases were calculated with DFT/6-311g(2d,2p) and their possible molecular electronic properties were searched. The results were compared with those experimental values.

Keywords: Tautomers, o-hydroxy Schiff bases, Molecular electronic properties, MOPAC2016, DFT.

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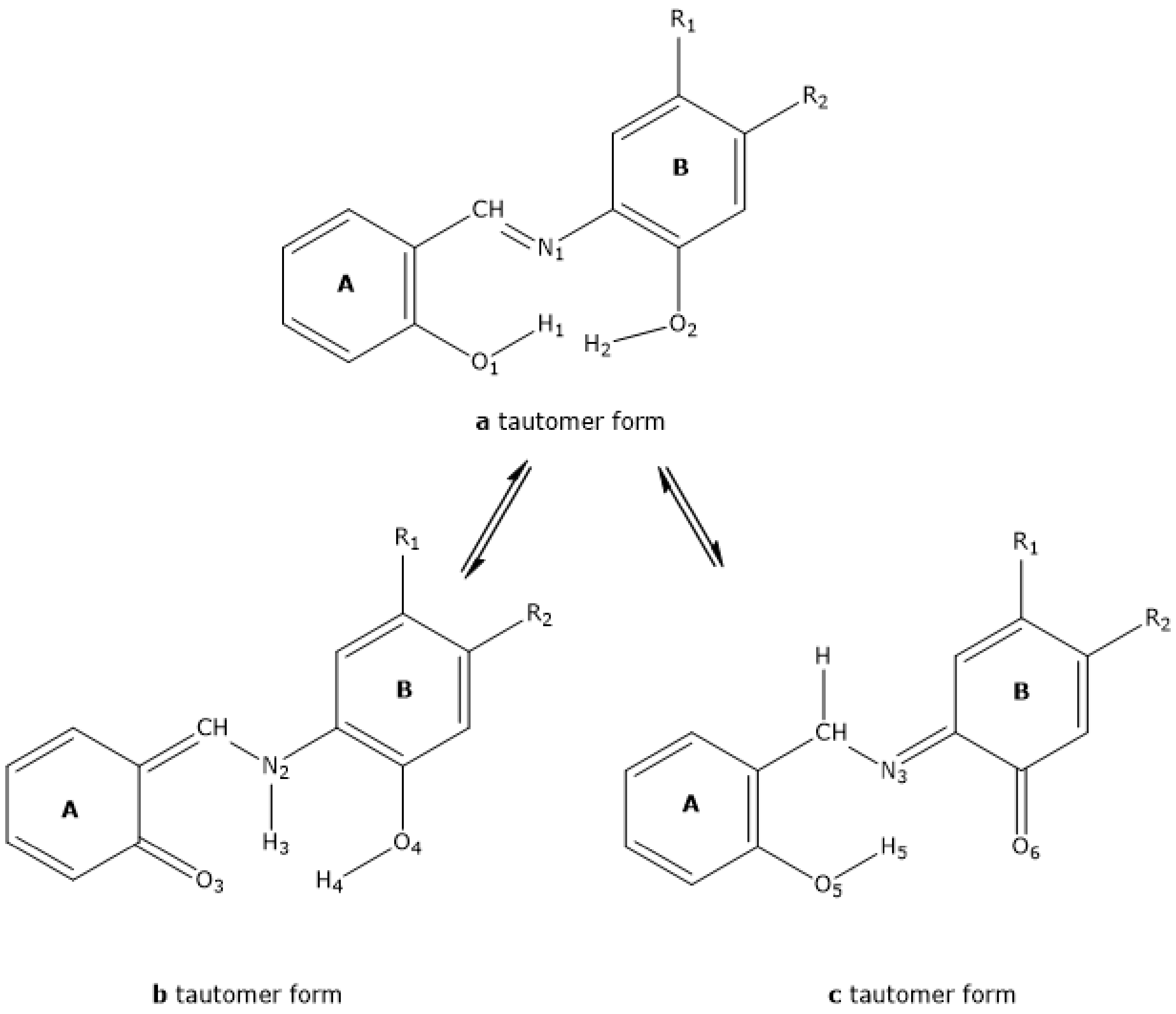
INTRODUCTION

