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# Resonance Assisted Intramolecular Hydrogen Bond in Schiff Bases*

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The intramolecular hydrogen bond, the proton transfer equilibrium and related properties of Schiff bases are discussed.

**Key words:** Schiff bases, hydrogen bond, proton transfer equilibrium, structure, photo- and thermochromism

## 1. Introduction

The Schiff bases derived from salicylaldehyde and other hydroxy-aromatic aldehydes have received considerable attention due to their properties of great practical importance, various applications in organic synthesis and coordination chemistry as well as their role played in biological systems. The properties that have attracted noticeable interest are photo- and thermochromism [1]. Since the first publication by Senior [2] at the beginning of the century, a voluminous literature on various aspects of these properties has appeared [3–6]. Photochromic properties of Schiff bases received a considerable interest in the last years due to recent development in optical recording technology [1,7]. Salicylidene aniline has been proposed as a possible candidate for reversible optical switching devices [7]. There are also other promising properties of Schiff bases directly related to the electronic structure of these compounds, due to non-linear responses in terms of their molecular hyperpolarizabilities, which creates the possibility of their application in many areas such as second harmonic generation and linear electro-optic modulation [8]. Some Schiff bases, where the proton-electron coupling is possible, have been recently suggested to be applied as material with a novel type of electronic properties [1,9]. On the other hand, the Schiff bases derived from pyridoxal and lysine act as co-enzyme for a variety of enzymes, chemical reactions of which are involved in aminoacids metabolism, as well as in glycogen phosphorylase [10].

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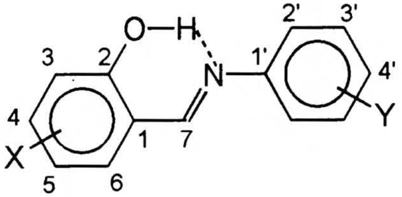
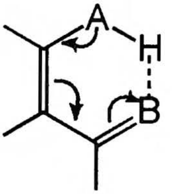
* Dedicated to Prof. L. Sobczyk on the occasion of his 70th birthday.

## 2. Intramolecular hydrogen bonding in Schiff bases

Intramolecular hydrogen bonding OH...N is a crucial factor in determining the physical, chemical and biological properties of salicylidene anilines and related Schiff bases:



Protonodonor OH and proton acceptor C=N groups in these compounds are linked by the planar π-electron system to form a quasi-aromatic chelate ring. This type of hydrogen bonding has been called by Gilli [11] the resonance assisted hydrogen bond (RAHB):



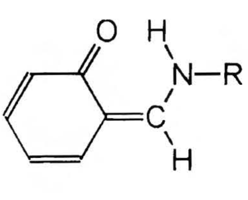
π electron delocalization in the conjugated system increases the proton donor properties of the AH group and proton donor properties of the atom B, leading to strengthening the hydrogen bond [11–13]. It influences also the dynamic properties of the hydrogen bond and the shape of the proton potential surface [13]. Formation of RAHB induces changes in the bond lengths and the bond angles in molecules [11–14]. Gilli *et al.* [11–12] found a correlation between the hydrogen bond length and the geometric parameter describing the π conjugation [11,12]. The interrelation between the strengthening of the hydrogen bond and π-system delocalization is very characteristic for RAHB [11–13]. The charge delocalization, which sometimes is extended over the whole molecules, leads to the very specific properties of RAHB and as well as the chemical and physical properties of compounds with quasi-aromatic chelate ring.

The X-ray studies of salicylidene anilines and related Schiff bases show that the OH...N hydrogen bond is non-linear and relatively short (2.64–2.51 Å). The planar quasi-aromatic ring is found to be present in all Schiff bases. Woźniak *et al.* [15] show that in the Schiff bases the mesomeric effect is dominant for changes in geometry of the molecule due to RAHB OH...N, on the ground of the structural relationships present in the N-salicylidene fragment. The value 2.2 of slope of the plot $C_2$–O *vs.* averaged $C_2$–$C_1$ and $C_2$–$C_3$ was close to 1.7 found for model phenole–amine complexes, where the mesomeric effect dominates. The complete crystallographic data can be retrived from Cambridge Structural Database [16]. Some representative data are shown in Table 1.

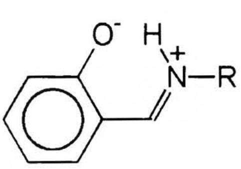
**Table 1**. Example of geometric parameter of intramolecular hydrogen bond in Schiff bases.

| No. | Compounds | $R_{O...N}$ (Å) | $R_{O...H}$ (Å) | $R_{H...N}$ (Å) | ∠OHN (°) | Ref. |
|---|---|---|---|---|---|---|
| 1. | N-(salicylidene)-pentafluoroaniline | 2.632(7) | 0.91(7) | 1.89(7) | 136(7) | 17 |
| 2. | N-(salicylidene)-3-aminopyridine | 2.572(5) | 1.02(5) | 1.73(5) | 137(4) | 18 |
| 3. | N-(3,5-dichlorosalicylidene)-4′-diethylaminoaniline | 2.595(3) | 0.87(4) | 1.78(4) | 155(3) | 15 |
| 4. | N-(3-nitrosalicylidene)-4′-diethylaminoaniline | 2.550(3) | 0.91(4)<br>2.01(8) | 1.64(4)<br>0.71(7) | 157(2)<br>134(7) | 15 |
| 5. | N-(2-hydroxynaphthylidene)-4′-diethylaminoaniline | 2.545(3) | 1.38(4) | 1.29(4) | 145(3) | 15 |
| 6. | N-(salicylidene)-2-hydroxyaniline | 2.600(2) | 1.83(2) | 0.91(2) | 137.7(9) | 20 |
| 7. | N-(5-nitrosalicylidene)-methylamine | 2.644(2) | 1.95(2) | 0.90(2) | 133(2) | 21 |

