

Research Article

Highlighting of Properties of Thermochromy and Photochromy in Salicylideneamines

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Abstract

This research aimed to understand the effects induced by PP, PQ and QQ complexes on the geometry, thermodynamic stability and vibration frequencies of salicylideneamines. It planned to determine the interactions within them. It envisaged identifying the impact of the solvent during the creation of these dimers by analyzing variations in electronic energies and associated dipole moments. To do this, the study utilized exploited DFT combined with sets of basis functions such as those of Pople and the HF method to optimize the geometries of P or Q monomers and PP, PQ or QQ dimers. The results obtained were employed for the calculations of NBO and QTAIM in the case of isopropyl amine N-(2,3-dihydroxybenzylidene) structures. For the last objective, SPSS Statistics v27 software was used to compare variations in energies or electronic moments during transitions from monomers to dimers. This methodological approach made it possible to prove that the electronic transitions $\sigma \rightarrow \sigma^*$ and $\pi \rightarrow \pi^*$ improve the equilibrium of the P and Q monomers. Their “dimeric” associations are steadied by those of the $Lp \rightarrow \sigma^*$ and $Lp \rightarrow \pi^*$ type with the heteroatoms of the PP, PQ and QQ complexes. These phenomena are obtained thanks to the hydrogen bonds established between the latter and the hydrogen favourable to these interactions. The observed “thermochromic” and photochromic trends can be explained by the stability of the PQ. The presence of the thermodynamically disadvantaged Q tautomer is also justified. The nature and polarity of the solvents don't significantly influence these latter results.

Keywords

Salicylideneamines, Interactions, Quantum Calculations, Tautomers, NBO, QTAIM

1. Introduction

Salicylideneamines are Schiff bases obtained by condensation of a primary amine with the substituted salicylic aldehyde [1]. The observation of reversible colours in the solid state, under the effects of light irradiation (“photochromy”) [2,

3] and temperature (thermochromy) is one of their remarkable properties.

This property is linked to structural changes within these molecules [4], attributed to isomerism between the enol and

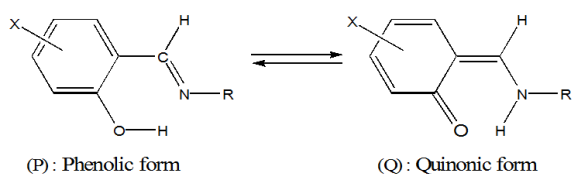
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Received: 12 February 2025; **Accepted:** 24 February 2025; **Published:** 7 March 2025



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ketone forms [5, 6], as illustrated in Figure 1. A proton transfer from the phenolic to the quinone genre of salicylideneamines [7] is revealed through the tautomeric equilibrium. The tautomer (P) stability present in all states of matter is highlighted in studies of these compounds using several experimental. The characteristics of the quinone form (Q), thermodynamically disadvantaged, are observed by the infrared spectroscopic analyses.



X = Substituant R is an alkyl or aryl radical or a hydrocarbon radical which may contain heteroatoms

Figure 1. Tautomeric equilibrium in salicylideneamines.

The proton transfer explanation of the phenomenon remains inadequate. Other factors may contribute to the coexistence of the two forms. This work conjectures that the latter results from the possible association of tautomers into symmetric dimers such as PP (Phenolic-Phenolic), PQ (Phenolic-Quinonic) and QQ (Quinonic-Quinonic). It raises the question of their stability conditions, and their frequencies induced by the dimerization. The answer to this question will lead to rationalizing the assignment of infrared vibration bands in salicylideneamines. Specifically, this research ini-

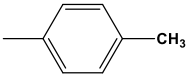
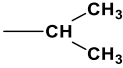
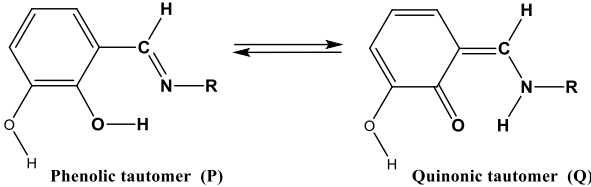
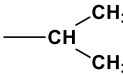
tially aims to suggest a better one in which dimers in the keto-enol balance are affiliated. Secondly, it targets to relate the intermolecular interactions between tautomers to the “thermochromic” and photochromic properties of salicylideneamines. The latter part of these specific objectives is the main focus of this article. Following this introduction, the results are presented and discussed. It ends with a conclusion. Beforehand, it summarizes the compounds studied and the methods used.

2. Materials and Methods

The mono hydroxylated monomer structures submitted for calculation are shown in Table 1. Salicylideneamine geometries are optimized employing standard parameters. Tautomer configurations are respected in Z-matrix constructions utilizing GaussView06. Gaussian 03 software was exploited to implement HF (Hartree-Fock) and DFT (Density Functional Theory) calculations. This work deploys the DFT-level density functional associated with basis sets of functions such as Pople's. The findings of DFT-optimized N-(2,3-dihydroxybenzylidene) isopropylamine structures were used for NBO (Natural Bond Orbitals) and QTAIM (Quantum Theory of Atoms in Molecule) computations. All optimized geometries were validated using vibration frequency estimates. SPSS v27 statistical software was employed to compare the variations of the dipole moment and electronic energies during the formation of PP, PQ or QQ dimers. This methodological approach leads to the results and their discussion.

Table 1. The Salicylideneamines Studied.

