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NMR Spectroscopy of 2-Hydroxy-1-naphthylidene Schiff Bases with Chloro and Hydroxy Substituted Aniline Moiety

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Schiff bases, products of the reaction of primary amines and carbonyl compounds, are involved in many metabolic processes. Hence, physicochemical studies of Schiff bases as model substances can contribute to a better understanding of biological systems. In this work, the one- and two-dimensional homo- and heteronuclear ^{1}H and ^{13}C NMR spectra of 2-hydroxy-1-naphthylidene Schiff bases with differently chloro- and hydroxyl- substituted aniline moiety were studied. The spectra were analyzed on the basis of chemical shifts, substituent effects, spin-spin couplings as well as connectivities. It was established that the investigated Schiff bases exist as NH tautomers in DMSO-d_6 solution with NH group orientated in *cis* position relative to the carbonyl of naphthylidene moiety. The positions of substituents on aniline ring were found to be in agreement with intra- and intermolecular hydrogen bond formation. Influence of substituents on planar or nonplanar conformation of compounds is discussed as well.

Keywords
Schiff bases
2-hydroxynaphthaldehyde
chloro and hydroxy anilines
^{1}H and ^{13}C NMR spectroscopy

INTRODUCTION

Schiff bases, products of the reaction of primary amines and carbonyl compounds, are involved in many metabolic processes. They mediate in connective tissues formation, in eye-sight biochemistry and elsewhere, having a role in various enzymatic reactions. One of the most important enzymatic reactions *via* Schiff bases is transamination of amino acids with pyridoxal phosphate (PLP).[1]

Schiff bases are involved as intermediates in the processes of non-enzymatic glycosylations. These processes are normal during aging but they are remarkably accelerated in pathogeneses caused by stress, excess of metal ions or diseases such as diabetes, Alzheimer's disease and atherosclerosis. Non-enzymatic glycosylation begins with an attack of sugar carbonyls or lipid peroxydation fragments on amino groups of proteins, aminophospholipids and nucleic acid, causing tissue damages by numerous oxidative rearrangements. One of the consequences is cataract of lens proteins.[2,3]

Schiff bases are also involved in reactions between some aldehydes and amines associated with preparation and storage of food. Numerous products of further fragmentation and crosslinking are responsible for colour, flavour and taste of foods and drinks.[4]

Metal ions play a catalytic role in reactions of Schiff bases. Copper participates in transamination and collagenation, and other metals participate in natural biological systems.[5] They also exert influence on non-enzymatic

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glycosylation. Schiff bases, as complexes or as free ligands, take part in *in vitro* antibacterial, antifungal and anticancer activities.[6–12]

Aromatic Schiff bases with an *ortho*-hydroxy substituent possess a very interesting characteristic – reversible color changes induced by irradiation (photochromism) or by a change in temperature (thermochromism).[13] Salicyliden- and 2-hydroxynaphthylideneamines have been the subject of particular interest because some of their complexes are found in nature and biological activities have been recorded for the synthesized ones.[5,8–10] Photochromic properties of such structures have received considerable interest due to the recent development of optical technology[14,15] and some of them manifest catalytic behaviour for polymerization.[16]

The change of colour of thermochromic compounds is ascribed to the tautomerism between the OH and NH forms resulting from intramolecular proton transfer between an enolimine and a ketoamine tautomer, which can be *cis* or *trans* relative to the C=N bond (Figure 1). *Cis-trans* isomerization is photo induced, upon irradiation in UV light, a consequence of such substances.[15,17]

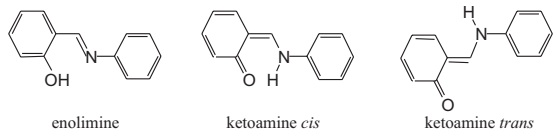


Figure 1. Three molecular species involved in thermochromism and photochromism of anilines.