Schiff bases are compounds containing an azomethine (-C=N-) group having biological activity (1, 2). Their anticancer, antiamoebic, antibacterial, antifungal, antinociceptive, antiviral, antidepressant, anti inflammatory and anti-HIV activity have been reported (3-9). An activity study has also been reported against tuberculosis (10). Schiff bases are important in many areas such as non-linear optics (NLOs) (11), optical limiting switching (12), electrochemical sensor technology (13), polymer technology (14) and medicine (15). Schiff bases have been widely used as ligand thanks to the high stability of their coordination compounds with different oxidation states and exhibiting unusual structural properties of their complexes (1). The pi system of a Schiff base affects both the electronic structure of complexes and geometric construction. Transition metal Schiff base complexes have been studied as catalysts in organic redox and electrochemical reduction reactions (16). Especially, Schiff bases derived from aromatic o-hydroxyaldehydes have received special attention due to their interesting thermochromism and/or photochromism, biological properties and variety of potential applications (17). For these reasons, the theoretical study on the stability, acidity constants and molecular electronic properties of o-hydroxy Schiff bases and their tautomers have big importance for determining the behavior of compounds. There are certain studies about spectroscopic and theoretical investigation of these compounds (5, 18-20).

The aim of the present study was to perform theoretical calculations (HOMO-LUMO, possible molecular electronic properties, *etc*) of novel o-hydroxy Schiff bases which were synthesized by our group (21) and their possible tautomer forms (Figure 1) by DFT/6-311g(2d,2p) (22, 23) in both vacuum and polar solvent, and determine acidity constants of them with PM6 method by MOPAC2016 (24). To the best of our knowledge, no theoretical study on o-hydroxy Schiff bases synthesized earlier by our group and their tautomeric forms exists.



R_1=Cl, R_2=H (**A1**); R_1=CH_3, R_2=H (**A2**); R_1=H, R_2=Cl (**A3**); R_1=H, R_2=CH_3 (**A4**)

Figure 1. The studied Schiff bases and their possible tautomer forms.

MATERIAL AND METHODS

Theoretical Calculations

CS ChemBioDraw Ultra 12.0 for Microsoft Windows (25), Gaussian09 (26), GaussView 5.0.9 (27) 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 of the compounds were determined with "opt=modredundant rb3lyp/6-311g(d,p)" method. Thermodynamic calculations and electronic absorption spectra were calculated with "freq rb3lyp/6-311+g(d,p) and DFT (TD-DFT rb3lyp/6-311+g(2d,2p)) scrf=(iefpcm, solvent) methods, respectively. Firstly, stable conformations of –CH=N- bond and tautomer forms belong to this bond were determined during the geometric determination step. Hydroxyl and carbonyl oxygens in **A** and **B** rings of each were determined stable conformation. Theoretical calculations were done by considering the geometries of the determined most stable conformations. Five different solvents have been used in the solvent phase calculations (chloroform, methyl alcohol, ethyl alcohol, dimethyl sulfoxide and water). The acidity constants of all of the compounds were calculated with PM6 method by MOPAC2016 (24).

RESULTS AND DISCUSSION

Sum of Electronic and Thermal Free Energies

The Sum of Electronic and Thermal Free Energies (SETFE) of the studied compounds and their tautomer forms in vacuum and different solvent phases (chloroform, methyl alcohol, ethyl alcohol, dimethyl sulfoxide and water) have been given in Table 1.

Tautomeric Equilibrium

The tautomeric equilibrium constants have been given for the compounds and their possible tautomeric forms in vacuum and different solvent phases (chloroform, methyl alcohol, ethyl alcohol, dimethyl sulfoxide and water) in Table 2.

