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The energy of the intramolecular hydrogen bond in chloro-substituted *N*-methyl-salicylidene imines

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Abstract

The energetic effects of the conformational rearrangement of eight Schiff bases, differently chloro-substituted, are discussed on the basis of the results of B3LYP/6-31+G(d,p) calculations. The proton transfer tautomers as well as "open"-non-hydrogen-bonded forms were considered. It was found, that the hydrogen-bonded forms have the lowest energy, but the second most stable were the proton transfer states with an O...H—N intramolecular hydrogen bond. The proton transfer in Schiff bases dominates in comparison to other conformational rearrangements. This is important for the understanding of thermochromic and photochromic properties of these molecules.

By using a thermodynamic cycle, the steric effects connected with chelate ring formation are estimated to be up to 5 kcal/mol, much higher than in related Mannich bases (~1 kcal/mol) which do not form resonance assisted hydrogen bonds. Accounting these effects the "real" value of the energy of hydrogen bond formation was estimated to be 15 kcal/mol which increases with growing number of chlorine atoms up to 16.5 kcal/mol for 4,5,6-trichloro substitution.
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Keywords: Hydrogen bonding; Schiff bases; Intramolecular hydrogen bond energy; Structural effects

1. Introduction

Salicylidene imines (*ortho*-hydroxy Schiff bases) reveal very interesting thermochromic and photochromic properties. Because of various applications, they became a topic of numerous recent publications [1–12]. These substances are able to form intramolecular hydrogen bonds with the possibility of ground- and excited-state proton transfer. This process is the basis of the above mentioned photo- and thermochromic properties of these compounds.

A specific feature of these hydrogen bonds is a direct π-electron coupling between acid base groups [13] which occurs also after proton transfer [14].

In this work, we aim to estimate the energy of the intramolecular hydrogen bond using the technique previously proposed for Mannich bases [15], as well as to describe the structure modifications resulting from the formation of the hydrogen bond. We are going to continue the comparison of these two classes of compounds – with electron coupling – Schiff bases and without – Mannich bases.

A potential ability for the proton transfer in hydrogen bonds is generally characterized by ΔpK_a ($= pK_a$ (BH^+) − pK_a (AH)) parameter, because it is proportional to the difference between the proton attraction by two A^- and B centers in A—H···B system [16]. Numerous structural and spectroscopic parameters of hydrogen-bonded systems correlate with ΔpK_a [17], which in this sense appears to be a potential measure of the strength of hydrogen bonding interactions. The energetic measure of the strength of these interactions ($\Delta E°_{HB}$) is another property of hydrogen bonding, interesting to know, but not easy to determine, even to define, especially of intramolecular hydrogen bonds [18].

In the case of intramolecular hydrogen bonds it is not possible to define $\Delta E°_{HB}$ as a difference between the energy of two separate components of the hydrogen-bonded com-

plex and the complex at minimum energy. An alternative approach in this case is to compare the energy of the structure with intramolecular hydrogen bond and an open form, with broken hydrogen bonds [18,19]. However, often there are a few conformers without intramolecular hydrogen bonds and the problem arises which of them should be used as a reference structure. To solve this problem, the energy of all possible conformers should be compared [19]. We have previously proposed an approach using a thermodynamic cycle scheme [15].

It consists of a hydrogen-bonded form (**2** in Scheme 1), the forms with the O—H group turned around the C—O bond by 180° (**1**) or the methylimine group turned around the C—C bond (**3**). The form **4** has the lowest energy of all open conformers and, generally, is the best possible reference state.

Using such a cycle, one is additionally able to estimate the steric contributions to the energy differences between **1**, **3** and **4** forms, which should also be included while going from conformer **4** to **2**. Otherwise, the absolute value of the energy of the intramolecular hydrogen bond established as a difference between conformer **2** and **4**, will be decreased by the value of the enhancement of the steric interaction between two approaching acid base groups. In our previous work [15], we successfully applied such a procedure to intramolecular hydrogen bonds in Mannich bases.

We aim to compare these results with the behaviour of a wide series of chlorine-substituted Schiff bases. In that way, the uniform character of the substitution and the structure of the complexes will be kept in broad range of ΔpK_a values. The studies of substituent effects on intramolecular hydrogen bonding in Schiff bases were performed earlier, but with emphasis on the changes of the substituents at the nitrogen atom of salicylidene imines [20,21].

Additionally, Mannich bases substituted at the 3 position form a different class of systems with enhanced

stability of intramolecular hydrogen bonds [22]. In the approach of this work, we included all eight differently chloro-substituted derivatives of Schiff bases without substitution at position 3 (see Scheme 2).

We also want to learn to what extent the more rigid structures of Schiff bases influence the steric components of the energy of states. One should account the differences resulting from the O—H···Cl hydrogen bond in some open forms of Schiff bases. To answer this question, independent calculations for 6-chloro-substituted phenols were performed, for both the closed and open forms.