For salicylaldimine, the NH form is generally less stable due to the loss of ring aromaticity,[18] which is the reason for the predominance of the OH tautomeric form of salicylaldimines in the crystalline state. 2-Hydroxynaphthylidene derivatives, containing an extended aromatic ring compared to the benzene ring of the salicylaldehyde Schiff bases, exhibit both ketoamine and enolimine tautomeric forms. The tautomerization induced by intramolecular proton transfer is accompanied by a π-electron configurational change, *i.e.,* different π-electron distributions of the two tautomers. Due to the resonance and delocalization energy in the retained aromatic structure, the NH form population of naphtaldimine Schiff bases is expected to be larger than that of salicylaldimine derivatives.[19, 20] The role of electron density of the lone pair of the imino nitrogen atom was noted by Hadjoudis[14] and Rontoyianni.[17] Among the 2-hydroxynaphthaldimine Schiff bases derived from substituted amines, the NH form has been established by X-ray single crystal diffraction in structures with 3-carboxy substituted anilines,[21] α-naphtylamines[22] and some aliphatic amines.[23,24] The OH tautomer has been detected in aniline structures with substituents: 3-chloro,[25] 3,5-dichloro,[26] 2-methyl,[27] 3-nitro,[28] 2-amino[29] and 2-bromo-4-methyl[30] as well as in aliphatic amine, threonine.[31] In some cases, both tautomeric forms are found in the crystal.[32,33]

An important role in stabilization of one or another tautomeric form is the possibility of hydrogen bond formation (intra- or intermolecular), depending on substituents. Strong influence of temperature on the character of the hydrogen bond consequently determines the type of tautomer detected by IR spectra in the solid state and solutions.[34] The final molecular structure, involving *cis* or *trans*, planar or non-planar conformation, under defined conditions depends directly on hydrogen bond formation, and there is no simple relation with the type of tautomer.[8] Thus, salicylidenaniline Schiff bases (although mostly as OH tautomers with intramolecular OH–N bonding) can also exist in NH form (intramolecular NH–O bonding) at low temperature (15 K), being stabilized by intermolecular hydrogen bond formation. The first structure determination of a pure NH form of salicylidenaniline was described by Ogawa in 2000.[35] In general, intermolecular hydrogen bond formation contributes to planarity of the molecule, but planarity or non-planarity do not determine the thermochromic or photochromic behaviour and are not in strong correlation with the type of tautomer either.[14,36] Enolimine tautomer of naphthaldimines with *N*-aryl substituents can be planar,[26,28] as well as non-planar in crystals.[25,27,29,30] NH tautomer can be regarded as a resonance hybrid of two canonical structures, the quinoid and zwitterionic forms, as shown in Figure 2.[37]

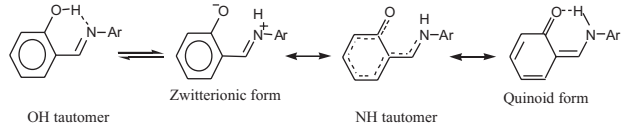


Figure 2. Proton transfer equilibrium in Schiff bases.

Polar solvents move the equilibrium to the NH tautomer. One of the explanations is that protonated solvents cause protonation of the imino bond, forming several intermediates, including the zwitterionic form which favours molecular polarity and electrostatic intermolecular interactions become stronger.[33,37,39] Zwitterionic form, which was found in predominance over the quinoid form, can stabilize the NH tautomer in salicylaldimines, retaining the phenyl ring aromaticity and location of the hydrogen atom at the nitrogen site at the same time. Tautomeric equilibrium in Schiff bases in solution reveals that tautomerization is not an exclusive crystal structure property. It was established that the tautomeric equilibrium, depending on the polarity of solvent and pH, is more expressed for naphthylidene than for salycilidene Schiff bases.[33]

In this work, we have investigated types of tautomers for some prepared 2-hydroxynaphthylidene Schiff bases that contain mono- and disubstituted hydroxy and chloro anilines in their structures. We have determined positions of the corresponding substituents on the aniline ring with regard to the naphthalene ring. NMR investigations were

substantiated by measurements of IR spectra of the same substances in the solid state and by our earlier X-ray single-crystal diffraction results.[21,25]

EXPERIMENTAL

Materials

Aniline, 2-aminophenol(2-hydroxyaniline) 99 %, 3-chloroaniline 99 %, 4-chloroaniline 98 %, 2-amino-4-chlorophenol (5-chloro-2-hydroxyaniline) 97 %, 2,4-dichloroaniline 99 %, 2-hydroxy-1-naphthaldehyde 98 %, copper(II) acetate monohydrate 99.99 % and zinc acetate dihydrate 99.99 %.