It is determined that the tautomer form **a** has the most stable form among the whole tautomer forms of the all compounds. It is estimated that **c** form is not possible because of high value of tautomeric constant (K_{T2}) (from 27 to 33) between **a** form **c** form. It is also estimated that the direction of the equilibrium can be from **b** to **a** due to low value of tautomeric constant (K_{T1}) (from 0.2 to 2.9) between **a** form **b** form. The stabilities of the **a** tautomer forms for the studied compounds have been given in Table 3. The order of the stabilities for the compounds in all the solvents are the same except for in chloroform. Tautomer forms, **A2a** and **A4a,** did not comply with the order in chloroform. The stabilities of for the studied compounds and their tautomer forms have been given in Table 4. As seen from Table 4, the tautomer forms, **A3** and **A1,** have the highest stabilites, and **A4** and **A2** have lowest stabilities among the compounds**.** The stabilities are affected from the variation of the molecular geometry resulted from substituent and the bonding position of the molecule.

Table 1. The energies (SETFE*, in kcal/mol) of the studied Schiff bases and their possible tautomer forms (298 K).

Compounds	Vacuum	Chloroform	Ethyl alcohol	Methyl alcohol	Dimethyl sulfoxide	Water
A1a	-732062.483	-732068.519	-732070.015	-732070.100	-732070.183	-732070.261
A1b	-732059.527	-732066.525	-732068.350	-732068.456	-732068.559	-732068.655
A1c	-732028.550	-732037.028	-732039.438	-732039.586	-732039.733	-732039.871
A2a	-468306.256	-468314.042	-468314.962	-468315.033	-468315.104	-468315.169
A2b	-468305.609	-468311.710	-468313.431	-468313.531	-468313.630	-468313.721
A2c	-468275.737	-468285.530	-468285.317	-468285.457	-468285.594	-468285.721
A3a	-732062.537	-732068.704	-732070.265	-732070.355	-732070.443	-732070.524
A3b	-732059.722	-732066.708	-732068.563	-732068.671	-732068.777	-732068.875
A3c	-732028.871	-732037.255	-732039.561	-732039.697	-732039.830	-732039.953
A4a	-468308.830	-468313.694	-468315.099	-468315.179	-468315.259	-468315.332
A4b	-468306.184	-468312.787	-468314.711	-468314.829	-468314.945	-468315.053
A4c	-468275.941	-468284.790	-468287.257	-468287.402	-468287.545	-468287.677

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

The lower SETFE value, the more stable the compound is. In this condition, the activity of the compound decreases.

Table 2. The calculated tautomeric equilibrium constants (K_T) for the compounds and their tautomeric forms.