In the top line in Scheme 2, the labels of the compounds are given. In contrast to Mannich bases and many other compounds with intramolecular hydrogen bonds like for example *ortho*-hydroxy benzaldehyde [25], the calculations show that in Schiff bases the intramolecular proton transfer reaction in the ground-state can proceed comparatively easy [14,26]. It is also seen from the results of this work. Therefore, also the states with proton transfer (PT) were included (**5**), as well as the states obtained by opening the hydrogen bond in the PT tautomer (**6**, Scheme 1). In that way, one also can estimate the energy of the intramolecular hydrogen bond in PT state, as well as the energy of intramolecular proton transfer reaction. Results of this work (Table 1) show, that the difference of the energy of these tautomers relative to the energy of tautomer **2** drops with the number of chloro-substituents, reaching, in the gas phase, 2 kcal/mol for 4,5,6-trichloro-substituted Schiff base. Both structures **5** and **6** are used to represent the proton transfer reaction in the ground-state as well as the open form of this hydrogen bond. This graphical presentation uses only one of the conceivable resonance structures. The results of the calculations, given below, clearly point out, that in **5** the content of the zwitterionic form is about 40% in the ground-state while in **6**, the keto-amine (*ortho*-quinoid)
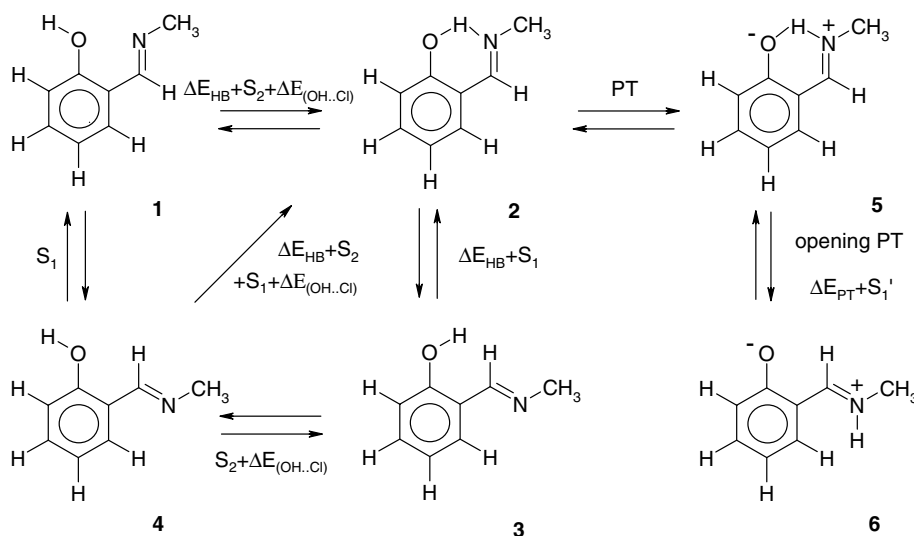
Scheme 1.

position	0 (9.92)	a (9.37)	b (8.73)	c (8.52)	d (8.61)	e (7.90)	f (7.70)	g (6.97)
3	H	H	H	H	H	H	H	H
4	H	Cl	H	H	Cl	Cl	H	Cl
5	H	H	Cl	H	Cl	H	Cl	Cl
6	H	H	H	Cl	H	Cl	Cl	Cl

Scheme 2. Labelling system in chloro-substituted Schiff bases. (The numbers in brackets are pK_a values of the corresponding phenols, which were used in the correlations throughout [23,24].)

Table 1
Dependence of calculated energies (kcal/mol) of six particular states (Scheme 1) on Cl-substitution

Conformer	**1**	**2**	**3**	**4**	**5**	**6**
Substituent						
H-	13.95	0.0	11.60	9.93	4.33	15.12
4-Cl-	13.97	0.0	11.53	9.89	3.97	14.41
5-Cl-	14.18	0.0	11.74	10.12	3.26	13.94
6-Cl-	11.17	0.0	12.05	7.00	3.02	13.61
4,5-diCl	14.01	0.0	11.62	9.94	3.41	13.93
4,6-diCl-	11.24	0.0	11.97	7.00	2.73	12.95
5,6-diCl-	11.38	0.0	12.16	7.07	2.01	12.67
4,5,6-triCl-	11.18	0.0	12.02	6.85	2.21	12.36

ΔE values are presented as differences to the most stable intramolecularly hydrogen-bonded structures (**2**).

resonance forms participate stronger in the resonance description of the ground-state (about 70%). The proton transfer reaction is defined as it is shown in Scheme 3.

Also experiments (electron absorption spectra [27] and crystallography [28]) state, that the π-electron coupling in Schiff bases facilitates the proton transfer along the intramolecular hydrogen bond, especially with substitution of electron withdrawing groups. Such a possibility was not accounted for Mannich bases; the calculations do not predict a second minimum on the potential energy curve in non-polar and weak-polar surrounding [26].

2. Calculation procedure

The energies and structures of six conformers, presented in Scheme 1, for eight molecules were calculated with Gaussian03 program [29] at the B3LYP/6-31+G(d,p) level. This approach, especially since the papers of Hargittai [30–34] is widely used in the literature [35–37]. Localization of minima was controlled by vibrational spectra calculations.
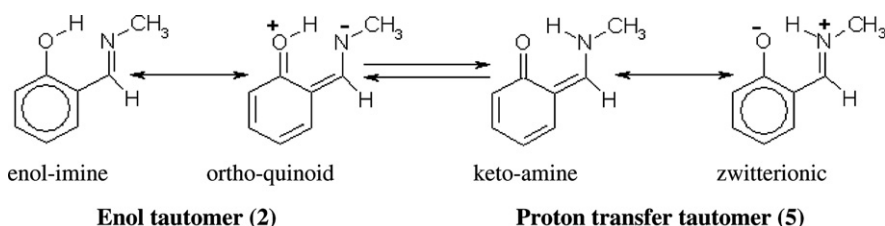
The energetic relations between all six structures are defined in Scheme 1. The partitioning of particular energy differences is also presented in this scheme. The energy of steric repulsion of the C=N—CH$_3$ group when approaching the oxygen and carbon atoms of the C—O bond is represented as S_1. S_2 is equal to the difference in energy between conformers **3** and **4** and describes the non-bonded interaction of the OH group, when it is in *syn* arrangement to the second substituent. When there is a chlorine substituent located at position 6 one has to account additionally the energy required for the breaking of the intramolecular O—H...Cl hydrogen bond in **4** and **1**. The values of this ΔE(O—H...Cl) interactions were independently estimated by comparison of the energy of a "parent" chloro-phenol in bonded and open conformation (cf. [15]).