Reagents were purchased from Aldrich (USA) and CIBA Chemical Corporation (Switzerland) and were used without further purification, except for aniline which was freshly distilled before use.

Physicochemical Measurements

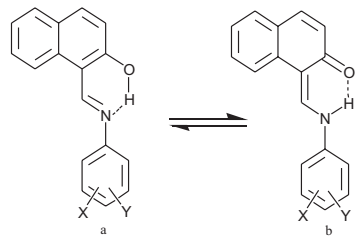
Melting points (m.p.) were determined on a Tottoli apparatus (Switzerland) and were not corrected. Synthesis and purity of compounds were examined by TLC plates, silica gel 60 F_{254} on glass (S) from Merck (Germany), as well as on plastic TLC plates: silica gel N-HR/UV_{254} (MN) from Macherey-Nagel (Germany). IR spectra were recorded as KBr pellets with a Paragon 500FT-IR Perkin-Elmer spectrophotometer and are given in cm^{-1}.

One- and two-dimensional ^1H and ^{13}C NMR spectra were measured with a Varian Gemini 300 spectrometer, operating at 75.5 MHz for the ^{13}C nucleus. Samples were recorded from DMSO-d_6 solutions at 25 °C (298 K) in 5 mm NMR tubes. Chemical shifts, in ppm, were referred to TMS as internal standard. Digital resolution in ^1H NMR spectra was 0.25 Hz, while it was 0.78 Hz per point in ^{13}C NMR spectra. The following techniques were used: standard ^1H, ^{13}C broadband proton decoupling, ^{13}C gated proton decoupling, COSY-45, NOESY and HETCOR. Proton decoupling was performed using the Waltz-16 modulation. COSY-45 spectra were measured in the magnitude mode using 1024 points in F_2 dimension and 256 increments in F_1 dimension, subsequently zero-filled to 1024 points. Each increment was recorded with 16 scans, 3000 Hz spectral width and a relaxation delay of 1 s. Digital resolution was 5.9 Hz/point and 11.7 Hz/point in F_2 and F_1 dimensions, respectively. NOESY spectra were measured in the phase-sensitive mode with 1024 points in F_2 dimension and 256 increments in F_1 dimension, subsequently zero-filled to 1024 points. Each increment was recorded with 16 scans, 3000 Hz spectral width and a relaxation delay of 1 s. Thus, the digital resolution was 5.9 Hz per point and 11.7 Hz per point in F_2 and F_1 dimensions, respectively. NOESY spectra were measured at several mixing times (0.45–1.2 s). HETCOR spectra were recorded with 2048 points in F_2 dimension and 256 increments in F_1 dimension, zero-filled to 512 points. Increments were recorded with 64 scans, relaxation delay of 1 s and spectral width of 20000 Hz in F_2 dimension and 4500 Hz in F_1 dimension. Digital resolution was 19.53 and 17.6 Hz/point in F_2 and F_1 dimensions, respectively.

IR spectral data were recorded as KBr pellets with a Paragon 500FT-IR Perkin-Elmer spectrophotometer. Data are given in cm^{-1}.

Preparation of Schiff Bases

The investigated Schiff bases **1**–**6** (Figure 3) were synthesized from the corresponding aromatic amines and aldehydes by the reaction of mono- and disubstituted derivatives of aniline with 2-hydroxynaphthaldehyde, according to the modified procedure of Senier and Clark.[40]



	X	Y
1.	H	H
2.	2-OH	H
3.	3-Cl	H
4.	4-Cl	H
5.	2-OH	5-Cl
6.	2-Cl	4-Cl

Figure 3. Molecular structure of compounds **1**–**6**.

General Procedure. – 2-Hydroxynaphthaldehyde (1 mmol) was dissolved by stirring in methanol (10 mL) and 1 mmol of aniline derivative was added slowly to the aldehyde solution. Substituted anilines were used in powdered form, except those for Schiff bases **1** and **3**, which were dissolved in a small amount of methanol before being added to aldehyde solution. Nicely coloured precipitates (yellow to red) were formed after a short time. The products were separated and purified by washing with water or/and by crystallization from methanol. The purity was controlled by TL chromatography and checked by melting points or/and by elemental analysis. Structures **1**–**4** were confirmed by metal complexes formation. Copper(II) complexes were made using copper acetate monohydrate and the zinc(II) complex was made using zinc acetate dihydrate.