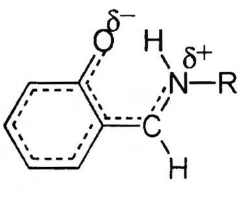
Most of the Schiff bases studied so far have the OH distance typical of the phenolic group, which indicates that the proton is localized at the oxygen atom. In some cases [9,15,19,22,23] a proton disordered over the two sites was found. The electron density map of hydrogen bond has shown that in some cases, like N-(3-nitrosalicylidene)-4′-diethylaminoaniline (**4,** Table 1), the occupation factor of the proton near the oxygen has been estimated to be 75% [15]. In N-bis-(2-hydroxy-naphthylylidene)-p-phenylenediamine the proton has been found to be the broadly distributed near the centre of the hydrogen bridge [9]. In anils of 2-hydroxynaphthaldehyde [15,24] the NH distance was found to be shorter than the OH distance. These data clearly indicate the coexistence of both tautomeric forms in the crystal and suggest the possibility of the proton transfer along the intramolecular hydrogen bond. A few Schiff bases have been found to exist in the crystal in a tautomeric form with proton, linked to the nitrogen atom [5,6,20,21]. The problem of the structure of this tautomeric NH-form has been the object of controversies [1,5]. Most frequently they are presented as a quinoide form (Q) or a zwitterionic (Z) one:



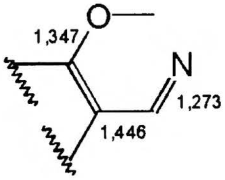
Q



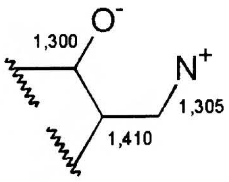
Z

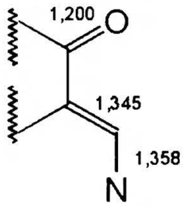


Analysis of the interatomic distances in the molecules of Schiff bases permitted to establish the molecular structure of several Schiff bases existing in a NH-form in the crystal [5,20,21]. A comparison made between the interatomic distances in chelate ring of N-(salicylidene )-2′-hydroxyaniline (**6**, Table 1) and those of the Schiff base existing in a phenolic form (OH-form) enabled Lindeman *et al.* [20] to present its structure as superposition of the resonance structures Q and Z. Z-conformer of anilide of 3-hydroxy-2-benzothiophenealdehyde with an appreciably short CO distance (1.22 Å) can be considered to exist in a quinoide form (Q-form) [5]:



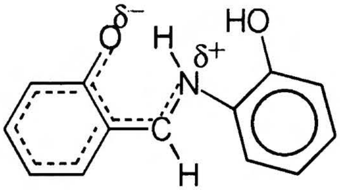
OH-form





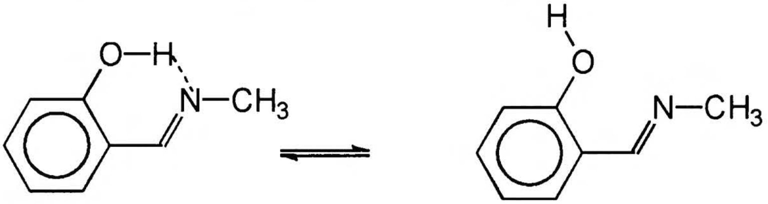
Q-form

The alternation of the bond length in the phenolic ring confirms the contribution of the quinoide resonance form to the molecular structure of **6** (Table 1).



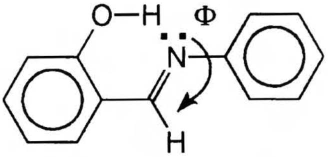
Woźniak [15] and Krygowski [21] have applied the HOSE model [25] for estimation of the weight of the resonance structures of Schiff bases. Krygowski *et al.* [21] have found that the quinoides structures contribute considerably to the molecular structure of N-(5-nitrosalicylidene)-methylamine (**7**, Table 1). The shortening of the CO bond length as well an alternation of the bond length in the salicylidene ring have been used as an indication of the presence of the NH tautomer in the crystal [9,23].

The energy of the intramolecular hydrogen bond, estimated by measuring of the chemical shift values (12.9–17 ppm) using the Schaefer's formula [26] $E = (\Delta\delta + 0.4)$ 4.184 kJ/mol, is about 35–50 kJ/mol. Millefiori and Millefiori [27] have analyzed RAHB in salicylidene-methylamine using the CNDO/2 energy partitioning scheme of Fischer and Kollman. The intramolecular hydrogen bond energy $\Delta E^T = 40$ kJ/mol was calculated as the difference between the total energy of the conformer with the intramolecular hydrogen bond and the conformer which differs from the previous one by the rotation of the OH group around the CO bond:



The formation of the hydrogen bond leads to changes in the charge redistribution not only in the hydrogen bridge OH...N but also in the whole molecule [27].

In Schiff bases the extent of the π electron delocalization and consequently several properties of the compound are directly related to the conformation of the molecule. In salicylidene anilines and related Schiff bases two competitive conjugative systems n-π and π-π are present [1–5]:



The n-π coupling and steric effects favour the non-planar form with aniline ring twisted by about 45°. In salicylidene anilines, which adopt this structure, the lone pair of the nitrogen overlaps the π electrons of the aniline aromatic ring, which results in a decrease of the basicity of the N atom and hence the OH...N hydrogen bond strength. In planar molecules of Schiff bases the lone pair of the nitrogen atom is not involved in the coupling with the π electron of the aniline ring, and consequently the hydrogen bond energy is greater than that in the previous case. Both types of Schiff bases have been found to exist in solid state and in solutions. The existence of the conjugative interaction between the two phenyl rings in some Schiff bases [28,29] in solutions has been evidenced by the high correlation coefficient for the relationship between the $^{13}$C chemical shift of the C-4 and C-7 atoms and Hammett constants of the substituents in the aniline ring. The values of the chemical shift C-4 and C-7 are also linearly dependent on the chemical shift of the proton engaged in the intramolecular hydrogen bond. These results indicate also the interdependence between the charge distribution in the whole molecule and the hydrogen bond strength.