The differences between **2** and **3** as well as between **2** and **1** states contain a "real" energy of hydrogen bond ΔE_{HB} corrected for S_1, S_2 and ΔE(O—H...Cl) interactions, respectively. Using the rules of a thermodynamic cycle, there are two ways of the estimations of ΔE_{HB}

$$\Delta E_{HB} = [E(2) - E(3)] - [E(1) - E(4)] \qquad (1)$$
$$\Delta E_{HB} = [E(2) - E(1)] - [E(3) - E(4)] \qquad (2)$$

which are identical from a numerical aspect. Another aim of this study is the estimation of the S_1 and S_2 parameters, which represent the steric decrement of the energy of the intramolecular hydrogen bond when calculated as a difference between **2** and **4** conformers, as it is proposed in the literature [19]. According to Scheme 1, S_1 can be obtained directly as a difference between energy of **1** and **4**. To estimate S_2, an independent way of ΔE(O—H...Cl) interaction in the open forms of the compounds containing a 6-chloro-substituent was applied, assuming that it is equal to the difference in energy of related phenols in theirs closed and open conformations;

enol-imine　　　　ortho-quinoid　　　　keto-amine　　　　zwitterionic

Enol tautomer (2)　　　　　　　　**Proton transfer tautomer (5)**

Scheme 3. [26,40].

$$S_1 = E(1) - E(4) \qquad (3)$$
$$S_2 = E(3) - E(4) + \Delta E(\text{O—H} \ldots \text{Cl}) \qquad (4)$$

and

$$\Delta E_{HB} = E(2) - E(4) - S_2 - S_1 + \Delta E(\text{O—H} \ldots \text{Cl}) \qquad (5)$$

3. Results and discussion

3.1. Energy of states

Table 1 presents the results of the calculations of the energy of all eight compounds, which were not substituted at position 3. Fig. 1 shows the dependence of the energies of states on pK_a of phenols.

For the structures **1** and **4**, Fig. 1 also shows the values corrected for the energy of the intramolecular hydrogen bond of the O—H···Cl form (**1″** and **4″**, respectively, dotted lines). The correction energy was calculated for particular phenols with *cis* and *trans* arrangement of the OH group with respect to 6-chloro-substituent. We have included into Fig. 1 also the direct (not corrected) values for the structures of **1** and **4**.

The lowest energy, next to **2**, has the state **5** – the form, obtained after proton transfer. In molecules with π-electron coupling proton transfer is much easier than in Mannich bases. Direct coupling between acid base centers decreases the increment of dipole moment upon the proton transfer as well as the work of charge separation in non-polar solvents which becomes much less than in Mannich bases, where charge on oxygen and nitrogen atoms are more localized. In related Mannich bases transfer of proton requires more than 15 kcal/mol, in the gas phase [26].

Another interesting observation is that the slope of the energy dependencies on pK_a is weak for all molecular forms and only becomes significant for the proton transfer states. The substituent effects are compensated to some extent, because the energy is calculated relative to the structure **2** with the same pattern of chloro-substitution as in all conformers of a given substance. Most importantly, however, the substituents influence the basicity of the imine component and the acidity of phenol often in opposite direction, which results in moderate changes of ΔpK_a upon substitution [35–37]. The double open structure **4** has the second lowest energy. After correction on the O—H···Cl hydrogen bond it makes the line almost parallel to the line for **2**, located 10 ± 0.1 kcal/mol higher. Related values for Mannich bases were about 2 kcal/mol less [22]. The difference between curves **4** and **2** represents the energy of intramolecular hydrogen bonds, but not corrected for steric S_1 and S_2 effects. In contrast, the energy difference between HB(**2**) and the proton transfer forms (PT-**5**) clearly decreases with incoming substitution. An increase of the number of chloro-substituents facilitates the proton transfer. This is important for the thermochromic and photochromic properties of Schiff bases [1]. The energy required for the proton transfer in gas phase drops systematically from 4.3 to 2.2 kcal/mol, upon decreasing the pK_a values by three units.

As mentioned in the Section 1, in order to obtain more reliable values of the energy of the intramolecular hydrogen bond, one should estimate the steric factors S_1 and S_2. Such estimations were performed according to the procedure given above (cf. also [15]) using the data of Table 1. The results are presented in Fig. 2.

These parameters depend on the acidity of the phenolic part of a complex. S_1 is regularly increasing with the acidity of phenol; S_2 also grows, but slower with decreasing pK_a. The complexes split into two groups – those containing a chlorine atom at position 6, and those not. A similar tendency is observed also in the S_2 dependence on pK_a. That might be the result of steric pushing of 6 Cl atom on the chelate ring which makes the hydrogen bridge shorter. In Mannich bases, S_1 was within the 1–1.5 kcal/mol range
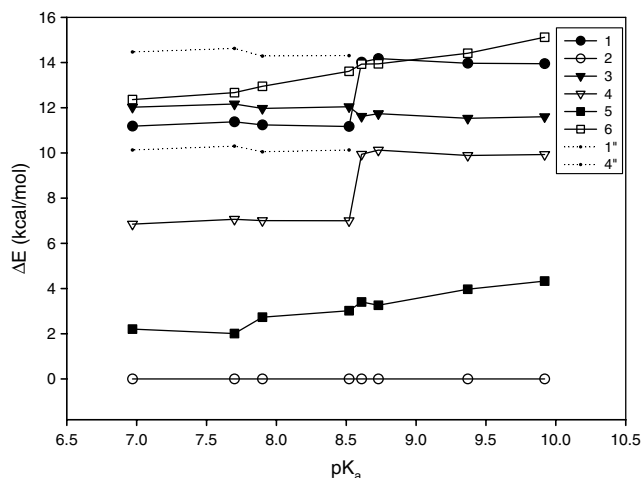