Reaction	K_T (kcal/mol)	Reaction	K_T (kcal/mol)	Reaction	K_T (kcal/mol)	Reaction	K_T (kcal/mol)
Vacuum							
$A1a \overset{K_{T1}}{\rightleftharpoons} A1b$	2.9562	$A2a \overset{K_{T1}}{\rightleftharpoons} A2b$	0.6476	$A3a \overset{K_{T1}}{\rightleftharpoons} A3b$	2.8150	$A4a \overset{K_{T1}}{\rightleftharpoons} A4b$	2.6456
$A1a \overset{K_{T2}}{\rightleftharpoons} A1c$	33.9329	$A2a \overset{K_{T2}}{\rightleftharpoons} A2c$	30.5192	$A3a \overset{K_{T2}}{\rightleftharpoons} A3c$	33.6668	$A4a \overset{K_{T2}}{\rightleftharpoons} A4c$	32.8887
Chloroform							
$A1a \overset{K_{T1}}{\rightleftharpoons} A1b$	1.9936	$A2a \overset{K_{T1}}{\rightleftharpoons} A2b$	2.3324	$A3a \overset{K_{T1}}{\rightleftharpoons} A3b$	1.9961	$A4a \overset{K_{T1}}{\rightleftharpoons} A4b$	0.9067
$A1a \overset{K_{T2}}{\rightleftharpoons} A1c$	31.4906	$A2a \overset{K_{T2}}{\rightleftharpoons} A2c$	28.5125	$A3a \overset{K_{T2}}{\rightleftharpoons} A3c$	31.4492	$A4a \overset{K_{T2}}{\rightleftharpoons} A4c$	28.9047
Ethyl alcohol							
$A1a \overset{K_{T1}}{\rightleftharpoons} A1b$	1.6648	$A2a \overset{K_{T1}}{\rightleftharpoons} A2b$	1.5317	$A3a \overset{K_{T1}}{\rightleftharpoons} A3b$	1.7018	$A4a \overset{K_{T1}}{\rightleftharpoons} A4b$	0.3872
$A1a \overset{K_{T2}}{\rightleftharpoons} A1c$	30.5763	$A2a \overset{K_{T2}}{\rightleftharpoons} A2c$	29.6451	$A3a \overset{K_{T2}}{\rightleftharpoons} A3c$	30.7043	$A4a \overset{K_{T2}}{\rightleftharpoons} A4c$	27.8417
Methyl alcohol							
$A1a \overset{K_{T1}}{\rightleftharpoons} A1b$	1.6441	$A2a \overset{K_{T1}}{\rightleftharpoons} A2b$	1.5022	$A3a \overset{K_{T1}}{\rightleftharpoons} A3b$	1.6842	$A4a \overset{K_{T1}}{\rightleftharpoons} A4b$	0.3508
$A1a \overset{K_{T2}}{\rightleftharpoons} A1c$	30.5136	$A2a \overset{K_{T2}}{\rightleftharpoons} A2c$	29.5761	$A3a \overset{K_{T2}}{\rightleftharpoons} A3c$	30.6585	$A4a \overset{K_{T2}}{\rightleftharpoons} A4c$	27.7770
Dimethyl sulfoxide							
$A1a \overset{K_{T1}}{\rightleftharpoons} A1b$	1.6240	$A2a \overset{K_{T1}}{\rightleftharpoons} A2b$	1.4740	$A3a \overset{K_{T1}}{\rightleftharpoons} A3b$	1.6660	$A4a \overset{K_{T1}}{\rightleftharpoons} A4b$	0.3138
$A1a \overset{K_{T2}}{\rightleftharpoons} A1c$	30.4502	$A2a \overset{K_{T2}}{\rightleftharpoons} A2c$	29.5096	$A3a \overset{K_{T2}}{\rightleftharpoons} A3c$	30.6134	$A4a \overset{K_{T2}}{\rightleftharpoons} A4c$	27.7137
Water							
$A1a \overset{K_{T1}}{\rightleftharpoons} A1b$	1.6052	$A2a \overset{K_{T1}}{\rightleftharpoons} A2b$	1.4489	$A3a \overset{K_{T1}}{\rightleftharpoons} A3b$	1.6491	$A4a \overset{K_{T1}}{\rightleftharpoons} A4b$	0.2792
$A1a \overset{K_{T2}}{\rightleftharpoons} A1c$	30.3893	$A2a \overset{K_{T2}}{\rightleftharpoons} A2c$	29.4487	$A3a \overset{K_{T2}}{\rightleftharpoons} A3c$	30.5707	$A4a \overset{K_{T2}}{\rightleftharpoons} A4c$	27.6547

$K_T=G_{(a)}-G_{(b,\,c)}$. It is seen that **a** form is more stable than the other form for each equilibrium in Table 2. Negative sign means **a** forms are more stable than the other forms for all equilibria. Lower K_T means more stable for the compounds.

Table 3. The stability order of the possible **a** tautomeric forms.

Compounds	**Vacuum SETFE kcal/mol**	**Compounds**	**Methyl alcohol SETFE kcal/mol**
A3a	-732062.537	**A3a**	-732070.355
A1a	-732062.483	**A1a**	-732070.100
A4a	-468308.830	**A4a**	-468315.179
A2a	-468306.256	**A2a**	-468315.033
Compounds	**Chloroform SETFE kcal/mol**	**Compounds**	**Dimetyl sulfoxide SETFE kcal/mol**
A3a	-732068.704	**A3a**	-732070.443
A1a	-732068.519	**A1a**	-732070.183
A2a	-468314.042	**A4a**	-468315.259
A4a	-468313.694	**A2a**	-468315.104
Compounds	**Ethyl alcohol SETFE kcal/mol**	**Compounds**	**Water SETFE kcal/mol**
A3a	-732070.265	**A3a**	-732070.524
A1a	-732070.015	**A1a**	-732070.261
A4a	-468315.099	**A4a**	-468315.332
A2a	-468314.962	**A2a**	-468315.169

Table 4. Stabilities of the compounds and their all tautomeric forms (**a, b, c**).