The π electron delocalization in quasi-aromatic ring accounts for some peculiar properties of the RAHB in Schiff bases. One of the very specific properties, observed in the IR spectra of salicylideneanilines (Fig. 1), is the low integral intensity of the protonic absorption. This integral intensity of the νAH stretching band results from the compensation of charge transfer in the hydrogen bridge by π electron shift along the conjugative system. Hence the dipole moment changes accompanying the proton vibration ($\delta\mu/\delta\Theta$) are small.

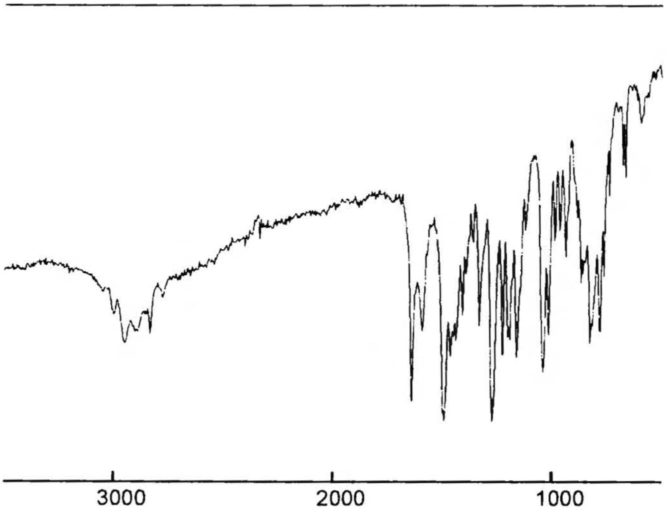
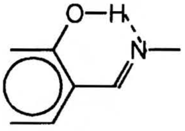
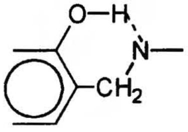
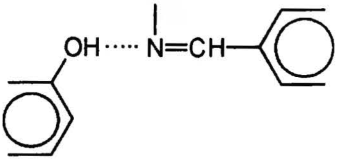


**Figure 1.** IR spectrum of N-(5-methoxy-salicylidene)-methylamine in KBr.

Comparison made between the IR data for N-(5-methylsalicylidene)-methylamine, Mannich base with similar OH...N intramolecular hydrogen bond base without quasi-aromatic ring and the complex of 2-ethylphenol with N-benzylidenemethylamine illustrate these effects [30].

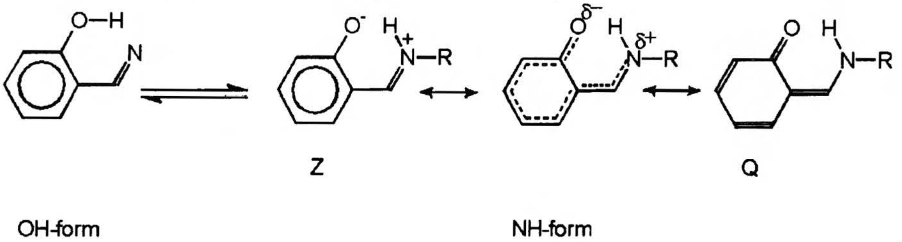
**Table 2.** The spectral parameters of the νOH band in the IR spectra of Schiff base, Mannich base and 2-ethylphenol-benzylidenemethylamine complex and calculated δμ/δΘ values [30].

| |  |  |  |
|---|---|---|---|
| νOH [$cm^{-1}$] | 2793 | 2901 | 3045 |
| A × $10^4$ [cm/mmol] | 3.45 | 5.57 | 10.31 |
| (δμ/δΘ) [D/A] | 2.97 | 3.77 | 5.13 |

Extensive vibrational couplings, which occur in the molecules of Schiff bases, being typical for RAHB, make the analysis of the IR and Raman spectra very difficult. In spite of many papers devoted to the assignment of the IR and Raman spectra of Schiff bases, some questions are still controversial, particularly in cases where the proton transfer equilibrium occurs [31–38]. Yuzawa *et al.* [37] have measured the IR spectra of N-salicylidene-aniline and their $^{15}N$ and $^{18}O$ analogues in acetonitrile. They have proved the coupling of the stretching νC=N with some ring vibration. The bands at 1320 $cm^{-1}$ and 1368 $cm^{-1}$ were assigned to the νCO and νCN vibrations, respectively. In the IR spectrum of salicylidene aniline in hexafluoroethanol solution νC=N frequency increases due to protonation, and a new band at 1543 $cm^{-1}$ appears. The observed $^{15}N$ and $^{18}O$ isotope effect suggests that $\nu C{=}NH^+$ and $\nu CO^-$ vibrations are strongly coupled through delocalization of the electrons in the O–C–C–C–N frame. The π electron delocalization in quasi-aromatic ring affects the dynamic properties of the hydrogen bond in Schiff bases [13]. The dynamic aspect of H-bonding is very important for those physico-chemical and biochemical mechanisms which are based on the proton transfer equilibrium.