Monohydroxylated salicylideneamines		
Tautomeric equilibrium		
	Phenolic tautomer (P)	Quinonic tautomer (Q)
acronyms	Radical R	Molecular structure name
A		N-(2-hydroxybenzylidene) benzylamine
B		N-(2-hydroxybenzylidene)-2-chlorobenzylamine
C		N-(2-hydroxybenzylidene) cyclopropylamine

Monohydroxylated salicylideneamines		
D		N-(2-hydroxybenzylidene) paramethyl benzylamine
E		N-(2-hydroxybenzylidene) isopropylamine
Dihydroxylated salicylideneamines		
	 Phenolic tautomer (P) \rightleftharpoons Quinonic tautomer (Q)	
Radical		N-(2,3- dihydroxybenzylidene) isopropylamine

3. Results and Discussion

This section looks at the effects of solvents on the stability of salicylideneamine tautomers. NBO calculations are analyzed to determine the electronic factors likely to influence them. The initial focus is on salicylideneamine dimers.

3.1. Relative Stability of Salicylideneamine Dimers

Intermolecular geometric parameters of tautomeric salicylideneamine associations are summarized in Table 2. According to its data, the PQ complex is the steadiest. This is followed by the PP one. The QQ is the least stable. The energy differences between these tautomeric associations were 0.0866 kcal.mol⁻¹; 0.5202 kcal.mol⁻¹ and 0.4336 kcal.mol⁻¹ for (PQ-PP) (PQ-QQ) and (PP-QQ) respectively. The quinone form was steady through the electronic charge transfer founded by hydrogen bonds. The PQ complex was more polar than PP. The dipole moment of the QQ one entity was zero. This value is related to the symmetric configuration adopted by the optimized structure, and to the coplanarity of its two benzylidene groups. Interactions between the O-H of one complex's fragment and the oxygen of the other leads to the establishment of intermolecular hydrogen bonds. The three geometric parameters α , β and d in the Figure 2 below define them in salicylideneamine dimer complexes. α represents the angle of linearity. For a perfect hydrogen bond, its ideal value is 180°. When it's destabilized, it's modified. β suggests the direction angle. Its optimum number is 109.5°. Parameter d measures the length of the hydrogen bond. Its existence according to this criterion is $d \leq 2.62$ Å. its strengthening is indicated by the decrease in this parameter.

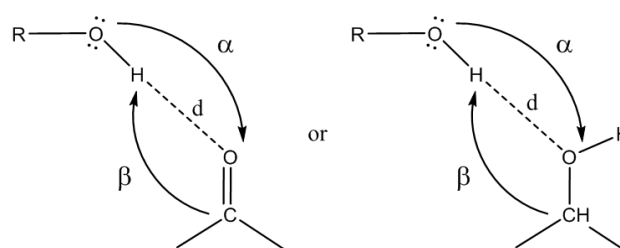


Figure 2. Geometric Parameters of Hydrogen Bond.

All distances between these elements were below 2.00 Å, in line with the conditions specified by [8]. The direction angles shown were 147.37° in the QQ complex and 159.58° in PP. In the QQ, the two ones were 155.51° and 152.06°. These angles deviate from the ideal value of 180.00°, however, they remain within the definitional limits of hydrogen bonding. In each pseudo-ring, this latter is expressed more strongly across a shorter distance.

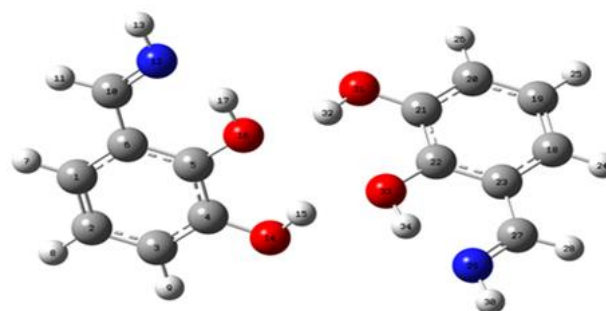


Figure 3. PP Complex.

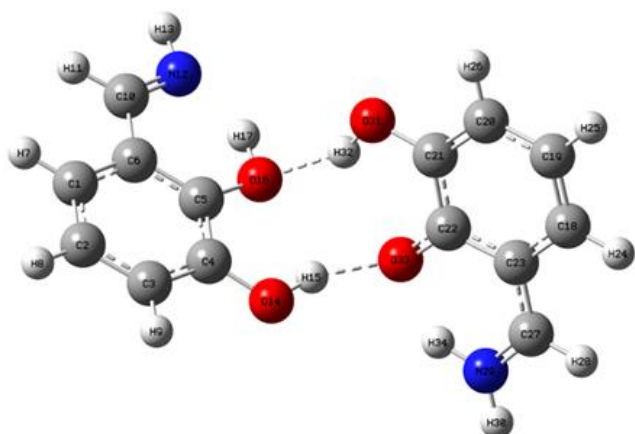


Figure 4. PQ Complex.

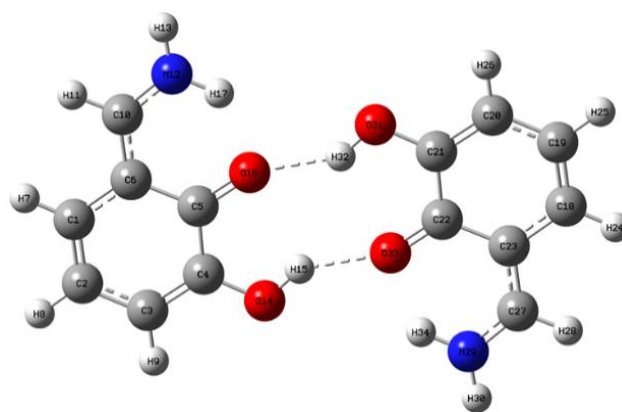


Figure 5. QQ Complex.

Table 2. Electronic Energies, Dipole Moments and Geometric Parameters of Intermolecular Hydrogen Bonds (HB) in PP, PQ and QQ dimers.