Compounds	**Vacuum SETFE kcal/mol**	**Compounds**	**Chloroform SETFE kcal/mol**	**Compounds**	**Ethyl alcohol SETFE kcal/mol**
A3a	-732062.537	**A3a**	-732068.704	**A3a**	-732070.265
A1a	-732062.483	**A1a**	-732068.519	**A1a**	-732070.015
A3b	-732059.722	**A3b**	-732066.708	**A3b**	-732068.563
A1b	-732059.527	**A1b**	-732066.525	**A1b**	-732068.350
A3c	-732028.871	**A3c**	-732037.255	**A3c**	-732039.561
A1c	-732028.550	**A1c**	-732037.028	**A1c**	-732039.438
A4a	-468308.830	**A2a**	-468314.042	**A4a**	-468315.099
A2a	-468306.256	**A4a**	-468313.694	**A2a**	-468314.962
A4b	-468306.184	**A4b**	-468312.787	**A4b**	-468314.711
A2b	-468305.609	**A2b**	-468311.710	**A2b**	-468313.431
A4c	-468275.941	**A2c**	-468285.530	**A4c**	-468287.257
A2c	-468275.737	**A4c**	-468284.790	**A2c**	-468285.317

Compounds	Methyl alcohol SETFE kcal/mol	Compounds	Dimetyl sulfoxide SETFE kcal/mol	Compounds	Water SETFE kcal/mol
A3a	-732070.355	**A3a**	-732070.443	**A3a**	-732070.524
A1a	-732070.100	**A1a**	-732070.183	**A1a**	-732070.261
A3b	-732068.671	**A3b**	-732068.777	**A3b**	-732068.875
A1b	-732068.456	**A1b**	-732068.559	**A1b**	-732068.655
A3c	-732039.697	**A3c**	-732039.830	**A3c**	-732039.953
A1c	-732039.586	**A1c**	-732039.733	**A1c**	-732039.871
A4a	-468315.179	**A4a**	-468315.259	**A4a**	-468315.332
A2a	-468315.033	**A2a**	-468315.104	**A2a**	-468315.169
A4b	-468314.829	**A4b**	-468314.945	**A4b**	-468315.053
A2b	-468313.531	**A2b**	-468313.630	**A2b**	-468313.721
A4c	-468287.402	**A4c**	-468287.545	**A4c**	-468287.677
A2c	-468285.457	**A2c**	-468285.594	**A2c**	-468285.721

H-bond

Intra-molecular H-bond lengths were given for the studied compounds and their tautomeric forms in Table 5. The stability of the **a** tautomer form can be explained with intramolecular H-bond between **H1** and **N1** atoms.

Table 5. H-bond for the studied compounds and tautomeric forms in vacuum phase at 298 K.

Compounds	a form			
	H1.....N1	**H1.....O2**	**H2.....N1**	**H2.....O1**
A1	1.748	3.116	2.254	3.044
A2	1.737	3.107	2.257	3.035
A3	1.748	3.115	2.250	3.043
A4	1.740	3.092	2.254	3.020
	b form			
	H3.....O3	**H3.....O4**	**H4.....O3**	**H4.....N2**
A1	1.578	2.581	2.627	2.423
A2	1.591	2.594	2.667	2.424
A3	1.577	2.581	2.617	2.419
A4	1.588	2.599	2.666	2.416
	c form			
	H5.....N3	**H5.....O6**		
A1	1.876	2.901		
A2	1.844	2.855		
A3	1.878	2.897		
A4	1.854	2.870		

Lower H-bond length means more stable double (interacted) compounds. As seen from Table 5, the strongest intramolecular H-bond was between **H1** and **N1** atoms for all the compounds and the tautomeric forms. This occasion supports that **a** tautomer form is most stable among those other forms. H-bond between **H5** and **N3** atoms is the most stable among the others for **c** tautomer for all compounds. As seen from Table 2, despite the strong H-bond for **c** tautomer form, the geometry of the **a** form for each compound is instable (K_{T1} and K_{T2} values are 1.6-2.9, 30-33 for **a** and **c** forms, respectively).