## 3. Proton transfer equilibrium in Schiff bases

Schiff bases are known to exhibit a tautomerization induced by the transfer of the proton from oxygen atom to the nitrogen atom along OH...N hydrogen bond with accompanying π electrons configurational changes:



(1)

The molecular structure of the proton transferred form is still an object of controversies. The best presentation of their molecular structure seems to be a superposition of the quinoide (Q) and zwitterionic (Z) resonance forms. The weight of the Q and Z forms depends on the electronic structure of the compound and intermolecular interactions. It seems that the extension of the π electron system and non-polar medium may favour the Q form. As it is known from the hydrogen bond studies, the proton transfer process along the hydrogen bridge is determined by the double minimum proton potential curve. The factors affecting the shape of the potential barrier in Schiff bases, like in the other RAHB, are not the same as these well established for hydrogen bonds without the quasi-aromatic chelate ring. While for the intermolecular hydrogen bond the ΔpKa value is the "driving force" of the proton transfer [39], for the RAHB the extension of the π electron delocalization seems to be a more important factor. Generally, the proton transfer causes the charge separation and an increase in the polarity of hydrogen bond [39]. With RAHB the π electron delocalization in the chelate ring and in the entire system may lead to a small increase of the dipole moment of the NH-form and sometimes to formation of non-charged tautomers. Having made calculations for N-salicylidene-methylamine by the MP2/6-31G** method, Filarowski [30] has shown that the proton transfer causes a small increase of the dipole moment, compared with the values obtained for Mannich bases and for a complex with the similar OH...N intermolecular bond. The calculation of the proton potential energy as a function of the OH distance in the OH...N bond has shown, that in the N-salicylidene-methylamine the proton is localized in one minimum (Fig. 2), but the energy difference between the two minima is lower than in the other two compounds. It results from the stabilization of the proton transferred form by the charge delocalization:

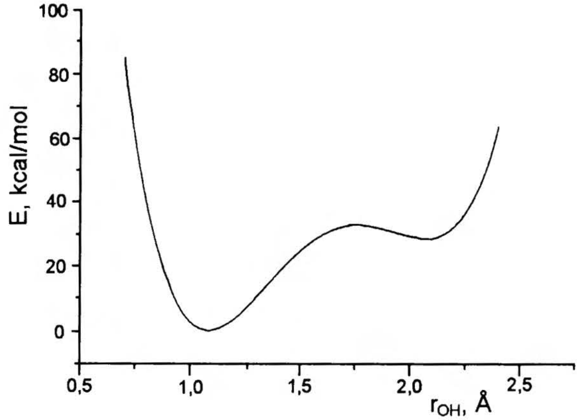
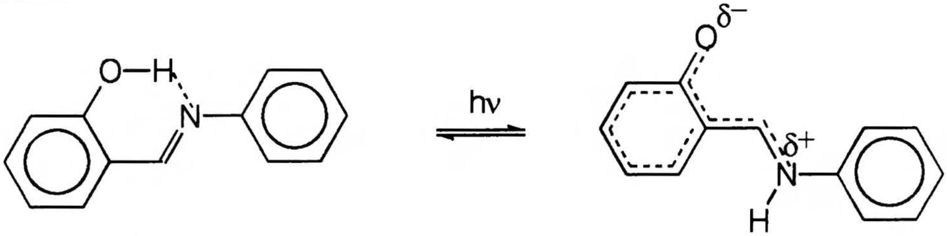
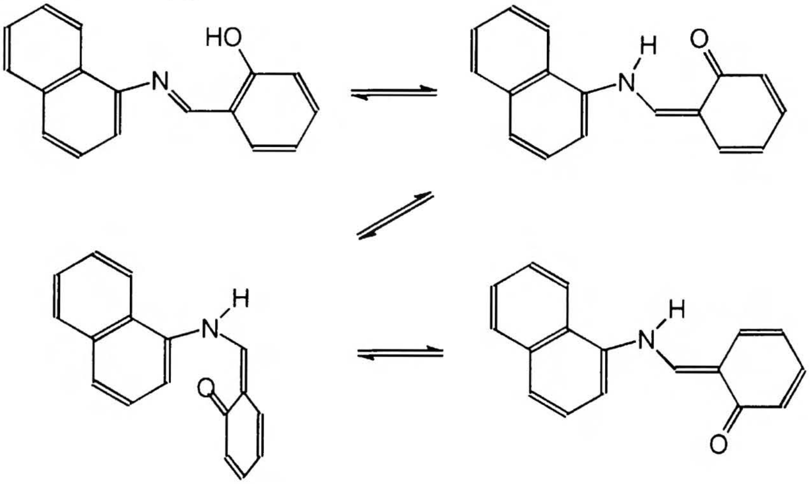


**Figure 2.** Potential energy surface of RAHB in N-salicylidene-methylamine [30].

The proton transfer equilibrium in the OH...N intramolecular hydrogen bond, being a crucial factor for properties of salicylidene anilines and related Schiff bases, has been extensively studied by both theoretical and experimental methods for about 50 years and is still an object of interest. This process can occur in the ground and the excited electronic states, leading to formation of coloured species. Thermochromism, exhibited by some Schiff bases, is directly related to the temperature sensitive equilibrium (1) and the formation of NH form. The studies carried out in several laboratories [1–5,40–46] revealed, that in the case of photochromic Schiff bases, the proton transfer occurs in excited electronic states and is followed by *cis-trans* isomerization:



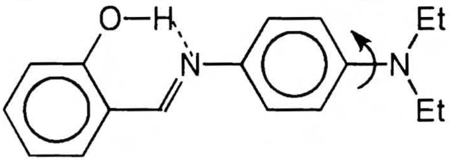
The flash photolysis studies have shown, that in the singlet excited state the proton transfer (in pico- or sub-picosecond time range) is followed by a rotation around the C–N form and the formation of a non-planar intermediate product, which in turn transforms into a *trans*-NH form. The structure of coloured species seems to be an open question [1,5,35–37,40–46]. Formation of the zwitterionic Z-form [1,5,32,43] for several Schiff bases in polar solvent has been proposed. Recently Grabowska *et al.* [43] have performed experimental and theoretical studies of photoisomerization of aliphatic Schiff bases: N-salicylidene-methylamine and -buthylamine and have shown the formation of this form in benzene solution. Stefan *et al.* [47] studied photoisomerization of the N-(salicylidene)-1-naphthylamine in 3-methylpentane using the nano-second flash photolysis, claiming the formation of the quinoide *trans* from (Q):