Parameters	Dimer (PP)	Dimer (PQ)	Dimer (QQ)
Electronic energies E (au)	-1188.531392	-1188.531530	-1188.530701
Dipole moments (D)	2.2139	3.7422	0.00028
Geometric parameters of HB			
O33 (Q)... H-O14 (P)	1.890	1.764	1.840
O16 (P)... H-O31 (Q)	1.890	1.960	1.840
<O33(Q)...H-O14(P)	159.58	155.51	147.37
<O16(P)...H-O31(Q)	159.58	152.06	147.37
Pseudo-cycle			
N... HO/O... NH	1.683	1.68979 (P)/1.738 (Q)	1.726
<O33(Q)...H-O14(P)	148.54	148.54 (P)/137.48 (Q)	137.63

The following section looks at the effect of solvents on the coexistence of tautomers.

3.2. Solvent Effects on Salicylideneamine Tautomerism

Water, for example, degrades salicylideneamines. For their spectroscopic treatment, strictly anhydrous media are sought. Respecting these conditions, these five molecules were analyzed in different solvents. They were dissolved in the cyclohexane, the CCl₄ or in the vacuum. The first one was nonpolar, while the second was weakly polar ($\mu=1.5$ D). In this section, their effect on the equilibrium number of tautomers during PQ transitions will be discussed. Calculations were performed for the CCl₄ and the cyclohexane liquids and the gas. The solvent influence on the tautomer pro-

portions is analyzed. In this perspective, the research was interested in determining whether the energies and the dipole moment variations associated with salicylideneamines were similar. Before, the two descriptive statistics' variables are summarized. The sample includes all five molecules. These were dissolved in cyclohexane or CCl₄ or under vacuum; the only factor was the solvent. Nonparametric tests are suggested. The Kruskal-Wallis [9] one was used to analyze its effects on the energy and dipole moment of the compounds, although the single-sample ANOVA criteria [10] were met.

3.2.1. Statistical Test Choice

The independence criteria of the observations were checked. The P or Q dipole moments and energies of each solution aren't influenced by those of the others. This premise is respected. The ΔE ($p = 0.184$) and $\Delta\mu$ ($p = 0.967$) were

normally distributed according to the one-sample Kolmogorov-Smirnov [11] test data (Table 3). Furthermore, the mol-

ecules come from populations of equal variance (see Table 4).

Table 3. One-Sample Kolmogorov-Smirnov Test.

Null Hypothesis	Sig.a	Decision
The distribution of ΔE is normal with mean 4.705 and standard deviation 1.122787.	0.184	Retain the null hypothesis.
The distribution of $\Delta\mu$ is normal with mean 1.974 and standard deviation .413118.	0.967	Retain the null hypothesis.

According to [12], samples are obtained from populations with equal variances. The variability of the score for each of the solvents was similar for ΔE ($p=0.988$) and $\Delta\mu$ ($p=0.989$) compared to the data from the Levene test (Table 10). For $\Delta\mu$, the residuals are normally distributed (Figure 6); they were

dispersed along the 1: 1 line of a quantile-quantile (Q-Q) plot [13] In addition, the variances were homogeneous ($p=0.155$) according to the results of the Bartlett test [14] (Table 4) [12]. On the other hand, some ANOVA prerequisites were violated.

Table 4. KMO and Bartlett's Tests associated with ΔE and $\Delta\mu$.

Tests	ΔE	$\Delta\mu$
Kaiser-Meyer-Olkin Measure of Sampling Adequacy.	0.500	0.500
Bartlett's Test of Sphericity		
Approx. Chi-Square	4.008	2.025
Df	1	1
Sig.	0.045	0.155

The variances associated with ΔE aren't equal according to the Levene test scores (Table 5). The residuals of ΔE weren't randomly distributed (Figure 7). The nonparametric

Kruskal-Wallis one [13] is used; the sample size was small ($n=5$). The molecules were also not chosen arbitrarily from the salicylideneamines family [12].

Table 5. Tests of Variances Homogeneity for ΔE and $\Delta\mu$.

Variables		Levene Statistic	df1	df2	Sig.
ΔE	Based on Mean	0.012	2	12	0.988
$\Delta\mu$	Based on Mean	0.011	2	12	0.989

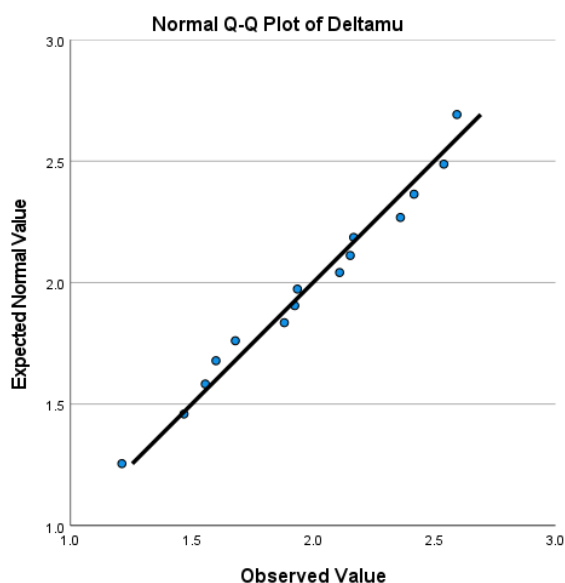


Figure 6. Q-Q diagram associated with $\Delta\mu$.