Dipole moment

Dipole moments of the studied Schiff bases and their tautomeric forms were given in Table 6. As seen from Table 6, tautomer forms can affect the dipole moments for the compounds. Especially, the significant variation for **c** tautomer form is observed when it is compared with that original molecule.

Table 6. The dipole moments (Debye) of the studied compounds and their tautomeric forms in vacuum phase at 298 K.

Compound	a form	b form	c form
A1	3.223	2.814	4.902
A2	4.064	4.837	8.064
A3	5.115	4.834	5.872
A4	3.776	4.584	7.921

As seen from Table 6, the compound **A1**, **A2**, **A3** and **A4** have high dipole moments. Higher dipole moment means stronger H-bond and/or stronger dipole-dipole interaction.

HOMO and LUMO energies

HOMO, LUMO and E_{GAP} values for **a** tautomer forms of the studied compound were given in Table 7.

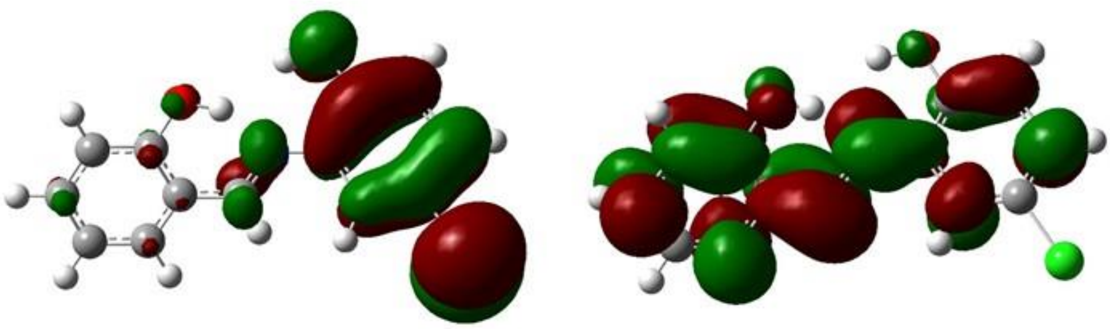
Table 7. HOMO, LUMO and E_{GAP} values for **a** tautomer forms of the studied compounds at 298 K in vacuum phase.

Compound	HOMO (eV)	LUMO (eV)	E_{GAP}* (eV)
A1a-g	-8.033	-5.924	2.109
A2a-g	-8.629	-5.918	2.710
A4a-g	-8.610	-5.894	2.716
A3a-g	-8.109	-5.831	2.278

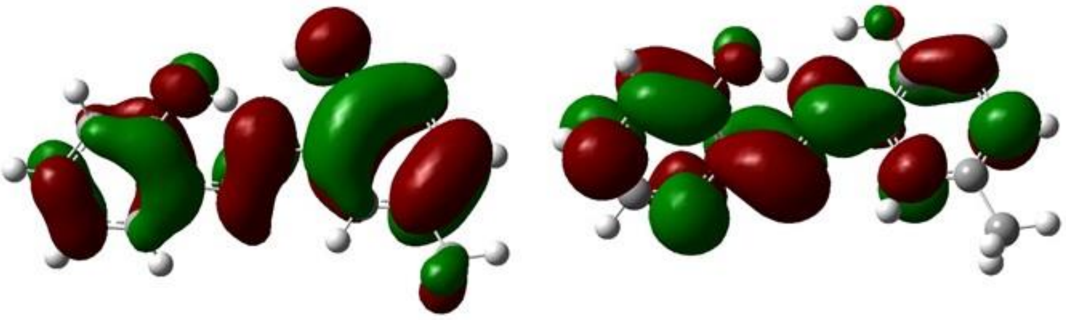
*E_{GAP} =LUMO-HOMO

As seen from Table 7. E_{GAP} value for each compound is about the same (2.1-2.7 eV). The low values show that these compounds are semiconductive (28-30).