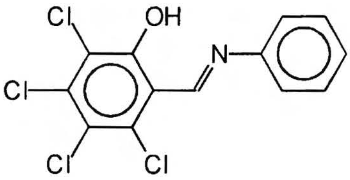
Yuzawa [37] studied the structure of the photocoloured form of N-salicylidene aniline in acetonitrile solution by the time resolved IR spectroscopy and proposed the molecular structure as a superposition of the Q and Z resonance structure. Schiff bases have also been extensively studied in order to find the structural factors influencing the proton transfer equilibrium. This problem is important from both theoretical and practical point of view [1,7,9,10]. Taking into account the historical aspect and the possible technical applications of Schiff bases, we start this discussion by pointing out to the influence of the crystal structure on the proton transfer equilibrium.

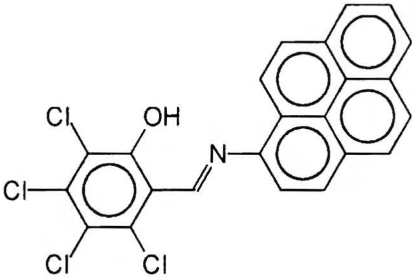
### 3.1. Crystal structure and proton transfer equilibrium

The structural studies on salicylidene anils, undertaken by Cohen and his co-workers [47,48] about 30 years ago, showed the existence of two different types of the crystal structure (α,β), directly related to the spectroscopic properties of the compounds. Crystalline Schiff bases of α type, which adopt a non-planar conformation with twist angle of aniline ring of 40–45°, exhibit photochromic properties. Schiff bases of the β type, whose molecules are planar and are packed face-to-face with short intermolecular contacts, show reversible colour changes as a result of temperature change. Cohen *et al.* [48,49] suggested that the photo- or thermochromism of Schiff bases was a topochemically determined process, since no apparent relationship between the photosensitivity and the electronic characteristic has been observed. As has been shown above, in non-planar molecules of salicylidene anilines the basicity of the nitrogen atom is considerably reduced, due to coupling with the π electrons of the aniline aromatic ring. Consequently, the potential energy barrier is high and the proton transfer process can proceed only in a singlet excited state. In the case of planar Schiff bases the nitrogen lone pair is not involved in this coupling, therefore the potential energy barrier is lower than in the preceding case and the proton-transfer is a thermally activated process. The planar conformation of thermochromic Schiff bases is stabilized by the π-π coupling and by the parallel packing through van der Waals, or dipole-dipole or charge transfer intermolecular interactions. In this case the transfer of the proton along the hydrogen bond cannot be followed by *cis-trans* isomerization, because the crystal structure is not sufficiently "open". In liquid crystal and solutions all these bases acquire photochromic properties. Kawato *et al.* [41] have shown, that an introduction of the bulky tert-butyl substituent into the molecule of thermochromic salicylideneanilines leads to photochromic properties. This effect is attributed to an increase in the open space, enabling a *cis-trans* isomerization in the crystal lattice. Hadjudis *et al.* [49] have shown that a similar result may be achieved by the complexation of the thermochromic Schiff bases in β and γ cyclodextrin and their permetylated derivatives. On the other hand, the increase in the intermolecular interactions in a crystal facilitates the proton transfer in the ground state. Aldoshin *et al.* [50] have calculated the conformational energy of salicylidene anilines and found that the non-planar forms are energetically favoured. However, the energy differences between the planar and non-planar forms are small, with values comparable to the energy of intermolecular interactions in the crystal lattice. For example, N-salicylidene-4′-dimethylaminoaniline [50]

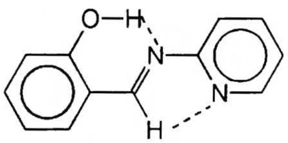


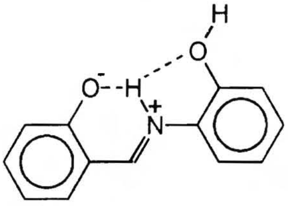
crystallizes in two polymorphic forms, of which one – the "yellow" exhibits photochromic properties and the other – "red" is thermochromic. In the last form the presence of some quantity of the NH-form at room temperature has been suggested. X-ray analysis has shown, that in the molecule of the "yellow" form the $N(CH_3)_2$ group is twisted from the molecular plane. The molecule of the "red" form is planar, which leads to shorter intermolecular distances and consequently to an increase in the energy of intermolecular interactions (about 54 kJ/mol found for the nearest neighbouring molecules in "red" form against 27 kJ/mol for the "yellow" one). Inabe *et al.* [23] have shown that the charge transfer π-π interactions in crystal N-tetrachlorosalicylidene-1-pyrenamide, where the inter-planar distances between the mean plane of the entire molecule are very short (3.37 and 3.39 Å), are responsible for lowering the proton potential barrier and for diminishing the energy difference between both minima, compared with N-tetrachlorosalicylidene-aniline.





In several cases the planar conformation of the Schiff molecules results from the additional intramolecular interactions. Hadjoudis *et al.* [51] have attributed the thermochromic properties of series of N-(salicylidene)-2-aminopyridines to the stabilization of the planar form by the intramolecular interaction C(7)–H...N





The nearly planar conformation of the molecule of N-(salicylidene)-2′-hydroxyaniline (**6**) [20] (ϕ = 0.9 (1.6)°) is achieved by the formation of the additional intramolecular hydrogen bond between the NH and the oxygen atom of the OH group on the aniline ring (NH...O = 2.668 (20) Å). Planarity of the molecule and the intermolecular hydrogen bonds O(2)H...O stabilize the NH tautomeric form [20,52]. The above results are an example of "crystal engineering": by applying structure – directing effect to producing planar or non-planar structure one can achieve the desired properties. It seems to be very important in view of possible applications, on the one hand, of the photochromic Schiff bases as new organic materials, which can store information and on the other hand, the thermochromic bases – with extended conjugative systems – as a charge conductor, which could be utilized in versatile electronic devices.