Fig. 1. Dependence of the energy of particular conformers (labelling as in Scheme 1) on pK_a; **1″** and **4″** present the values corrected on the effect of O—H...Cl interactions.
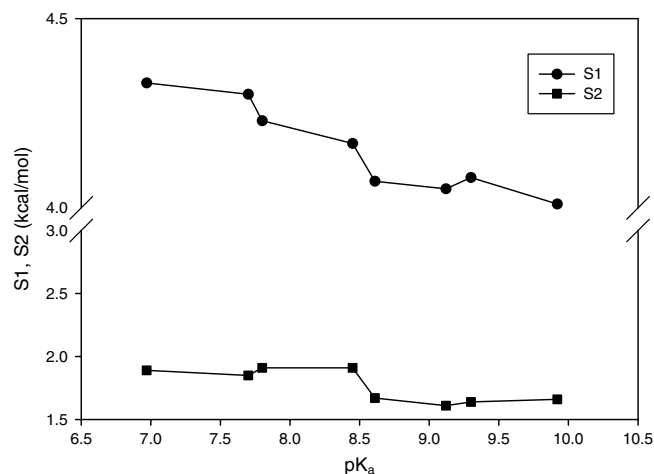

Fig. 2. Energy of non-bonded interactions of methylamine (S_1) and hydroxy groups (S_2) with the core of chelate ring, estimated according to the thermodynamic cycle presented in Scheme 1.

[15], while in Schiff bases it amounts to 4–4.3 kcal/mol. This is due to π-electronic coupling to the C=N—R group. Turning the benzylidene group out of the ring plane requires much more energy than in Mannich bases [38]. S_2 in Mannich bases was within the range 0.9–1 kcal/mol, while in Schiff bases it becomes 1.6–1.9 kcal/mol, again a slight increase due to the planarity of chelate ring in the Schiff bases.

After correcting for S_1 and S_2 factors the estimated values of the energy of the hydrogen bond (ΔE_{HB}) in the enol forms (OH...N) of Schiff bases show the dependence on pK_a, increase with acidity of phenol, Fig. 3.

In Mannich bases [22], for similar phenols the energy of the hydrogen bond was 10–11 kcal/mol and for Schiff bases it is clearly larger in the average 15.7 for the substances without 6-substitution and 16.3 kcal/mol for the compounds with 6-Cl.

Using the results of our calculations, one can also estimate the energy of the formation of hydrogen bond in the zwitterionic form. It can be defined as $\Delta E(6-5) + S_1'$ (Scheme 1). Because of the lack of an appropriate information on S_1', it can be assumed that the S_1' value is close to S_1, which was already used to characterize the steric effects in the reaction $3 \rightarrow 2$.

Fig. 3 demonstrates that the estimated energy of the formation of the zwitterionic hydrogen bond from appropriate ions depends weakly on pK_a. The slope is negative (stronger phenol–weaker interactions). An ionic character of the interaction in such a hydrogen bond is a probable reason. The presented numerical values also show that the intramolecular hydrogen bond in proton transfer form is generally weaker than for the molecular form (2). The difference is, however, of the order of 1–2 kcal/mol, only, from less acidic phenol to more acidic, respectively.

Nevertheless, the energy required for opening the intramolecular hydrogen bond is similar in both forms, of the order of 10 kcal/mol (Table 1). Both intramolecular hydrogen bonds are thermodynamically stable in a similar way. For molecules with 6-Cl-substituent, however, the difference in energy of bonded and open (4) form drops to 7 kcal/mol, due to formation of the competitive O—H...Cl hydrogen bond. The energy of intramolecular proton transfer reaction is 4.4 kcal/mol for non-substituted Schiff base and gradually drops with Cl-substitution down to about 2 kcal/mol for the strongest acids.

3.2. Structural effects

In this work, we aim to discuss the structure changes in relation to substitution in Schiff bases. As we stated previously for Mannich bases [39], these effects can be rationalised as the response to the change of the strength of the hydrogen bond (dependence on ΔpK_a).

In this approach, we also want to answer the question what differences in behaviour of intramolecular hydrogen bonds in Schiff bases result from the direct electronic coupling between acid base groups in these compounds in relation to what was observed in Mannich bases. One specific question is, if the observed effects are larger in Schiff bases in comparison to Mannich bases.

The most direct answer to the question about structural effects resulting from the formation of hydrogen bonds give the structural parameters related to atoms directly involved into A—H—B bridge formation. There are O—H, C—O, H···N and O···(H)N distances (Scheme 4).

Fig. 4 illustrates how the distance (d(OH)) changes upon consecutive chloro-substitution, as the function of pK_a. For the lines of structures 1 and 3, a slight increase of d(OH) is observed, of the order 0.004 Å due to O···H—Cl hydrogen bond like in Mannich bases. A very pronounced increase of phenol d(O—H) is observed when going to structures 2 as a result of hydrogen bond formation. Comparing the results of this paper with those of Ref. [39] one can recognize the larger effects in Schiff bases. Lines 5 and 6 of Fig. 4 present the N—H bond distances evolution. These distances are pronouncedly longer in hydrogen-bonded structures (5) than in open ones (6). The N—H distance in the form 6 changes very little with pK_a, while the N—H distances of forms 5 are seriously extended and show an increase with decreasing acidity of phenol.
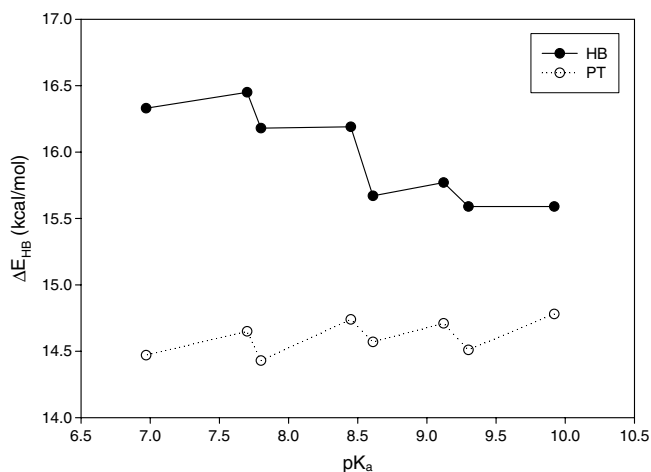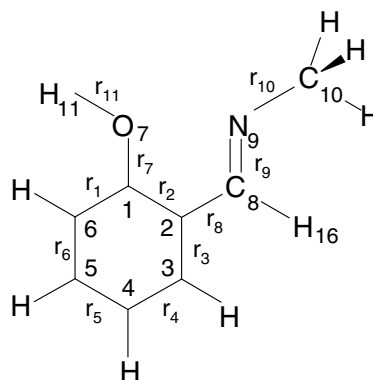