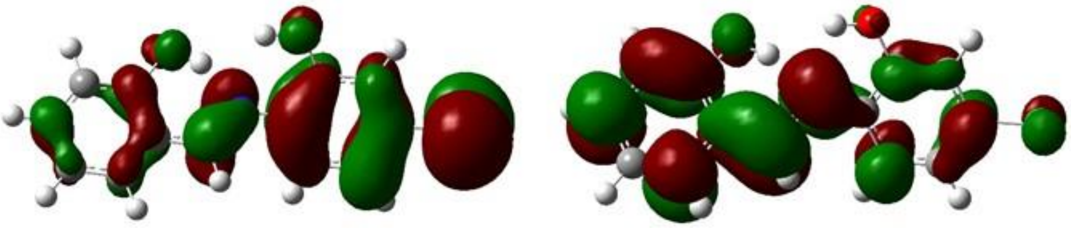
HOMO and LUMO shapes for **a** tautomeric forms of the studied compounds at 298 K in vacuum phase were given in Figure 2.



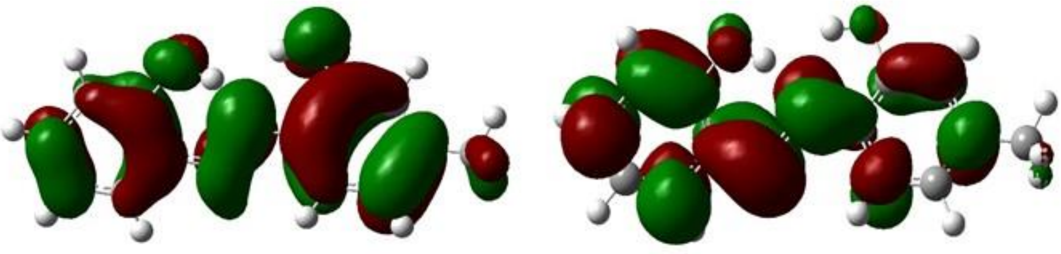
A1a-HOMO A1a-LUMO



A2a-HOMO A2a-LUMO



A3a-HOMO A3a-LUMO



A4a-HOMO A4a-LUMO

Figure 2. HOMO and LUMO shapes for **a** tautomer forms of the studied compounds at 298 K in vacuum phase (g).

It seen that electrons of HOMO and LUMO generally condense on aromatic ring in Figure 2.

