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Artículo científico

Theoretical Studies of (*E*)-2-[(2-Chloro-benzylimino)-Methyl]-Methoxyphenol, a Schiff base

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Resumen

En este trabajo se estudió, a través de los métodos semiempiricos PM3, AM1 y MNDO, la molécula (E)-2-[(2-clorobencilimino)metil]-metoxifenol, una base de Schiff. La geometría molecular y las frecuencias de vibración del infrarojo fueron analizadas a través de diferentes programas de modelaje molecular para evaluar cuál de ellos provee una mayor exactitud. Además, se calculó la energía LUMO-HOMO, la constante del equilibrio ceto-enólico, la entalpía de reacción y las cargas de Mulliken. Los resultados teóricos fueron consistentes con los reportados.

Palabras claves: Métodos semiempíricos; base de Schiff; geometría molecular; frecuencia vibracional

Abstract

In this work, (E)-2-[(2-chlorobenzylimino)methyl]methoxyphenol, a Schiff base, has been analyzed through theoretical studies by using Semiempirical PM3, AM1 and MNDO quantum chemical methods. The molecular geometry and infrared vibrational frequencies were analyzed through different molecular modeling software in order to evaluate which one provides a better accuracy. Also, the LUMO-HOMO energy gap, keto-enolic equilibrium constant, the enthalpy of reaction and Mulliken charges were studied. The theoretical results were consistent with the experimental data reported.

Keywords: Semiempiricals methods; Schiff base; molecular geometry; vibrational frequencies

Introduction

As we know, Schiff bases have been extensively studied because of their many interesting properties and their wide applications in chemical, optical communication and by their pharmacological and biological activity[1,2,3,4].

On the other hand, molecular modeling can facilitate to researchers the determination of the minima energy of a molecule and its optimal geometric structure. There are four main computational approaches: semi-empirical, *ab-initio*, density functional theory (DFT) and molecular mechanics (MM) methods[5].

Semi-empirical methods are the simplest based on quantum mechanics. They are applicable to molecules containing between 100 or 200 atoms. The Modified Neglect of Diatomic Overlap (MNDO), Austin Model 1 (AM1) and the Parameterized Model number 3 (PM3) are part of semi-empirical models that provide accurate geometries according with experimental crystallographic structure with low computer requirements in reasonable time of calculation[5,6,7,8]. Theoretical studies performed with AM1 or PM3 are as effective as an *ab initio* calculation using small basis set[9].

Many Schiff bases have been studied through computational calculation but under density functional theory (DFT) with the 6-311++G (d,p) basis sets[10,11,12]. In this work, we are going to study the Schiff base 2-[(2-chlorobenzyl-imino)methyl]methoxyphenol synthesized and reported by Ünver *et al.*[13] through semiempirical calculations. The geometric structure, vibrational frequencies, LUMO–HOMO energies, Enthalpy of reaction, Entropy & Gibbs free standard Energy, electric dipole moment and the tautomeric equilibrium constant, were all calculated using the AM1, PM3 and MNDO methods.

Theoretical Methods

Computational calculation were done through an Intel celeron CPU B 820, 1,7 GHz y 2GB RAM computer. The first task was to determine the optimized geometry of the compound (E)-2-[(2-chlorobenzylimino)methyl]methoxy-phenol; spatial coordinates of the X-ray structure reported by Ünver *et al.*[13] were used. Full geometry optimization was performed with the unrestricted Hartree-Fock basis, Polak-Ribiere conjugate gradient algorithm with a convergence limit of 0.01 kcal./Å.mol. Semi-empirical calculations for this structure were carried out *in vacuo* using AM1, PM3 y

MNDO Hamiltonians included in the computational packages HyperChem v 8.03[14] and Spartan'08[15]. Harmonic vibrational frequencies for the stable conformation were calculated on the same level of the optimized geometries. Computed frequencies for those levels contained systematic errors which had to be readjusted[16].

Additionally, a Molecular Dynamics study was done to determine the lowest energy conformation. Molecular structures were generated through simulated annealing under conditions similar to those reported by Lubes[17], it means 300 °K for 10 ps., using the force field MM+ with a posterior geometry optimization until a convergence limit of 0.01 kcal./Å mol using the Polak-Ribiere conjugate gradient algorithm.