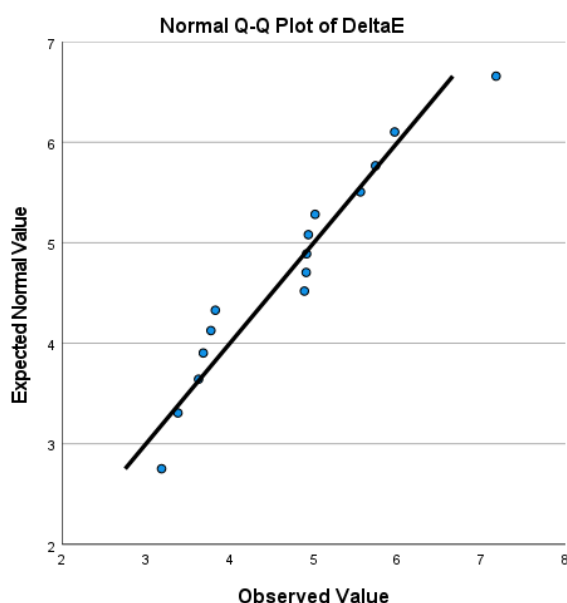


Figure 7. Q-Q diagram associated with ΔE .

3.2.2. Descriptive Statistics

The energies and the dipole moment variations associated with the tautomerism PQ are respectively summarized in the Tables 6 and 7.

Table 6. Energy variations ΔE in kcal.mol^{-1} During PQ Transition; $\Delta E = E_Q - E_P$.

Molecules	Gas phase	Cyclohexane	CCl ₄	Median
A	4.936	3.827	3.683	3.827
B	5.965	5.016	4.889	5.016

Molecules	Gas phase	Cyclohexane	CCl ₄	Median
C	7.174	5.737	5.557	5.737
D	4.910	3.774	3.627	3.774
E	4.915	3.381	3.186	3.381

Table 7. Dipole Moment Variations $\Delta\mu$ (in D) During PQ Transition $\Delta\mu = \mu_Q - \mu_P$.

Molecules	Gas phase	Cyclohexane	CCl ₄	Median
A	1.468	1.882	1.925	1.882
B	1.212	1.556	1.600	1.556
C	1.936	2.361	2.417	2.361
D	1.680	2.110	2.168	2.110
E	2.154	2.540	2.594	2.540

3.2.3. Effect of the Solvents on the Energy Variations During the PQ Transition

The PQ transition energies were modified according to the nature and solvent dipole moment. They were more important in the gas phase than in liquids (Table 8; Figure 8). In addition, the polar ones lowered them more significantly than nonpolar. These trends were contradicted by the Kruskal-Wallis's test; the differences between the results of the three solvents (vacuum, $n=5$; cyclohexane, $n=5$; CCl₄, $n=5$) weren't significant ($\chi^2(2, n=15) = 4.340$; $p=0.114$) (Table 8). The energy variations were of the same magnitude order in the three environments. A similar tendency was observed for the dipole moment.

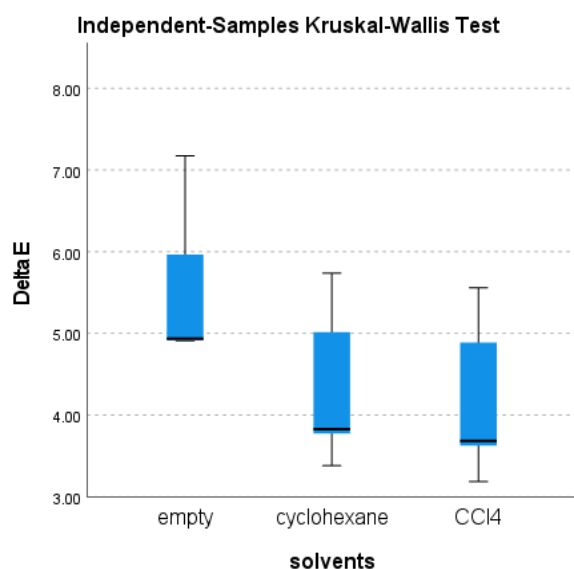


Figure 8. Simple Box of the Energy Variations ΔE (kcal.mol^{-1}) by the Solvents.

Table 8. ΔE across Solvents- Independent-Samples Kruskal-Wallis Test Summary.

Total N	15
Test Statistic	4.340 ^{a,b}
Degree of Freedom	2
Asymptotic Sig.(2-sided test)	0.114

a. The test statistic is adjusted for ties.

b. Multiple comparisons aren't performed because the overall test doesn't show significant differences across samples.

3.2.4. Effect of Solvent on Dipole Moment Variations During the PQ Transition

The dipole moments increased during the PQ transition with those of the solvents (Table 9; Figure 9). The more polar the latter, the more they grow (Figure 9, Table 9). This hypothesis was refuted by Kruskal-Wallis's test; the differences between the three dissolvers (vacuum, n=5; cyclohexane, n=5; CCl₄, n=5) weren't significant ($\chi^2(2, n=15) = 3.120$; p=0.2) (see Table 10).

Table 9. Dipole Moment Variations $\Delta\mu$ (in D) during the PQ transition.