Fig. 3. Energy of hydrogen bond formation in the enol (the 4–2 reaction) and proton transfer form (the 6–5 reaction) according to Scheme 1.
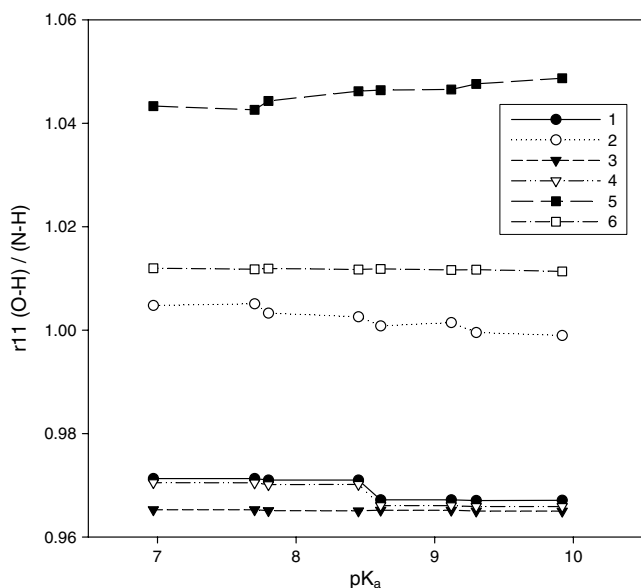

Scheme 4.

Fig. 4. Dependence of O—H distance on pK_a of phenols for all conformers of Schiff bases. Lines 5 and 6 concern the lengths of N—H distances.
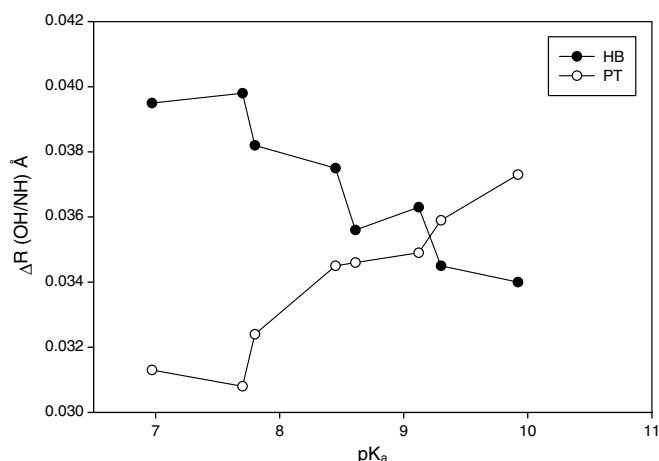

Fig. 5. Increments of O—H and N—H distances calculated as difference between bond lengths in **2** and **3** structures for O—H, and between **5** and **6** structures for N—H.

Fig. 5 shows these differences in a more pronounced way; the d(OH) increments were calculated relative to structure **3**, free of hydrogen bond. The effects are larger (0.034–0.040 Å) than in Mannich bases (0.023–0.028 Å), without 3-Cl-substituents. The effect systematically grows with the number of substituents. The compounds with 6-Cl-substituents form a separate class with larger 0.0375–0.040 Å d(OH) increases. The hydrogen bonding effects in the zwitterionic form are presented as the differences in N—H bond lengths in forms **5** and **6** (Fig. 5). It is clearly seen, that the effect decreases pronouncedly when the pK_a becomes lower. Weakening the acidity of a phenol means an increase of affinity of the O⁻ moiety to the proton – it makes stronger hydrogen bonds (in the sense of mutual

interaction of partners) and the natural consequence is the N—H⁺ bond extension.

C—O distances decrease systematically with the increasing number of chlorine substituents. As it was shown for Mannich bases [39], the changes are parallel for the structures with and without intramolecular hydrogen bond. The slope of this dependence reflects rather the direct influence of substituents on C—O bond length. Some discontinuity of the lines is observed when passing from molecules not containing the 6-Cl atom to compounds with this additional group. The C—O bond shortening due to this effect is of the order of 0.004 Å. Comparing the results presented here with those in [39], for the compounds not containing the 3-Cl group, one observes that the C—O bond lengths are shorter in Schiff bases than in related Mannich bases by about 0.011 Å.