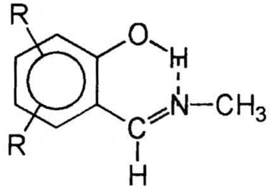
### 3.2 Electronic effects on the proton transfer equilibrium

The introduction of substituents into aromatic rings of salicylideneaniline and other chemical modifications of this molecule leads to modulation of the shape of the proton potential surface [15,19,21,23,53,54]. The ΔpKa values and the π electron delocalization are the key factors determining the proton transfer equilibrium in Shiff bases, similarly to the other systems with RAHB. The importance of basicity of the nitrogen atom, related to the planar conformation of the molecule has been discussed in the previous section. However, the planarity of the molecules appears not to be an indispensable condition of the presence of tautomeric equilibrium in the ground state. Hadjudis *et al.* [54] have determined the probability of finding Schiff bases in the NH form at 300 K by measuring the temperature dependence of the $^{14}$N NQR frequencies (Table 3). In photochromic compound **1** the low basicity of the N atom is responsible for a large energy difference between the OH- and NH-form.

**Table 3**. Probability of proton transfer in the OH...N RIHAB in Schiff bases [54].

| No. | Compound | ΔE [MeV] | P (300 K) |
|---|---|---|---|
| 1. | N-salicylidene-2-chloroaniline | 140 | 0.4 |
| 2. | 3,5-dichlorosalicylidene-benzylamine | 63 | 8.1 |
| 3. | 3-methoxysalicylidene-2-amino-6-methylpyridine | 86 | 3.1 |
| 4. | 3,5-dichlorosalicylidene-2-amino-6-methylpyridine | 56 | 10.3 |

In N-salicylidene-benzylamine (**2**) insertion of the methylene group between the C=N bond and the adjacent aromatic ring makes this molecule non-planar but, at the same time, leads to an increase in the basicity of the nitrogen atom; the $pK_b$ values for benzylamine being 4.62, while that of aniline is 8.4. In this case, the electron density of the lone pair is the factor which determines the thermochromism of this Schiff base. A considerable basicity of aliphatic amines makes possible the proton transfer equilibria at room temperature [55]. N-salicylidene methylamine in non-polar solvent exists in OH-form, but in a polar solution at room temperature the contribution of the NH form has been shown [35,44]. Recently, we have studied the proton transfer equilibrium in N-salicylidene-methylamines in chloroform solution by measuring the changes in $^{13}$C chemical shift, induced by the substitution of the proton involved in hydrogen bond by deuterium ($^{n}\Delta C(D)$). This method had been used by Hansen *et al.* [56] and Katritzky *et al.* [57] in studies of intramolecular hydrogen bonding in some Schiff bases. Large positive values of $^{2}\Delta C{=}O(D)$ and negative of $^{6}\Delta C{-}CH_3(D)$ observed in series of N-salicylidene-methylamines as well as their dependence on temperature are an evidence of the proton transfer equilibrium.



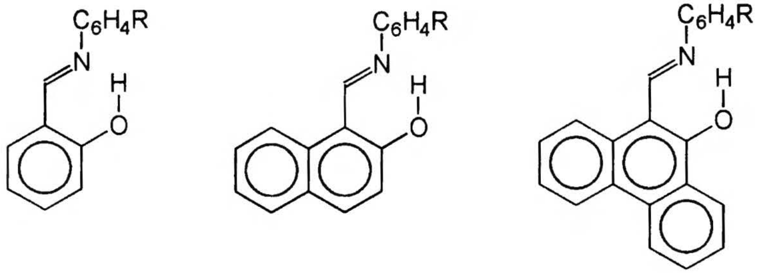
R = Cl, Br, $NO_2$, $CH_3$, $OCH_3$

The substituents on aromatic ring through the mesomeric and steric effects cause an increase in the acidity of the phenolic group, or alternately an increase in the basicity of the nitrogen atom. In case of 3-$NO_2$, 5-$NO_2$, tetra-chloro- and 4,6-di-methoxy-substituents the NH form predominates in chloroform solutions. These results indicate the importance of both factors: the acidity of the OH group and the basicity of the N atom for the position of the tautomeric equilibrium in Schiff bases. N-(5-$NO_2$-salicylidene)-ethylamine, as it has been shown above (Table 1), exists in solid state mainly as NH tautomer. Only a very small fraction of molecules in OH-form has been detected by $^{13}$C CPMAS NMR measurements [21]. The greater probability of the proton transfer (Table 3) in 3,5-dichlorosalicylidene-2-amino-3′-methylpyridine (**4**) compared to 3-methoxy- analogue (**3**) results from the increased acidity of the phenolic OH group in the former compound (pKa values of the respective phenols are 7.89 and 9.98). A multinuclear $^1$H, $^{13}$C and $^{15}$N NMR studies made on series of substituted N-salicylidene-anilines have shown that a suitably increased acidity is necessary to make possible the proton transfer in the ground state at room temperature (Table 4). While in the series of N-substituted anils of 3,5-dichloro-salicylaldehyde [28] the proton is located at the phenolic oxygen atom, in 3-nitro- and tetrachloro-salicylidene-anilines the equilibrium has been established. The weight of the N–H form, found by measuring the $J_{NH}$ values, ranges between 15–26% ( Table 4). Introduction of the electron donor substituent into the aniline ring, which increases the basicity of the nitrogen atom, shifts this equilibrium to the NH form side.