We also calculated the LUMO-HOMO energies, dipole moment of the molecule, heats of formation, Gibbs free energy, Mulliken charges of the tautomeric equilibrium constant and the enthalpy of reaction.

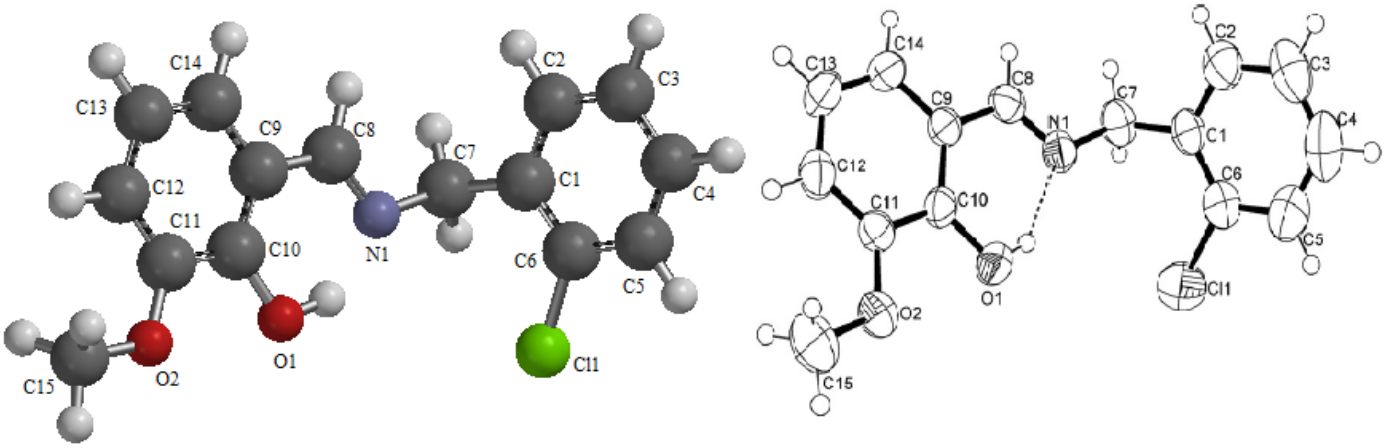


Fig. 1: Calculated optimized geometry of (*E*)-2-[(2-chlorobenzylimino)methyl]-methoxyphenol (left) and X-ray structure reported[13] (right).

Results and Discussions

Optimized geometry of (E)-2-[(2-chlorobenzylimino)-methyl]methoxyphenol are consistent with crystalline structure being non planar and belonging to the punctual group C1 (Figure1)

Structural analysis

The structural analysis referring to bonding distances, bonding angles and dihedral angles were performed through 3 different semi-empirical methods (Table 1). As seen before, PM3, AM1 and MNDO methods give us a good approximation for the system without the need to sacrifice excessive time before obtaining results. Results obtained through two computational programs were confronted in order to determine which of them provide the best approximation for the system.

In the table 1 we can see that the bond distances and the bond angles obtained using Spartan'08 are closer to reported than those obtained using HyperChem v.8.03, with deviations between 0.98 to 1.28% and 1.31 to 2.70%, respectively. In addition, the lowest dispersion is obtained when calculation were performed through PM3 method.
Computational data confirm the structure presented by Ünver *et al.*[13], where the reported C8-N1 distance is even smaller than calculated being a typical distance for C (sp^2)-N (sp^2). On the contrary, the distance C7-N1 is longer and consistent with a C (sp^3)-N (sp^2) bond. Finally the angle between C9 (sp^2)-C8 (sp^2)-N1 (sp^2) are close to 120º, while the N1 (sp^2)-C7 (sp^3)-C1 (sp^2) angle is close to 109º, usual for sp^3 hybridizations.

IR stretching frequencies analysis

In Table 2, we can see the analysis of the calculated IR stretching frequencies characteristic for the molecule through three semi-empirical methods using the Spartan'08 software. In addition, according with literature, correction factors of 0.94 were applied for the results obtained with PM3 method; 0.93 for AM1 method and 0.87 for MNDO[16]. The percent mean deviation is around 6.5 and 12.8% being these values close to estimated by the software manufacturer[15]. If the correction factor is applied, the mean deviation is reduced from 3.4 to 6.7%.