The distances between particular lines describe the effect of hydrogen bond formation. The difference between lines 2 and 3 is 0.0258 ± 0.0003 Å. This decrement was pronouncedly less in Mannich bases (0.017 Å), calculated at B3LY/P 6-31G(d,p) level [39]. However, a specific decrease of C—O bond lengths in conformers **1** seems to be not easy to interpret. Fig. 6 also demonstrates a very pronounced shortening of the C—O distances upon proton transfer. The effect is around 0.0727 ± 0.0003 Å, with no dependence on pK_a. This leads to the conclusion, that the C—O bond lengths hardly can be a measure of the hydrogen bond strength, compare for example the previously mentioned differences between **1**, **3** and **4** structures, but also the differences of C—O bond lengths between **5** and **6** structures. The effects of the formation of proton transferred hydrogen bonds are also weakly dependent on pK_a. One should mention very similar amplitude of changes of C—O bond lengths (0.0251 ± 0.0005 Å) in enol
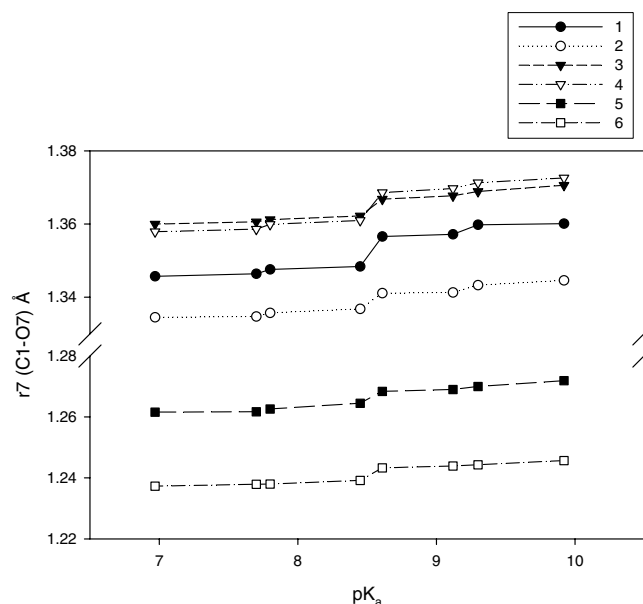

Fig. 6. Dependence of C—O bond lengths in six conformers (labelling as in Scheme 1) on the pK_a of phenols.

and proton transfer hydrogen bonds. Proton transfer leads to more double character of C—O bond, but in contradiction to molecular forms, opening the proton transferred hydrogen bond leads to further extension of the keto character of the states (see further).

The hydrogen bond lengths (O···(H)N) and (O)H···N distances are the direct measures of the character of hydrogen bonding. From this point of view, the results obtained are much more in favour of specific strengthening of hydrogen bond by 6-Cl-substitution. The bridge length is 2.63 Å in non-substituted Schiff base (2.72 Å in Mannich base [39]) and is decreasing with enhancement of the acidity of phenols to 2.62 Å, but for compounds with 6-Cl-substitution the obtained distances form a distinct separate group, they decrease with acidity within the range 2.61–2.60 Å. Parallel to those are changes of H···N distances, which form also two groups, one with values within 1.73–1.72 Å range and the second within 1.70–1.69 Å range. The groups do not overlap.

Fig. 7 presents the correlation between energetic and structural characteristics of hydrogen bonds. This correlation is not perturbed by the participation of the 6-Cl-substitution.

The ring bond distances are sensitive on the formation of intramolecular hydrogen bonding. Even in the non-resonance-enhanced hydrogen bonding (in Mannich bases, [41]) the structural effects can be described by the pattern of an *ortho*-quinoid structure. In the previous work [26] on solvent and substitution effects in three of the compounds presented here (non-substituted, 4- and 4,6-disubstituted) it was shown, that the *ortho*-quinoid character of the phenol ring structure was much more evident than in related Mannich bases.

Formation of the intramolecular hydrogen bond, upon going from structures **4** to **2**, leads to the increase of C1—C2 distance on 0.0125 Å in average (0.0071 Å in Mannich base [41]). It is interesting that steric repulsion alone,

when going from **4** to **1** give half of the effect (0.0075 Å). Proton transfer leads to further elongation of this bond on 0.043–0.039 Å, with the tendency to decrease upon increasing the acidity of the phenol. A similar tendency is observed in the next increase of C1—C2 distance, on 0.021–0.019 Å, while opening the proton transfer hydrogen bonds (**5 → 6**), Fig. 8.

These differences suggest a strong increase of the importance of the *ortho*-quinoid resonance form in describing the structure of the conformers on the way from the open form (**4**) through the hydrogen-bonded (**2**) to proton transfer (**5**) and at the end further to the open proton transfer from (**6**). Similar effects are seen for C1—C6 distance.

Hydrogen bond formation clearly decreases the length of C5—C6 and C3—C4 bonds, while increases the C4—C5 bonds length. These effects are enhanced when going to the proton transfer form and further to open proton transfer structure (**6**).

Some correlation lines of ring bond lengths with pK_a show irregularities related mostly to the local interaction of particular pattern of substituents, for example the C4—C5 bond length pronouncedly increases for a derivative, which contains the combination of 4,5-dichloro-substituents, the C5—C6 bond increases for combination of 5,6-substituents and so on. Nevertheless, the correlations of particular parameters on pK_a are of similar shape for all structures (**1–6**) (Fig. 9). The differences between correlation lines for different conformers also weakly depend on pK_a. They are substantial, however, and can be used to characterize relation between conformers, particularly the effects of hydrogen bonding.