**Table 4.** Proton transfer equilibrium in some substituted salicylideneanilines and 2-hydroxynaphthylideneaniline.

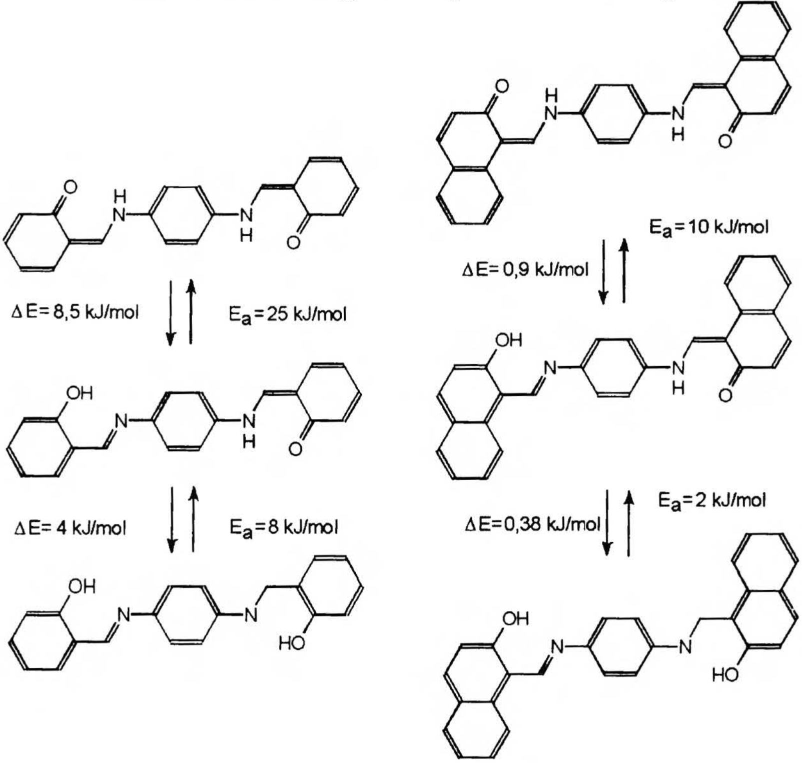
| No. | Compounds | $^1J_{NH}$ (Hz) | %NH form |
|---|---|---|---|
| 1. | N-(tetrachlorosalicylidene)-4′-diethylaminoaniline | 35.0 | 36.5 |
| 2. | N-(tetrachlorosalicylidene)-aniline | 22.6 | 23.5 |
| 3. | N-(3-nitrosalicylidene)-4′-diethylaminoaniline | 27.9 | 29.0 |
| 4. | N-(3-nitrosalicylidene)-aniline | 13.2 | 14.0 |
| 5. | N-(2-hydroxynaphthylidene)-4′-diethylaminoaniline | 35.8 | 37.5 |

The very specific properties of the RAHB system is the influence of the π electron delocalization on the hydrogen bond strength and on the stabilization of the proton-transferred form. The spectroscopic studies and calculations of the differences in the heat formation of the NH ond OH form (ΔH), carried out by Alarcon *et al.* [58,59], have shown that an extension of the π electron delocalization in Schiff bases by substitution of the benzene ring in the salicylidene part by the fused aromatic rings leads to the stabilization of the NH-form:



$\Delta H = \Delta H_{NH} - \Delta H_{OH}$ 17–18 kJ/mol  –4–(–9) kJ/mol  –25 kJ/mol

The NMR [53,55,58–64] (Table 4) and the UV studies [55,59] showed that anils of 2-hydroxynapthaldehyde exist as equilibrium mixture, containing appreciable amounts of OH- and NH-tautomers. The contribution of the NH form of N-(2-hydroxynaphthylidene)-aniline in $CDCl_3$ solution was estimated to be about 40% [55,61]. Replacement of the aniline group by methylamine causes an increase in population of the NH form up to 73%; ΔH values being 10.9 kJ/mol [55]. The X-ray analysis confirms the considerable contribution of the NH form [15,24]. The recent $^{13}C$ CPMAS NMR studies have shown that in the case of 2-hydroxy-1-naphthylidene anilines a fast tautomeric equilibrium exists also in the solid state [60]. Anils of 10-hydroxy-2-fenantrene-9-carbaldehyde exist primarily as NH-tautomer both in solid state and in solutions [59,60]. The solid state measurement of spin-lattice relaxation rates ($T_1^{-1}$) of the proton, performed by Inabe *et al.* [9], led to the determination of the activation energy of the proton transfer $\Delta E_a$ and of the energy

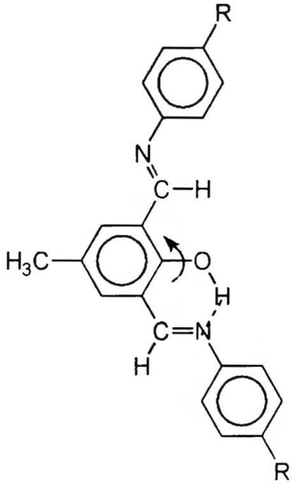


differences between the OH and NH forms in N,N-bis-(salicylidene)- and N,N-bis-(2-hydroxynaphthylidene)-p-phenylenediamine.

Resonance stabilization of the N–H form in 2-hydroxynaphthalene derivatives, when compared with salicylidene- derivatives, results in a decrease of ΔE. The collective proton motion and the almost equal population of both NH- and OH-forms has been suggested in this case.

An interesting low temperature effect has been noticed for several Schiff bases. Dudek [55] has observed that lowering of the temperature leads to an increase in population of the NH form and at the same time to a decrease in the δH values for of 2-hydroxynaphthylidene-methylamine. The tautomerization of N-salicylidene-methylamine to zwitterionic NH form in methanol solution at 195 K has been evidenced by Raman spectroscopic studies [35]. The appearance of the thermochromic band (about 400 nm) in the UV spectra at 70–150 K has been observed for several Schiff bases [1,65]. Various factors have been suggested as a cause of this "negative thermochromism".