In Figure 2 is shown the equation for the graph and the correlation between reported frequency values and the ones obtained through computational methods. For all the three systems, good correlations were obtained, being PM3 better than those obtained with AM1 and MNDO methods. The R^2 values were 0.994, 0.969 and 0.990, respectively.

Table 1: Some selected values of bond distances, bond angles and dihedral angles obtained through PM3, AM1 and MNDO with Spartan'08 and HyperChem v 8.03 computational programs. The distances are reported in Angstroms (Å), bond and dihedral angles in degrees.

	Reported[13]	**PM3[a]**	**AM1[a]**	**MNDO[a]**	**PM3[b]**	**AM1[b]**	**MNDO[b]**
O2-C11	1.365	1.370	1.363	1.370	1.385	1.381	1.370
O2-C15	1.417	1.419	1.441	1.419	1.407	1.420	1.400
N1-C8	1.264	1.290	1.291	1.290	1.295	1.287	1.287
N1-C7	1.463	1.469	1.473	1.469	1.464	1.440	1.457
C9-C10	1.396	1.403	1.426	1.403	1.409	1.401	1.427
C1-C6	1.368	1.404	1.406	1.404	1.397	1.399	1.415
C1-C7	1.510	1.509	1.513	1.509	1.498	1.500	1.519
Cl-C6	1.735	1.728	1.731	1.728	1.685	1.701	1.755
Mean deviation (%)		**0.822**	**1.252**	**0.822**	**1.427**	**1.260**	**1.400**
O1-C10-C11	118.0	118.20	116.15	118.20	117.01	114.40	122.70
N1-C8-C9	122.3	121.24	120.31	121.24	119.20	120.73	119.66
N1-C7-C1	109.5	111.98	111.98	111.98	110.04	112.49	109.73
C11-O2-C15	116.9	117.72	117.72	117.72	115.60	115.80	119.69
O2-C11-C12	125.6	124.75	124.36	124.75	123.40	125.00	120.91
O2-C11-C10	114.9	116.28	115.52	116.28	116.20	114.39	118.93
Mean deviation (%)		**0.98**	**1.28**	**0.98**	**1.31**	**1.49**	**2.70**
C9-C10-C11-O2	-178.6	179.93	179.94	179.93	176.70	179.72	-175.36
C14-C9-C10-O1	178.5	-179.77	-179.78	-179.77	-179.90	-179.70	177.10
C7-N1-C8-C9	-177.9	-179.60	-179.74	-179.60	178.90	-178.96	-178.98
C14-C9-C8-N1	-178.4	-178.89	-178.94	-178.89	-179.30	172.87	93.74
C15-O2-C11-C10	174.4	-179.56	179.57	179.56	155.40	-175.84	-108.70
C2-C1-C7-N1	-102.8	-101.25	-100.91	-101.25	-118.77	108.22	96.17

[a] Values obtained with Spartan' 08; [b] Values obtained with HyperChem v 8.03

Percent mean deviation: $100^* \ 1/n \ \sum |(d_{calc} - d_{report})/ d_{report}|$

Table 2: Some selected IR stretching values reported and obtained through semi empirical methods using the Spartan'08 software with their respective adjustments.

Stretching	**Reported [13] (cm^{-1})**	**PM3 (cm^{-1})**	**AM1 (cm^{-1})**	**MNDO (cm^{-1})**	**Adjust PM3 (cm^{-1})**	**Adjust AM1 (cm^{-1})**	**Adjust MNDO (cm^{-1})**
O-H	3414	3475	3181	3516	3262	2959	3059
C-H and Ar-H	3062-3008	3121- 3145	3263-3293	3427-3377	2934-2956	3035-3063	2981-2938
C-H	2907	3155	3231	3298	2966	3005	2869
C=N	1635	1867	1937	1933	1755	1801	1682
C=C	1471	1615	1712	1715	1518	1592	1492
Ar-O	1336	1362	1466	1463	1280	1363	1273
Ar-O-C	1082-1027	1146-1127	1273-1223	1216-1115	1077-1059	1184-1147	1058-970
Mean deviation (%)*		**6.5**	**12.8**	**11.8**	**3.4**	**6.7**	**3.7**

* Percent mean deviation: $100^* \ 1/n \ \sum |(\nu_{calc} - \nu_{report})/ \nu_{report}|$

The study for the simulated IR spectra was repeated using the HyperChem v 8.03 computer program in order to evaluate if this could provide a better approximation to the results reported by Ünver *et al.*[13]. The stretching frequencies using PM3, AM1 and MNDO and the readjusted ones obtained using the correction factors mentioned before are given in Table 3.