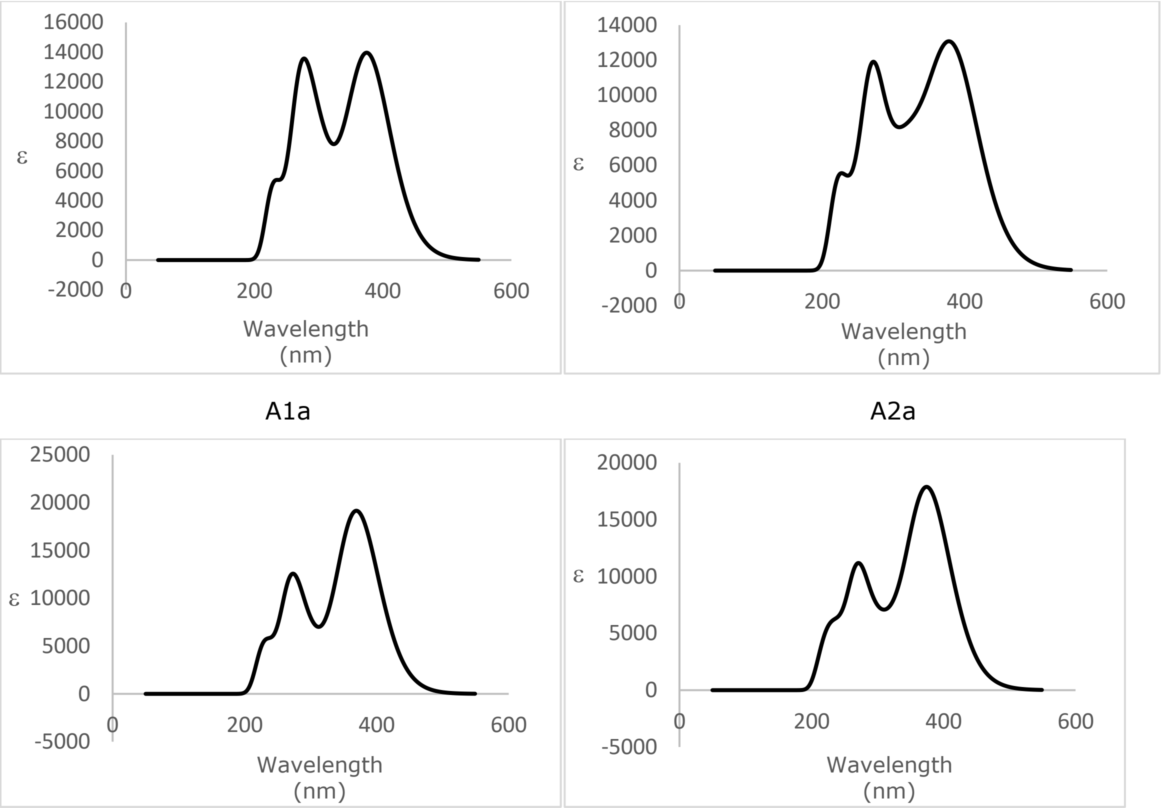
Electronic Absorption Spectroscopy

UV-Vis excitation energies for **a** tautomer forms of the compounds in different solvents were given in Table 8.

Table 8. UV-Vis excitation energies for **a** tautomer forms of the compounds in different solvents.

Solvent/Vacuum	**Excitation energies (nm)**		
	λ_1	λ_2	λ_3 **(shoulder)**
	A1a		
Dimethyl sulfoxide	373.020	275.060	234.470
Ethyl Alcohol	372.540	274.850	227.290
Vacuum	378.270	272.800	226.580
Chloroform	376.280	275.190	227.420
Methyl Alcohol	371.910	274.710	227.220
Water	371.700	274.730	227.240
	A2a		
Dimethyl sulfoxide	381.480	273.340	221.780
Ethyl Alcohol	381.020	273.140	221.730
Vacuum	384.650	271.510	222.120
Chloroform	384.480	273.570	222.130
Methyl Alcohol	380.430	273.000	
Water	380.230	273.000	221.640
	A3a		
Dimethyl sulfoxide	369.320	274.270	227.670
Ethyl Alcohol	368.730	274.050	227.540
Vacuum	370.760	271.760	226.070
Chloroform	372.260	274.300	
Methyl Alcohol	368.080	273.930	227.470
Water	367.910	273.950	227.490
	A4a		
Dimethyl sulfoxide	377.660	272.740	239.210
Ethyl Alcohol	376.990	272.570	
Vacuum	376.590	271.220	239.750
Chloroform	380.090	272.980	226.450
Methyl Alcohol	376.330	272.450	225.910
Water	376.210	272.450	225.890

Three peaks have been observed for almost all the compounds (Table 8). Representative theoretical UV-Vis spectra for **a** tautomer forms of the studied compounds at 298 K in vacuum phase have been shown in Figure 3.



A1a A2a

A3a A4a

Figure 3. Representative theoretical UV-Vis Spectra for **a** tautomer forms of the studied compounds at 298 K in vacuum phase.

It can be thought that the value of the higher wavelength (λ_1) belongs to the n-π* transition and the value of the lower wavelength (λ_2 and λ_3) belongs to the π-π* transition according to the UV-Vis spectra.

Calculated pK$_a$

The pK$_a$ values of the compounds and relevant possible tautomer forms were calculated with PM6 method by MOPAC2016 program and the results have been given in Table 9.

Table 9. pK_a values (vacuum phase) of the studied compounds and relevant tautomeric forms.

Compound	H (belonging to the –OH group in phenyl ring A)	H (belonging to the –OH group in phenyl ring B)
A1a	5.211	9.475
A1b		12.654
A1c	8.714	
A2a	5.078	10.880
A2b		13.938
A2c	7.863	
A3a	5.605	9.817
A3b		12.697
A3c	8.631	
A4a	5.271	9.876
A4b		11.168
A4c	8.177	

It is determined that H atoms bonded –OH group on phenyl ring **A** for tautomer form **a**. are more acidic and H atoms bonded –OH group on phenyl ring **B** is more basic. This situation shows H-bond between **N1** and **H1** can be strong (Table 5). It is understood that **H1** or **H2** hydrogen can be broken firstly during the formation of the metal complexes of these compounds.

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