More general statements can be made on the basis of collective characteristics of the structure of the phenol ring. They, according to the definitions given in [14], are the variance of bond lengths (*A*), which already in Mannich bases give pronounced increase on the closing the intramolecular hydrogen bonding, from 6.1 and 5.4 in phenol and benzyl-
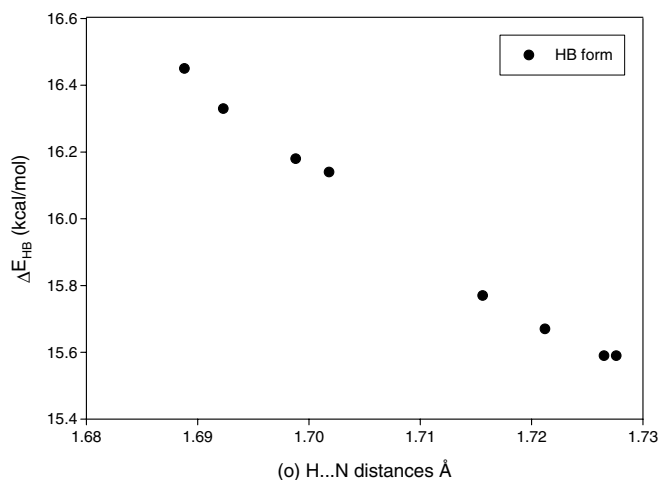
Fig. 7. Correlation of the calculated B3LYP/6-31G(d,p) energy of (O—H···N) form of the hydrogen bond in Schiff bases on (O)H···N distance.
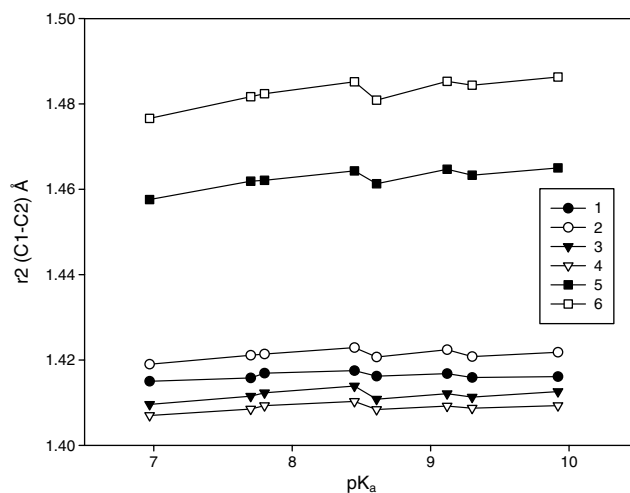
Fig. 8. Dependence of selected structural parameter (C1—C2 distance, in *A*) of ring on pK_a of phenols, for 6 conformers, numbering as in Scheme 1.
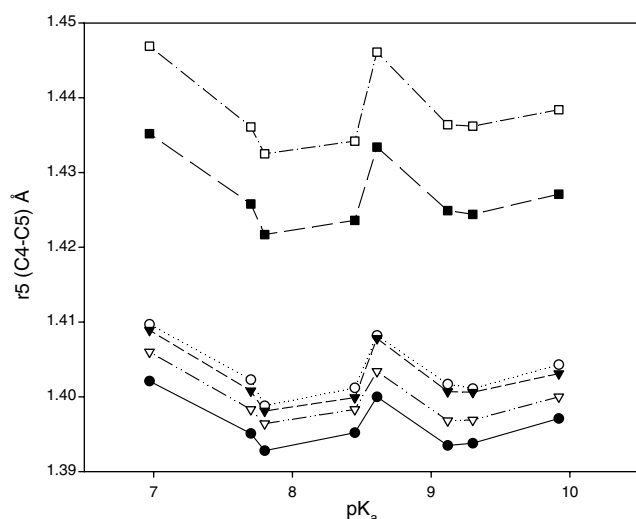
Fig. 9. Dependence of C4—C5 bond length on pK_a labelling as in Table 2.

amine, respectively, to 46.8 in Mannich base. It was interesting what difference introduces the π-electron coupling. In [26], values for three Schiff bases (see above, appropriately divided by 6 in this work) are 120–140. We can here verify its dependence on the strength of hydrogen bonding, in the series of eight compounds. In addition to the values presented in [26], we calculated here the related values for all conformers (Scheme 1).

There is no systematic dependence on the number of chloro-substituents. Some irregularities can be a result of different steric repulsions for specific arrangements of substituents (cf. Fig. 9, also [39]). A different picture was found in Mannich bases [39], where the *A* parameter grows systematically with substitution, except the case with full substitution of the phenyl ring, where *A* decreases. The participation in resonance in Schiff bases decreases the individual effects of particular substituents (cf. [35–37]).

3.3. Fraction of keto form

Very informative, collective characteristics of structure effects can be derived from the content of *ortho*-quinoid resonance forms in particular structures. Especially it is interesting to compare the molecules with internal coupling (Schiff bases) and without (Mannich bases). It is also interesting if this effect depends on substitution. The basic definitions, the model and preliminary results are given in [14,26,40]. The method consists in estimating the content of a few particular resonance forms of phenol ring (cf. Scheme 3). The reference bond lengths are taken from the calculations using the same basis set. It was found that in the open form of the non-substituted Schiff base there is about 6% of *ortho*-quinoid ("keto") form, in the bonded one it reaches 12%. For the proton transfer form it is around 40% and interestingly grows up to 70% [14] after opening of zwittertonic chelate hydrogen bond. Many results presented above are in agreement with the observa-

tion that the zwittertonic conformer with broken intramolecular hydrogen bond (**6**) appears to be mostly in "keto" form. In this work, we first calculated the amount of keto forms for all conformers of series of eight Schiff bases with various Cl-substitutions.

In the studies of permittivity influence on the first three Schiff bases of our series, it was found that the calculated fraction of keto form weakly depends on pK_a.

To verify this observation we used wider pK_a range for eight Schiff bases.

The results are presented in Table 3. As in the case of the bond variance (*A*) parameter, one observes a weak dependence of the content of keto form on substitution pattern. The resonance stabilization is the most effective at 50% of keto and "aromatic"(-like in phenol) resonance forms. The systems studied here seem to reach such a state at less than 50% of keto form, but in proximity of such state. The resonance stabilization effect diminishes the influence of phenol acidity [35–37]. Additional support comes from the fact, that in the open form, when resonance stabilisation of hydrogen bond does not act, the contents of one (-keto) form drastically grows.