As we can see, the value of the percent mean deviation is around 4.2 to 11.8% while the adjustment improves these values reducing them around 3.4 and 4.8%. On the other hand, to evaluate if a linear correlation is given, reported experimental frequencies were plotted against those obtained theoretically. On Figure 3, can be seen that the linear regression coefficient (R^2) for the PM3 method is 0.995, for the AM1 method is 0.989 and for the MNDO method is 0.988. Again, the values obtained using the PM3 method was better.

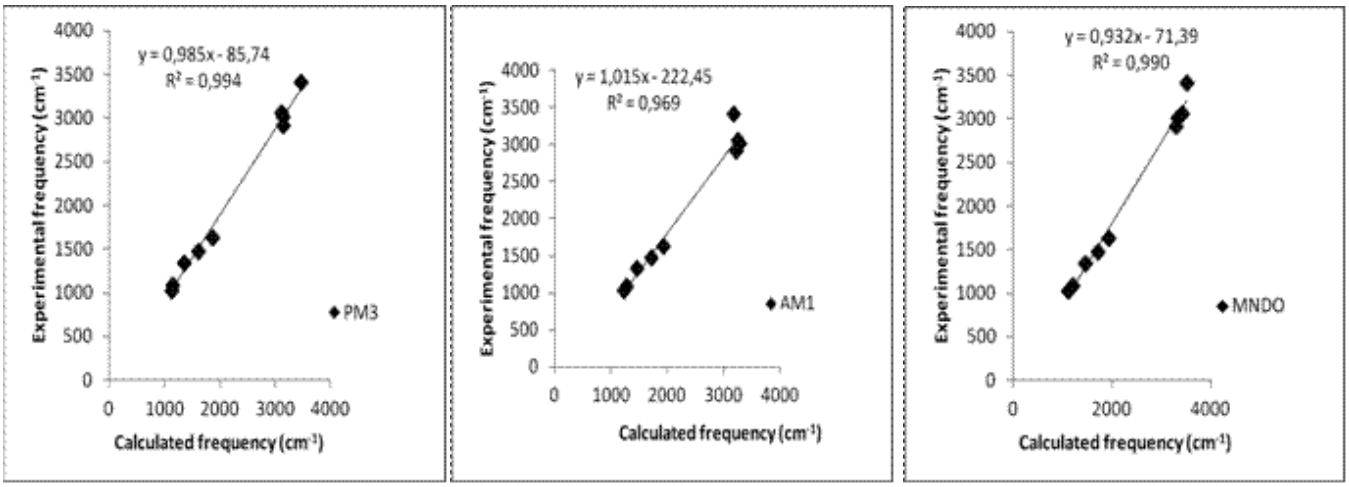


Fig. 2: Correlation between the values of the reported IR frequency vs. calculated IR frequency using the PM3, AM1 and MNDO semi-empirical methods and the Spartan'08 software.

Table 3: Some selected values of the reported IR stretching frequencies and those obtained through HyperChem v 8.03 software using PM3, AM1 and MNDO methods and with its respective adjustments.

Stretching	Reported[13] (cm^{-1})	PM3 (cm^{-1})	AM1 (cm^{-1})	MNDO (cm^{-1})	Adjusted PM3 (cm^{-1})	Adjusted AM1 (cm^{-1})	Adjusted MNDO (cm^{-1})
O-H	3414	3596	3357	3976	3380	3122	3459
C-H Y Ar-H	3062-3008	3077-3026	3148-3188	3217-3416	2892-2844	2928-2965	2799-2972
C-H	2907	3002	2943	3179	2822	2737	2766
C=N	1635	1843	1958	1973	1732	1821	1717
C=C	1471	1527	1554	1746	1435	1445	1519
Ar-O	1336	1409	1444	1450	1324	1343	1262
Ar-O-C	1082-1027	1117-1055	1123-1155	1108-1156	1050-992	1044-1074	964-1006
Mean deviation (%)*		**4.2**	**6.4**	**11.8**	**3.4**	**4.0**	**4.8**