Structures	Gas phase	Cyclohexane	CCl ₄	Median
A	1.468	1.882	1.925	1.882
B	1.212	1.556	1.600	1.556
C	1.936	2.361	2.417	2.361
D	1.680	2.110	2.168	2.110
E	2.154	2.540	2.594	2.540

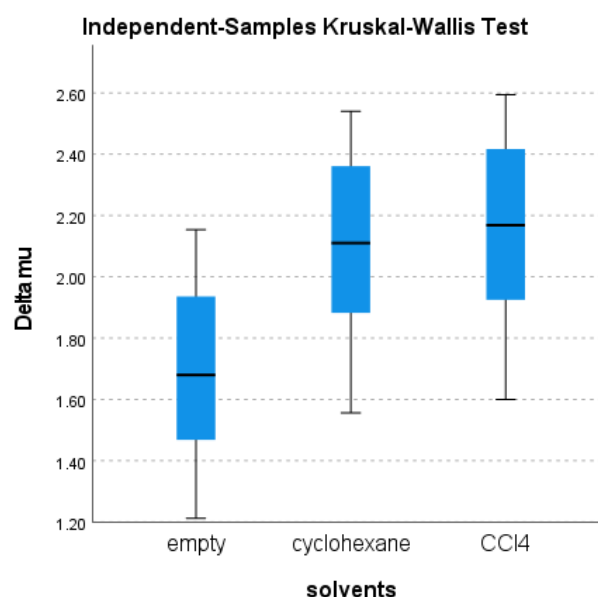
$$\Delta\mu = \mu_Q - \mu_P$$

Table 10. $\Delta\mu$ across solvents- Independent-Sample Kruskal-Wallis Test Summary.

Total N	15
Test Statistic	3.120 ^{a,b}
Degree of Freedom	2
Asymptotic Sig.(2-sided test)	0.21

a. The test statistic is adjusted for ties.

b. Multiple comparisons aren't performed because the overall test doesn't show significant differences across samples.

**Figure 9.** Simple Box of the Dipole Moments Variations $\Delta\mu$ (D) by the Solvents.

The differences $\Delta\mu$ in the three dissolvers (vacuum, n=5; cyclohexane, n=5; CCl₄, n=5) weren't significant; the test conduit at $\chi^2(2, n=15) = 3.120$; p = 0.210. Under these conditions, the solvents had no effect on the energies or dipole moments associated with the salicylideneamines PQ transition. In a word, the number of phenolic or quinones compounds linked to this process was hardly modified by their polarities.

3.3. Analysis and Interpretation of NBO Calculations

The variations in electron density contribute to the stabilization of molecular structures. NBO were used to characterize them. In this work, the electronic transitions of the following types were concerned: σ to σ^* , π to π^* , σ to LP and from π to LP, LP to σ^* and finally from LP to π^* . The stabilization energy threshold adopted was set at 1 kcal.mol⁻¹ to eliminate very insignificant ones [15]. The aim was to determine the steadying electronic transitions of the tautomers, as well as those that strengthen the cohesion of their associations into dimers.

3.3.1. σ to σ^* Type Transitions

The bonds between carbon, oxygen, nitrogen and hydrogen atoms participate in these types of transitions. Those selected with the stabilization energy threshold E(2) greater than 1 kcal.mol⁻¹ have proven that these represent a substantial proportion in each complex. Their values didn't exceed 9 kcal.mol⁻¹. These electronic transitions took place within the same entity. They didn't contribute to their stabilization.

3.3.2. π to π^* Transitions

Electronic transitions from π to π^* type involved nitrogen and oxygen atoms, ensuring conjugation in each part of the complex. In all salicylideneamines, their stabilization energies were higher than those of the σ to σ^* categories except for a few like $E(2) \leq 5$ kcal.mol⁻¹. Fragments of the QQ complex were stabilized; all these transitions were intramolecular. The benzylidene rings were steadied. The conjugation of the π -system with the imine chain was reflected. P monomers were further strengthened by these electronic transitions.

In the PQ complex, each tautomer was steadied by electronic transitions from π to π^* . The greatest stabilization came from these:

$\pi(\text{C18-C19})$ to $\pi^*(\text{C20-C21})$ of $E^{(2)} = 30.06$ kcal.mol⁻¹ with charge transfer 92.29 me.

$\pi(\text{C20-C21})$ to $\pi^*(\text{C18-C19})$ of $E^{(2)} = 27.73$ kcal.mol⁻¹ with charge transfer 84.68 me.

The Q tautomer was only concerned. However, other transitions such as those with lone pairs of oxygen or nitrogen atoms were also involved.

For the QQ dimer, stabilization energies associated to benzylidene rings and branching chains were low. This result was consistent with the energy levels of the P and Q monomers.

3.3.3. LP to σ^* and LP to π^* Transitions

These transitions are summarized in Table 11. The intramolecular, intermolecular and pseudo-cycle charge transfers of the P or Q tautomers and the P-Q or Q-P salicylideneamines were shown. The role of heteroatoms in fragment stabilization was highlighted.

For the P tautomer, the Lp of N12, O14 and O16 and the σ^* orbitals of the C10-H11, C4-C5, C5-C6 bonds were respectively involved by the intramolecular transfers of the Lp type to σ^* . In detail, that of the O16-H17 was also moved by N12. For the first three, the stabilization energies were in the same order, 13.15, 10.96 and 9.54 in kcal.mol⁻¹. Their charge transfers were respectively 16.73, 11.11 and 9.45 in me. The contribution of the latter to P stabilization was less than that of the Lp to π^* transitions from C6 carbon to the π^* orbitals of C1-C2 and C10-N12 bonds. The stabilization energies were respectively 104.29 kcal.mol⁻¹ and 66.40 kcal.mol⁻¹, with charge transfers of 849.82 me and 612.88 me. For tautomer Q, the Lp of O33, O31 and C23 atoms concerned to the intramolecular ones. The Lp(1)O33 and the σ^* orbitals of the C21-C22 and C22-C23 bonds, with respective stabilization energies of 19.07 and 14.39 kcal.mol⁻¹, and charge transfers of 26.07 and 19.67 me were involved to the Lp to σ^* transitions. The O31 atom moved electronic charges from its Lp(1) to the σ^* orbital of the C21-C22 bond, with a stabilization energy of 10.08 kcal.mol⁻¹ and a TC=10.58 me. It was implicated in another, much more stabilizing electronic transition to charge transfer to the π^* orbital of the C20-C21 bond. The stabilizing

energy of this transition was 38.53 kcal.mol⁻¹ with a TC=98.91 me. The C23 atom participated in a strong stabilization through electronic charge transfers from Lp(1)C23 to the π^* orbitals of the C18-C19 and C27-N29 bonds. The corresponding stabilization energies were 78.91 kcal.mol⁻¹ and 205.70 kcal.mol⁻¹ with respective TC of 512.58 me and 1910.12 me.