In di-Schiff bases like para-substituted anils of 5-methyl-isophthaldehyde (4-methyl-2,6-bis-(4′-R-phenylimino-methyl)-phenols) OH group rotates around the C–O bond at room temperature. The rotation is inhibited (in the NMR time scale) at 250 K, as has been shown by $^{15}$N, $^{1}$H and $^{13}$C NMR spectroscopy [66]; the rotational barrier, determined by the NMR line shape analysis, is 47.2–49.5 kJ/mol. At low temperature the structure with two non-equivalent aniline groups has been proposed. The recent X-ray IR and $^{13}$C CPMAS NMR analyses of 4-methyl-bis-(phenylimino-methyl)-phenol have shown that this compound adopts a similar conformation in solid state [67].



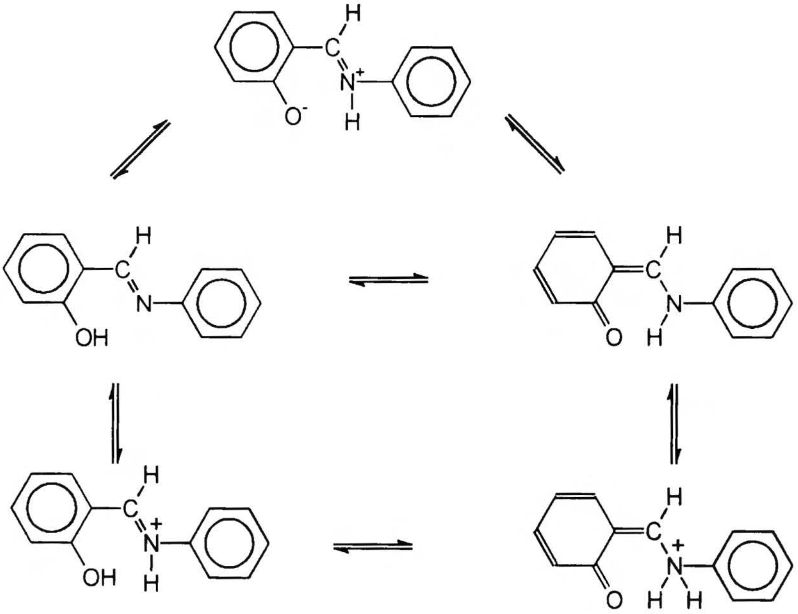
### 3.3. The solvent effect on proton transfer equilibrium

Influence of the solvent on intramolecular hydrogen bond in Schiff base and proton transfer equilibrium has been studied for several systems [35,38,41,55,62,64]. It has been shown that protondonor solvents stabilize the NH form and accordingly increase the population of this form (Table 5).

**Table 5**. Solvent effect on population of the NH-form of 2-hydroxynaphthylidene methylamine (%) [55].

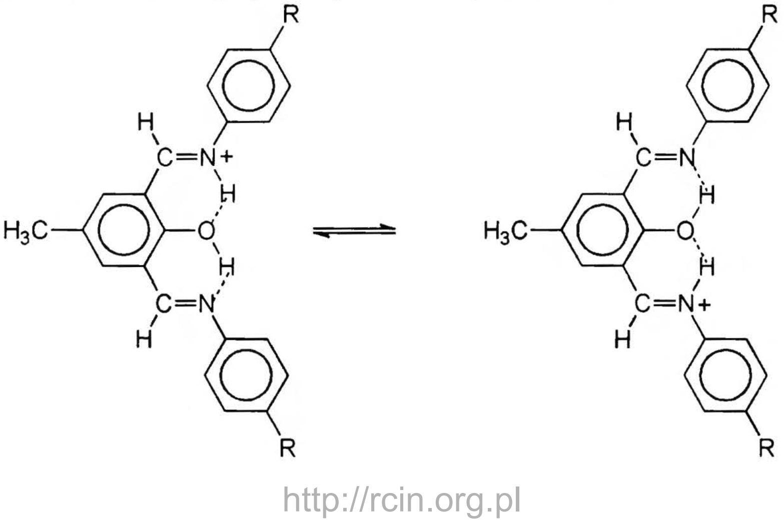
| Solvent | $CH_3OH$ | $CDCl_3$ | $C_5D_5N$ | $CCl_4$ |
|---|---|---|---|---|
| % of NH form | 90 | 73 | 66 | 22 |

It has also been suggested that in these solvents the proton transferred NH-form has a zwitterionic molecular structure [35]. In acidic 2,2,2-trifluoroethanol or hexafluoro-2-propanol several equilibria may be established [32,61]:



Carles [68] has found that N-(2,3-dihydroxybenzylidene)-aniline exists in water solution mainly in NH form, and she stated that there are intermolecular hydrogen bonds, which stabilize this form.

Recently we have studied the protonated form of di-anils of 4-methyl-isophthaldehyde by FTIR and NMR spectroscopies [69]. Hydrogen bonded systems with fast proton fluctuations and large proton polarizability were found:



Prototropic equilibrium in simple Schiff bases, as a model for active site of pyridoxal enzymes, has been widely studied [10]. The enzymatic activity of these enzymes depends on the protonation site of the cofactor [10].

## 4. Conclusion

The biological activity as well as technical application of salicylidene anils still stimulates its investigation [1]. This review does not cover all aspects, but its goal was to show that the importance of salicylidene anilines and related Schiff bases is accounted for by the presence of the RAHB. The variety of intra- and intermolecular factors enable to modulate the hydrogen bond energy and the position of the proton in the hydrogen bridge O...N.

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