* Percent mean deviation: $100^* 1/n \sum |(\nu_{calc} - \nu_{report})/ \nu_{report}|$

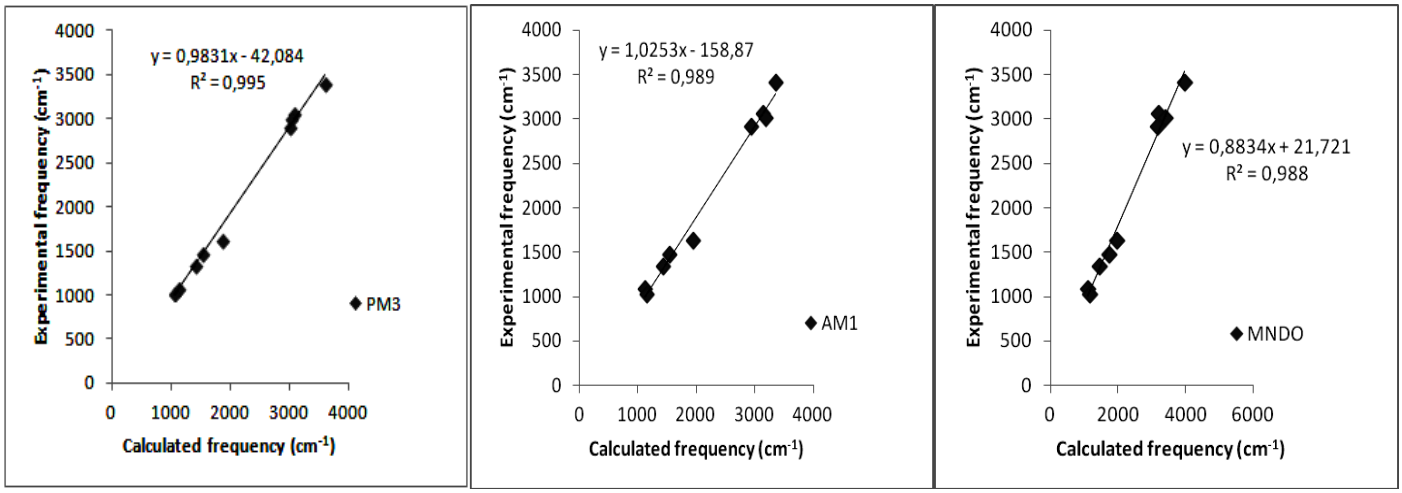


Fig. 3: Correlation between the values of the reported IR frequency vs. calculated IR frequency using the PM3, AM1 and MNDO semi-empirical methods and the HyperChem v 8.03 software

On the contrary to the work reported by Arora *et al.*[5], where a Schiff base is studied through semi-empirical methods too, the best adjustment in this work is obtained with the PM3 semi-empirical method.

Based on the percent mean deviations, Spartan'08 gives a better approximation for the structure of this molecule, while HyperChem v 8.03 provides more exacta data for IR spectra. In both cases is recommended the application of a correction

factor to obtain a mean deviation below 5%. Anyway, choosing one of these software programs depends on the criteria of the user and the properties desired to evaluate.

Study of the Keto-Enolic equilibrium

The molecule under study can compromise in a tautomeric equilibrium passing from the Enolic form to the Ketonic form as in Figure 4.

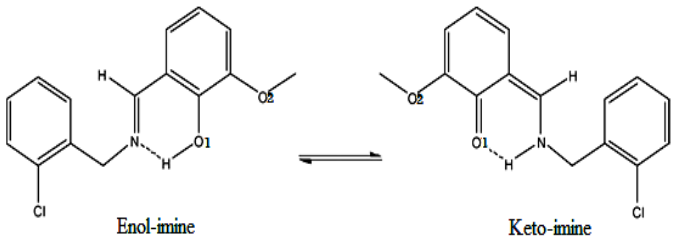


Fig. 4: Keto-Enolic equilibrium of the (E)-2-[(2-chlorobenzyl-imino)methyl]methoxyphenol.

On Table 4, we can see that the enolic form is thermodynamically more stable than the ketonic form. Heat of formation values, under the three semiempirical methods, are between -16.868 to -64.167 kJ/mol on the enol form while on the keto form is around -11.292 and 21.899 kJ/mol.