The most effective were of the LP type of π^* . The most decisive were Lp(1)C23 to $\pi^*(\text{C27-N29})$. Its energy reached 205.7 kcal.mol⁻¹. It was associated with a CT of 1910.2 me. The next three had energies of 104.29 kcal.mol⁻¹, 76.91 kcal.mol⁻¹ and 66.4 kcal.mol⁻¹. Their TC were equalled to 849.82 me, 512.58 me and 612 me respectively. They're intramolecular. The fragments Q and P were concerned. Only one transition of this nature remained less stabilizing than that from Lp to σ^* . Its energy dropped to 38.53 kcal.mol⁻¹ with a TC of 98.91 me. It followed that of Lp(1)N12 to $\sigma^*(\text{O16-H17})$. The transition was associated with an energy of 45.26 kcal.mol⁻¹ and a TC of 56.24 me. It was one of the few presents in pseudo-cycles.

The other two were Lp(2)O33 to $\sigma^*(\text{C21-C22})$ and Lp(1)O33 to $\sigma^*(\text{N29-H34})$. They corresponded respectively to energies of 23.75 (CT= 33.44 me) and 9.43 kcal.mol⁻¹ (CT = 9.1 me). There were 11 intramolecular transitions. Of these, seven concerned the P or Q fragments. The additional four referred to the Q-P or P-Q dimers. The tautomerism in salicylideneamines was favoured by these transitions of the LP to π^* type; moreover, these occurred within the P or Q shards. The most decisive was Lp(1)C23 to $\pi^*(\text{C27-N29})$. It arose in a Q fragment. These transitions can also arrive in P-Q or Q-P dimers.

Q-P dimers are stabilized by two double transitions: Lp(1)O16 to the $\sigma^*(\text{O31-H32})$ orbitals and LpO33 to $\sigma^*(\text{O14-H15})$. Their energies were 15.73 kcal.mol⁻¹ (TC = 14.61 me) and 9.69 kcal.mol⁻¹ (TC = 15.43) respectively. Those in favour of P-Q were: Lp(1)O16 to $\sigma^*(\text{O31-H32})$ and Lp(1)O16 to $\sigma^*(\text{O31-H32})$. They were intermolecular, suggesting the hydrogen bonds presence between the P and Q fragments of salicylideneamine. Moreover, these transitions were the least influential of 18 selected.

Electronic charge transfer interactions of the type Lp to σ^* and Lp to π^* also occurred within the PQ dimer. The most significant were those with the highest stabilization energies. They're grouped in Table 12. The intramolecular, intermolecular and pseudo-cycle charge transfers for each tautomer are shown. In the QQ complex, they appear with the same charge transfers in both fragments. The strongest stabilizing transitions were as follows: $\pi(\text{C3-C4})$ to $\pi^*(\text{C5-O16})$ and $\pi(\text{C21-C20})$ to $\pi^*(\text{C22-O33})$ of $E^{(2)} = 49.35$ kcal.mol⁻¹ and charge transfer CT= 190.59 me.

$\pi(\text{C3-C4})$ to $\pi^*(\text{C1-C2})$ and $\pi(\text{C21-C20})$ to $\pi^*(\text{C19-C18})$ of $E^{(2)} = 27.63$ kcal.mol⁻¹ and charge transfer CT= 84.68 me.

$\pi(\text{C1-C2})$ to $\pi^*(\text{C3-C4})$ and $\pi(\text{C19-C18})$ to $\pi^*(\text{C21-C20})$ of stabilization energy $E^{(2)} = 28.48$ kcal.mol⁻¹ and charge transfer CT= 84.42 me.

$\pi(\text{C5-O16})$ to $\pi^*(\text{C3-C4})$ and $\pi(\text{C22-O33})$ to $\pi^*(\text{C21-C20})$ with $E^{(2)} = 4.18 \text{ kcal.mol}^{-1}$ and charge transfer $\text{CT} = 10.62 \text{ me}$.

The first reflected a higher electron density on the oxygen atoms, while the second and third illustrated each entity of the complex's stabilization by conjugation of the π -system. The last confirmed charge transfer to this atom. Between the two compounds, their contributions were predominantly low energy. These energies didn't exceed $0.6 \text{ kcal mol}^{-1}$. Charge transfers were less than 0.8 me . Apart from this majority, two steadying intermolecular transitions of $E^{(2)} = 14.52 \text{ kcal.mol}^{-1}$ reinforced the stability of the complex: $\text{Lp}(\text{O33})$ to $\sigma^*(\text{H15-O14})$ and $\text{Lp}(\text{O16})$ to $\sigma^*(\text{H32-O31})$. They were associated with a charge transfer of 13.63 me . They evi-

denced that the two fragments of the QQ structure's stabilization occurred via intermolecular hydrogen bonds. These interactions were weaker than their intramolecular counterparts formed with the oxygen atoms O33 and O16.

For the PP complex, the steadying transitions referred to the π to π^* type. Their stabilization energies ranged from 29 to 49 kcal.mol^{-1} . They're listed in Table 11. π conjugation within the benzylidene ring was demonstrated by these electronic transitions. The nitrogen of the six-membered pseudo-ring was considered. Charge transfers of 105.80 me and 31.95 me corresponded to electronic transitions $\pi(\text{C5-C6})$ to $\pi^*(\text{C10-N12})$ in the first entity and to $\pi(\text{C18-C23})$ to $\pi^*(\text{C27-N29})$ in the second.