It is interesting that the content of the keto form in Mannich bases was between 2.5% and 6% and clearly increased with substitution [26]. Substituents influence simultaneously the acidity as well as the basicity of the groups forming the hydrogen bond in a complicated way that depends on the pattern of substitution. This can act in opposite direction on ΔpK_a [37], disturbing in our case

Table 2
The values of $A = 1/6 \sum_i (d_i - \bar{d})^2 \cdot 10^6$, calculated by B3LYP/6-31+G(d,p)

Conformer	**1**	**2**	**3**	**4**	**5**	**6**
Substituent						
H-	67.4	120.1	84.5	36.6	1174s.3	2117.3
4-Cl-	80.7	130.8	96.6	45.8	1232.1	2187.9
5-Cl-	78.5	131.8	89.3	39.8	1218.0	2161.5
6-Cl-	88.9	131.1	89.2	48.0	1235.3	2214.8
4,5-di-Cl-	58.2	113.7	80.9	33.0	1161.8	2088.1
4,6-di-Cl	98.2	139.1	99.6	53.9	1297.0	2280.4
5,6-di-Cl	81.6	122.8	84.5	43.2	1238.8	2176.8
4,5,6-tri-Cl-	57.7	102.4	73.0	37.7	1049.5	2082.1

Table 3
Content of keto form in particular conformations (**1**–**6**) of eight chloro-derivatives of Schiff bases

Conformer	**1**	**2**	**3**	**4**	**5**	**6**
Substituents						
H-	6.7	12.3	8.2	3.6	44.0	68.3
4-Cl-	6.6	12.3	8.3	3.6	44.2	68.6
5-Cl-	6.3	12.4	8.1	3.3	45.7	68.3
6-Cl-	7.2	11.8	7.9	3.7	42.5	67.4
4,5-di-Cl-	6.3	12.1	8.4	3.5	45.2	68.0
4,6-di-Cl	7.1	11.8	8.0	3.8	43.1	67.7
5,6-di-Cl	7.1	12.1	7.9	3.7	45.2	67.6
4,5,6-tri-Cl-	7.0	11.6	8.0	4.0	42.6	67.7

the dependences on pK_a of acidic component. On the other hand, it is an interesting feature of the interactions in resonance assisted hydrogen bonds, that some other characteristics like position of the v(OH) band gravity center [41], and its intensity depends regularly on pK_a. In this work also such dependences of the of O—H distance on pK_a are presented.

4. Summary

In the present work, we have studied the energetic and structural differences between various possible tautomers and conformers of *ortho*-hydroxy Schiff bases, which reveal interesting properties, also from a practical point of view, photo- and thermochromic.

The study was performed for isolated molecules of *N*-methyl-salicylidene imine and seven chloro-substituted derivates based on the results of B3LYP/6-31+G(d,p) calculations. Modulation of the structure of the title molecule by substitution may be important for predicting materials of desired properties, especially in relation to the proton transfer tautomerism.

The six species, which can be distinguished for the ground-state of each of the molecules might be arranged into four groups: species not forming a hydrogen bond, species with an intramolecular hydrogen bond, proton transfer forms, and forms with opened proton transfer hydrogen bonds. This classification is based on energetic and structural differences and similarities between particular forms. Each of the presented conformers and tautomers is a stationary state, the structure of which is a consequence of quantum chemical resonance between two virtual resonance forms [14,26,40].

From the obtained results it becomes obvious that the most decisive is the intramolecular hydrogen bond, its formation and breaking. Three "open" conformers of enolic forms of Schiff bases reveal similar energetic and structural behaviour. Formation of intramolecular hydrogen bond leads to characteristic structural changes like extension of O—H distance and shortening the C—O distance as well as changes of structural parameters of the rings which generally can be classified as increase of the *ortho*-quinoid resonance structure in description of these molecules. The shortening and elongation of particular ring distances as well as C-alkyl/C-aryl and C═NC bonds follows such a pattern. Calculated on the basis of structural effects, the amount of keto forms in the structure of molecules is around 3–8% for open forms, 12% for O—H···N forms, 42–45% for O···H—N forms and interestingly about 68% in the open, non-hydrogen-bonded structure obtained after the proton transfer.

Influence of the increasing chlorine substitution was analysed from the point of view of the change of the acidity of the phenolic part of the hydrogen bond as well as of specific electronic and structural consequences of a given arrangement of substituents. Correlating the structural characteristics, including also bond length variance (A)

and content of *ortho*-quinoid resonance form (% keto) defined in this work, with the pK_a of phenols, we have found that the increase of acidity has a modest influence only, due to partial compensation of the acid base properties upon the substitution, which is characteristic for substances with direct π-electron coupling [35–37].

On the other hand, the acid base properties quite regularly correlate with the difference of the energy (ΔE_T) between enol-imine and proton transfer (keto-imine [35–37]) tautomers.

These results can be viewed as complementary to those obtained by Gilli et al. [35–37], where the modification of basicity by substitution was considered. They found, that the ΔE_T correlation on Hammett constants σ_R^0 of substituents has a different slope for the compounds with predominance of enol-imino and keto-amino structures [36]. In our case, where the acidity and basicity were modulated by chloro-substitution in the phenol ring, all derivatives reveal the same (enol-imine) type of hydrogen bonding, and correlations with pK_a look rather regular. We have stated that also other characteristics of hydrogen bonding are regularly changing with pK_a – these are – the extension of O—H bond lengths and the heat of formation of the hydrogen bond (especially when steric corrections were considered). This is in line with the previously experimentally stated correlation of the frequency and intensity of v(O—H) bands in Schiff bases on pK_a [42].

In our calculations we found the feature very specific for Schiff bases, that the next to tautomer **2**, from the energetic point of view, is the proton transfer structure with intramolecular hydrogen bond; thus, the easiest energetically process is the proton transfer, which becomes more easier when the number of chlorine substituents increases. For poly-substituted derivatives the difference in energy drops to 2 kcal/mol in the gas phase, which for Mannich bases is around 15 kcal/mol.

The opening of this form requires a similar amount of energy as breaking the O—H···N hydrogen bond. The dominant forms in possible equilibrium are hydrogen-bonded O—H...N and O···H—N forms. Correlations of particular parameters on the pK_a of phenols reveal additionally, some characteristic points, e.g. specific extension of the C4—C5 bond upon introducing the combination of two chloro substituents at 4 and 5 positions. We have found also a specific strengthening of hydrogen bonding by steric shortening of the chelate ring by 6-Cl-substituent. The 3-Cl-substituents influence the structure so strongly that they are selected as a special group which will be analysed in a following work.

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