Table 4: Heat of formation calculated for the enolic and ketonic forms. Bond distance (Å) between N and O1 and between N and the H atom from the –OH in its enolic form.

Method	$\Delta H°$ *enol* (kJ/mol)	$\Delta H°$ *ketone* (kJ/mol)	Interaction distance N·O1	Interaction distance N··H
PM3	-64.167	-11.292	2.666	1.820
AM1	-16.838	0.428	2.884	2.008
MNDO	-16.868	21.899	3.442	2.831

* The distance and thermodynamic values were determined using the Spartan'08 software because it provides better approximate values to the ones of the crystalline structure.

It is necessary to mention that, on the hydrogen transposition from the enol-imine to the keto-imine, the hydrogen atom has to be as closer as possible to the nitrogen atom. The minimum calculated distance for the N··H interaction is 1.820 Å (Table 4) while the distance N1··O1 is 2.666 Å in agreement with the 2.585 Å observed in the reported crystalline structure[13].

It is well known that the equilibrium constant of a reaction can be determined from its Gibbs free energy ($\Delta G_{reaction}$) according to the equation: $LnK = -\Delta G_{reaction}/RT$, where $\Delta G_{reaction}$ comes from the difference between free energy of formation of the products and reactants according to equation: $\Delta G_{reaction} = \sum n\Delta G_{f(products)} - \sum n\Delta G_{f(reactants)}$.

Table 5: Standard enthalpies, standard entropy and standard free energy values calculated through the semi-empirical methods PM3, AM1 and MNDO for the enolic and ketonic forms. Equilibrium constant calculated.

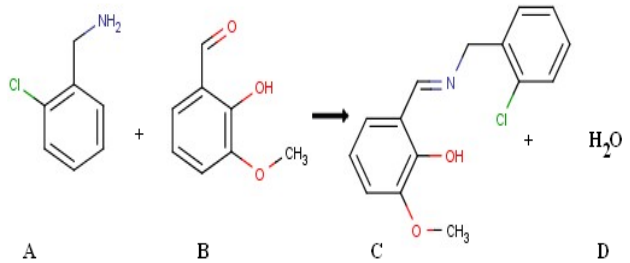
Method	H Enol kJ/mol	S Enol J/mol	G Enol kJ/mol	H Keto kJ/mol	S Keto. J/mol	G Keto kJ/mol	$\Delta G\Theta$ kJ/mol	K_{eq}
PM3	656.92	0.563	488.927	700.30	0.554	535.041	46.114	$8.3.10^{-09}$
AM1	717.87	0.490	571.615	736.04	0.503	586.014	14.398	$3.0.10^{-03}$
MNDO	739.76	0.468	600.229	775.94	0.466	637.109	36.881	$3.5.10^{-07}$

On Table 5 are presented the values of the functions of state and the calculated keto-enolic equilibrium constant (K_{eq}). As we can see, three very different values for the equilibrium constant are obtained. This is because of the different solutions obtained from every semiempirical Hamiltonian[18]. However, it has to be mentioned that, in all cases, the value of Keq is very small (Keq<<0) from which we can assume that the keto-enolic equilibrium is displaced to the enolic form.

Both results (heat of formation and the equilibrium constant) match with the spectroscopic results of the compound obtained by Ünver *et al.*[13] where the enolic form would be favored over the ketonic form.

Analysis of the heat of reaction

The title compound (**C**) was synthesized, as we can see on reaction 1, from the reactants 2-chloro-bencylamine (**A**) and 2-hydroxy-3-methoxybenzaldehyde (*o*-vanillin) (**B**), in the process is also required the loss of a water molecule (**D**). On Table 6 the values of the formation enthalpy obtained through the three methods for all the previously mentioned compounds can be seen. The heat of reaction was calculated using the following expression: $\Delta H_{reaction} = \sum nH_{products} - \sum nH_{reactants}$.



(1)

Table 6: Heats of formation obtained through the three semi-empiricals methods using the Spartan' 08 software for each of the compounds previously mentioned. The values are shown in kJ/mol.