Table 11. π to π^* type electronic transitions in PP complex.

Electronic transitions		$E^{(2)} (\text{kcal.mol}^{-1})$	CT (me)
$\pi(\text{C1-C2})$	$\pi^*(\text{C3-C4})$	37,57	123,10
$\pi(\text{C1-C2})$	$\pi^*(\text{C5-C6})$	33,46	113,81
$\pi(\text{C3-C4})$	$\pi^*(\text{C1-C2})$	39,58	133,47
$\pi(\text{C3-C4})$	$\pi^*(\text{C5-C6})$	46,62	162,57
$\pi(\text{C5-C6})$	$\pi^*(\text{C1-C2})$	40,43	134,35
$\pi(\text{C5-C6})$	$\pi^*(\text{C3-C4})$	31,99	103,97
$\pi(\text{C5-C6})$	$\pi^*(\text{C10-N12})$	29,01	105,80
$\pi(\text{C18-C23})$	$\pi^*(\text{C19-C20})$	35,25	120,87
$\pi(\text{C18-C23})$	$\pi^*(\text{C27-N29})$	31,95	113,29
$\pi(\text{C19-C20})$	$\pi^*(\text{C18-C23})$	48,04	180,00

Charge transfers within each fragment of the complex stabilized their tautomers. Two ensured balances between their pieces: $E^{(2)} = 6.32 \text{ kcal.mol}^{-1}$ and $E^{(2)} = 9.31 \text{ kcal.mol}^{-1}$ associated with the following electronic transitions:

Electronic transfers between oxygen atoms O16 and O33 to groups O31-H32 and O14-H15 reflect stabilization by hydrogen bonds between the two shards of the PP dimer.

For the P tautomer, the Lp of N12, O14 and O16 and the σ^* orbitals of bonds C10-H11, C4-C5 and C5-C6 were involved to intramolecular transfers of the Lp type to σ^* . The stabilization energies, in kcal.mol^{-1} , were 13.15, 10.96 and 9.54 respectively. They corresponded, in me, to charge transfers of 16.73, 11.11 and 9.45. Their contribution was less than that of the Lp type from C6 carbon to the π^* orbitals of C1-C2 and C10-N12. The stabilization energies were $104.29 \text{ kcal.mol}^{-1}$ and $66.40 \text{ kcal.mol}^{-1}$ in the same order, with charge transfers of 849.82 me and 612.88 me. For tautomer Q, the Lp of atoms O33, O31, C23 was concerned with the intramolecular ones. The $\text{Lp}(1)\text{O33}$ and the σ^* orbitals of the C21-C22 and C22-C23 were involved to Lp to

σ^* transitions. Their stabilization energies were $19.07 \text{ kcal mol}^{-1}$ and $14.39 \text{ kcal mol}^{-1}$ with their charge transfers of 26.07 and 19.67 me respectively. The O31 atom transferred electronic charges from its $\text{Lp}(1)$ to the σ orbital of the C21-C22, with a stabilization energy of $10.08 \text{ kcal.mol}^{-1}$ and a $\text{TC} = 10.58 \text{ me}$. It was involved in another, much more stabilizing electronic transition by transferring charges to the π^* orbital of the C20-C21. The steadying energy of this transition was $38.53 \text{ kcal mol}^{-1}$ with $\text{TC} = 98.91 \text{ me}$. The C23 atom participated in a strong stabilization through electronic charge transfers from $\text{Lp}(1)\text{C23}$ to the π^* orbitals of the C18-C19 and C27-N29 bonds. The corresponding stabilization energies were $78.91 \text{ kcal.mol}^{-1}$ and $205.70 \text{ kcal.mol}^{-1}$ with respective TC of 512.58 me and 1910.12 me.

The π systems contributed strongly to the stabilization of the P and Q tautomers in the PQ complex. The six-membered pseudo-cycle of the P was more steadied than that of the Q. This was reflected in their energies and their charge transfers. For the P, the electronic transition $\text{Lp}(1)\text{N12}$ to $\sigma^*(\text{O16-H17})$ from $E(2) = 45.24 \text{ kcal.mol}^{-1}$

was more stabilizing. It was more steady than Lp(2)O33 to $\sigma^*(\text{N29-H34})$ of $E(2) = 23.75 \text{ kcal.mol}^{-1}$. The latter concerned Q. Charge transfer was higher in the P pseudo-cycle than in the Q. The two tautomers in the complex interacted. Each molecular entity moved charges to the other. Their displacement contributed to the stability of the complex. The atoms O16 belonging to P and O33 to Q was their starting points. The steady intermolecular interactions were en-

sured by two double transitions. The first was that of Lp(1)O16 with $\sigma^*(\text{O31-H32})$ orbitals. The second was that of LpO33 at $\sigma^*(\text{O14-H15})$. The ($E^{(2)}$; CT) pairs were (7.12; 7.32) and (7.97; 10.43) for O16 and (15.73; 14.61) and (9.69; 15.43) for O33. The existence of hydrogen bonds between the two entities in the complex was proven by these electronic transitions.

Table 12. Lp-Type Electronic Transitions to σ^* or π^* Orbitals in PQ Complex.