Method	A	B	C	D	ΔH_{react}
PM3	63.885	-381.906	-64.167	-223.537	30.317
AM1	47.684	-375.412	-16.838	-247.861	63.029
MNDO	69.653	-377.129	-16.868	-254.966	35.642

The value of the enthalpy of reaction is positive in all the cases (Table 6), an endothermic reaction is carried on in which energy is consumed. This result matches with the rupture of two N-H bonds (2 x 391 kJ/mol) and the rupture of a C=O bond (799 kJ/mol) are more energetic than the formation of C=N (615kJ/mol) and H-O bonds (2 x 463 kJ/mol)[19].

Molecular Dynamics Analysis

In order to determine any other thermodynamically possible stable conformers, a Molecular Dynamics Analysis was performed using the HyperChem v 8.03 software. Using the Potential Energy map a second structure different to that reported was determined (Figure 5). This structure presents lower enthalpy of formation in comparison with that presented in Figure 1 (-81.17 kJ/mol and -64.17 kJ/mol respectively). Nevertheless, the information of bond distance, bond angles and torsion angles does not match with the crystallographic information; in fact the dispersion of these parameters are higher than the ones calculated for the structure 1 (Table 7). Considering the points exposed above, the intramolecular interaction N··H-O, might stabilize in some way the molecule favoring the formation of the crystal, as was reported by Ünver *et al.*[13].

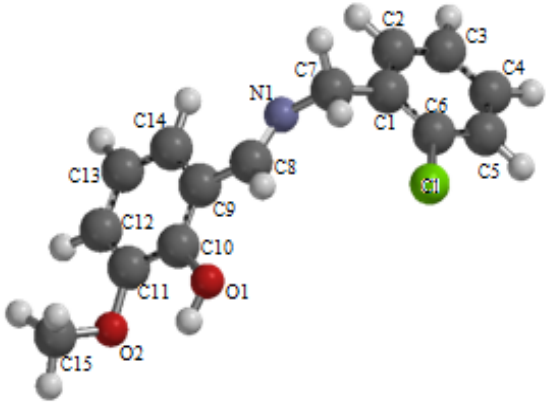


Fig. 5: Most stable conformer obtained through Molecular Dynamics studies.

A final analysis of the structure was performed in order to evaluate the position of the H atom respective to the O1 atom from which two possibilities were determined; both are shown in Figures 1 and 6.

Table 7: Bond distances, bond angles, torsion angles calculated using the semi-empirical PM3 method.

	Reported[13]	PM3[a]	PM3[b]
O2-C11	1.365	1.382	1.370
O2-C15	1.417	1.405	1.419
N1-C8	1.264	1.296	1.290
N1-C7	1.463	1.459	1.469
C9-C10	1.396	1.406	1.403
C1-C6	1.368	1.397	1.404
C1-C7	1.510	1.498	1.509
Cl-C6	1.735	1.687	1.728
Mean deviation (%)		**1.162**	**0.822**
O1-C10-C11	118.0	116,89	118.20
N1-C8-C9	122.3	119.67	121.24
N1-C7-C1	109.5	116.78	111.98
C11-O2-C15	116.9	117.10	117.72
O2-C11-C12	125.6	125.15	124.75
O2-C11-C10	114.9	114.82	116.28
Mean deviation (%)		**1.33**	**0.98**
C9-C10-C11-O2	-178.6	-179.35	179.93
C14-C9-C10-O1	178.5	-179.82	-179.77
C7-N1-C8-C9	-177.9	179.939	-179.60
C14-C9-C8-N1	-178.4	179.326	-178.89
C15-O2-C11-C10	174.4	-172.12	-179.56
C2-C1-C7-N1	-102.8	83.69	-101.25

[a] Obtained from the structure in Figure 5.
[b] Obtained from the structure in Figure 1

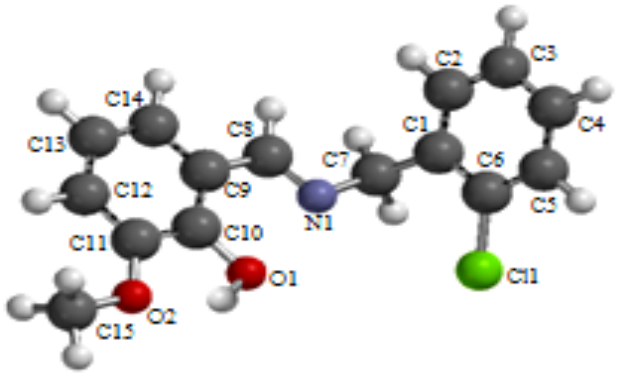


Fig. 6: Effect of the $-OCH_3$ group on the –OH group.

The heat of formation of the conformation reported on Figure 6 is thermodynamically less stable than those presented in Figure 1 (-42.39 kJ/mol and -64.17 kJ/mol, respectively). The difference can be attributed to the higher steric effect of the methoxy group over the –OH group.

Mulliken charges

The values of the Mulliken charges were used to determine the electronic density in the molecules atoms through the Spartan'08 software. On Table 8 can be seen the nitrogen atom presents higher electronic density than the O1 atom

and matches with the electronegative behavior observed experimentally[13]. because of this, the bond distance between C10 and O1 is the typical distance for a sigma bond allowing us to conclude again that the Enol-imine is more favored that the Keto-imine.

Table 8: Some selected values for the Mulliken charges calculated through the Spartan'08.

Atom	PM3	AM1	MNDO
O1	-0.161	-0.183	-0.237
O2	-0.262	-0.255	-0.249
N1	-0.131	-0.207	-0.298
C7	0.011	0.118	0.033
C8	0.007	-0.004	0.131
Cl	0.072	-0.013	-0.036

Other data obtained in this study

During the molecular modeling study some other interesting data was obtained such as bonding energy, dipole moment,Δ LUMO -HOMO, punctual group, polar surface area and volume. This data is shown in Table 9.

Table 9: Some calculated values such as total energy, bonding energy, electronic energy, nuclear energy, dipole moment, LUMO-HOMO gap, punctual group, polar surface area and volume.

	PM3	AM1	MNDO
Total Energy (kJ/mol)	-295058.90	-321622.43	-320420.34
Bonding Energy (kJ/mol)	-14959.87	-14929.10	-14978.36
Electronic Energy(kJ/mol)	-1922412.32	-1935657.45	-1923680.01
Nuclear Energy (kJ/mol)	1627353.411	1614035.02	1603259.67
HOMO (eV)	-8.61	-8.91	-8.88
LUMO (eV)	-0.40	-0.29	-0.37
Δ LUMO-HOMO(eV)	8.21	8.62	8.51
Dipole Moment (Debye)	3.43	3.85	4.27
Molecular Mass (uma)	275.735	275.735	275.735
PSA (A^2)	28.068	28.068	28.068
Volume (A^3)	274.48	274.48	274.48
Punctual Group	C1	C1	C1
Area (A^2)	296.37	296.37	296.37

Conclusions

Concerning to the structural study of the molecule, we have seen that the Spartan'08 software gets closer to the crystalline structure reported than the HyperChem v 8.03 computational package. The lower mean deviation was obtained with the semi-empirical method PM3 (0.98 and 1.31 with Spartan' 08 and Hyperchem v 8.03, respectively). On the other hand, Hyperchem v 8.03 showed better results on the study of the IR stretching frequencies. Again, the best dispersion was obtained with the semi-empirical method PM3. The adjustment of the IR vibrational frequencies, using the reported correction factors, diminishes the deviations obtained to values below 5%. Semi-empirical IR spectra simulations were very accurate and could be perfectly used as a tool that facilitates interpretation of the experimental spectra of Schiff base compounds.

Regarding to the equilibrium Keto-Enolic, results obtained on the thermodynamic stability analysis, the Mulliken charges calculated and the equilibrium constant calculated for the system studied, has confirmed the x-ray structure reported by Ünver *et al.*[13], where the enol tautomer is favored over the keto tautomer.

Molecular Dynamics study in vacuum through simulated annealing, reveals a possible conformer with lower formation energy (-81.17 kJ/mol) compared with the structure reported (-64.17 kJ/mol), but bond distances, bond angles and dihedral angles does not match with x-ray structure. It is possible that intermolecular and the intramolecular interaction N··H-O1, stabilize the molecule favoring the formation of the crystal.

It was also observed that the methoxy group has a steric effect on the –OH group that favors the conformer where the H atom is closest to the N atom. The difference on energy is -21.78 kJ/mol.

Finally, in the present study, the Δ LUMO-HOMO gap calculated of the molecule are 8.21, 8.62 and 8.51 eV for PM3, AM1 and MNDO respectively, which clearly indicates that the molecule is very stable.

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