Electronic transitions		$E^{(2)} (\text{kcal.mol}^{-1})$	CT (me)	Environment	Fragment
Lp(1)N12	$\sigma^*(\text{C10-H11})$	13,15	16,73	Intramolecular	P
Lp(1)N12	$\sigma^*(\text{O16-H17})$	45,26	56,24	Pseudo-cycle	P
Lp(1)O14	$\sigma^*(\text{C4-C5})$	10,96	11,11	Intramolecular	P
Lp(1)O16	$\sigma^*(\text{C5-C6})$	9,54	9,45	Intramolecular	P
Lp(1)O16	$\sigma^*(\text{O31-H32})$	7,12	7,32	Intermolecular	P-Q
Lp(1)O16	$\sigma^*(\text{O31-H32})$	7,97	10,43	Intermolecular	P-Q
Lp(1)O33	$\sigma^*(\text{O14-H15})$	15,73	14,61	Intermolecular	Q-P
Lp(3)O33	$\sigma^*(\text{O14-H15})$	9,69	15,43	Intermolecular	Q-P
Lp(1)O33	$\sigma^*(\text{N29-H34})$	9,43	9,1	Pseudo-cycle	Q
Lp(2)O33	$\sigma^*(\text{C21-C22})$	19,07	26,07	Intramolecular	Q
Lp(2)O33	$\sigma^*(\text{C22-C23})$	14,39	19,67	Intramolecular	Q
Lp(2)O33	$\sigma^*(\text{N29-H34})$	23,75	33,44	Pseudo-cycle	Q
Lp(1)O31	$\sigma^*(\text{C21-C22})$	10,08	10,58	Intramolecular	Q
Lp(2)O31	$\pi^*(\text{C20-C21})$	38,53	98,91	Intramolecular	Q
Lp(1)C6	$\pi^*(\text{C1-C2})$	104,29	849,82	Intramolecular	P
Lp(1)C6	$\pi^*(\text{C10-N12})$	66,40	612,88	Intramolecular	P
Lp(1)C23	$\pi^*(\text{C18-C19})$	76,91	512,58	Intramolecular	Q
Lp(1)C23	$\pi^*(\text{C27-N29})$	205,70	1910,12	Intramolecular	Q

3.4. Analyses and Interpretation of the Salicylideneamines Topological Properties: QTAIM Calculations

The analyses related to fragment interactions in the PP, PQ and QQ complexes of salicylideneamines. Their energies are shown in the last column of each table. The processing of the AIM calculations focused on the areas in which the two shards of the complexes had interacted. The critical connection points materializing the long-range interactions in these complexes have been specified. And PQ complexes were linked to the negative sign of the local electronic energy

density ($H(r) < 0$). This was accompanied by a weak electron density amplitude around 0.01. The three parameters were connected by the Abramov relation [17]. They obeyed the following equations:

$$2G + V = \frac{1}{4} \nabla^2 \rho \quad \text{with local energy density } H = G + V.$$

The kinetic energy density translates into the so-called Abramov relation [17].

$$G = \left(\frac{1}{10}\right) (3\pi^2)^{\frac{2}{3}} \rho^{\frac{5}{3}} + \left(\frac{1}{72}\right) \frac{(\nabla \rho)^2}{\rho} + \left(\frac{1}{6}\right) \nabla^2 \rho$$

The quantities $G(r)$ and $V(r)$ were of opposite sign. $V(r)$,

was negative while $G(r)$, was always positive. When $H(r) < 0$, the constraint was to respect the inequality $|V(r)| > G(r)$.

For all complexes, $G(r)$ was always positive and $V(r)$ negative. The signs of these two parameters were consistent with the ionic nature suggested for the long-range interactions within them. The relationship $\rho(r) > G(r)$ was respected. This relationship led to $G(r)/\rho(r)$ being less than unity. The interactions weren't purely ionic. In other words, they were partially covalent. The ratios $(-G(r)/V(r))$ had values between 0.81861475 and 0.99583146. They were all positive. They were framed by the relationship $0.5 < -G(r)/V(r) < 1$. This relationship, defined by [16, 18], confirmed that hydrogen bonds were partially covalent in these complexes.

4. Conclusion

Solvation contributed to strengthening the proportions of the quinone form. The variations in the dipole moments of the tautomers were such that $\Delta\mu = \mu_Q - \mu_P > 1$. For all molecular structures, the order of dipole moments was declined by $\Delta\mu_{vacuum} < \Delta\mu_{cyclohexan} < \Delta\mu_{CCl_4}$. The variations in dipole moments were greater than 2 Debye for molecular structures C, D and E in cyclohexane and CCl_4 . These tautomers can be characterized by their measurements. Solvation enhanced monomer stability, while dimer association provided additional equilibration. A few elements influenced the tautomerism of salicylideneamines.

Electronic factors highlighted the presence of intra- and intermolecular interactions. Their transitions of the $\sigma \rightarrow \sigma^*$ and $\pi \rightarrow \pi^*$ types reinforced tautomeric stability. Those of the $Lp \rightarrow \sigma^*$ and $Lp \rightarrow \pi^*$ type involved the heteroatoms of PP, PQ and QQ complexes. They steadied the dimer associations of tautomers. The existence of long-distance interactions characterized during AIM topological analyzes was confirmed. These entities were stabilized through hydrogen bonds established between heteroatoms and hydrogen favourable to these interactions. The energies of intramolecular hydrogen bonds in the six-membered pseudo-ring contributed to the relative stability of phenolic tautomers. Difficulties in resolving infrared spectra of salicylideneamines have been compounded by the addition of substituents on the imine nitrogen, particularly when these radicals contained phenyl or alkyl groups. Solvents influenced the characteristic vibration frequencies of tautomers.

Abbreviations

PP	Phenolic-Phenolic
PQ	Phenolic-Quinonic
QQ	Quinonic-Quinonic
HF	Hatree-Fock
DFT	Density Functional Theory
NBO	Natural Bond Orbitals
QTAIM	Quantum Theory of Atoms in the Molecule

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Conflicts of Interest

The authors declare no conflicts of interest.

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