2-Hydroxy-α-naphthylidenaniline (***1***)*:*

M.p. 97–99 °C (99 °C);[41] 99.1 % yield; R_f = 0.10 (petrol-ether, TS-MN).

2-Hydroxy-α-naphthylidene-2-aminophenol (***2***)*:*

M.p. 244–246 °C (248–250 °C);[40] 81.3 % yield; R_f = 0.15 (dichloromethane, TS-S).

Cu^{II} complex, dark olive green, 99.3 % yield.

Anal. Calcd. for $C_{34}H_{22}N_2O_4Cu_2$ (M_r = 649.64): C 56.82, H 2.80, N 3.89 %; found: C 56.82, H 3.07, N 3.79 %.

The same analysis was obtained from the complex made with CuCl instead of Cu^{II} acetate.

Zn complex, yellow, 77.2 % yield.

TABLE I. ^{1}H chemical shifts, δ/ppm, and coupling constants J/Hz of Schiff bases **1**–**6**

H atom	Chemical shifts, δ/cm^{-1} Coupling constants, *J*/Hz [a]					
	1	**2**	**3**	**4**	**5**	**6**
NH	δ 15.81 *J* 4.32 (d)	δ 15.72 *J* 9.55 (d)	δ 15.48 *J* 3.87 (d)	δ 15.59 *J* 3.30 (d)	δ 15.70 *J* 8.72 (d)	δ 15.54 *J* 2.66 (d)
OH_2,	–	*J* 10.33 (s)	–	–	*J* 10.56 (s)	–
C_aH	δ 9.65 *J* 4.65 (d)	δ 9.53 *J* 9.54 (d)	δ 9.69 *J* 3.89 (d)	δ 9.68 *J* 4.32 (d)	δ 9.53 *J* 9.00 (d)	δ 9.79 *J* 2.85 (d)
H_2,	δ 7.65 *J* 8.08 (d)	–	*J* 7.86 (s)	δ 7.69 *J* 8.64 (d)	–	–
H_3,	δ 7.51 *J* 6.99 (t)	δ 7.00 *J* 7.95 (d)	–	δ 7.55 *J* 8.39 (d)	δ 7.00 *J* 8.72 (d)	δ 7.78 *J* 2.26 (d)
H_4,	δ 7.32 *J* 7.97 (t)	δ 7.12 *J* 7.64 (t)	δ 7.36 *J* 7.50 (d)	–	δ 7.14 *J* 1.48 (d)	–
H_5,	δ 7.51 *J* 6.99 (t)	δ 6.96 *J* 7.79 (t)	δ 7.50 *J* 7.91 (t)	δ 7.55 *J* 8.39 (d)	–	δ 7.58 *J* 8.43 (d)
H_6,	δ 7.65 *J* 8.08 (d)	δ 7.94 *J* 7.95 (d)	δ 7.54 *J* 7.91 (d)	δ 7.69 *J* 8.64 (d)	*J* 8.14 (s)	δ 8.09 *J* 8.73 (d)
H_3	δ 7.00 *J* 9.05 (d)	δ 6.80 *J* 9.55 (d)	δ 7.04 *J* 9.15 (d)	δ 7.05 *J* 9.31 (d)	δ 6.81 *J* 9.34 (d)	δ 7.12 *J* 9.06 (d)
H_4	δ 7.93 *J* 9.23 (d)	δ 7.81 *J* 9.22 (d)	δ 7.96 *J* 9.23 (d)	δ 7.96 *J* 9.05 (d)	δ 7.84 *J* 9.33 (d)	δ 8.01 *J* 8.98 (d)
H_5	δ 7.79 *J* 7.73 (d)	δ 7.69 *J* 7.96 (d)	δ 7.81 *J* 7.95 (d)	δ 7.82 *J* 7.95 (d)	δ 7.68 *J* 7.78 (d)	δ 7.85 *J* 7.66 (d)
H_6	δ 7.35 *J* 8.18 (d)	δ 7.25 *J* 7.96 (t)	δ 7.37 *J* 7.73 (t)	δ 7.37 *J* 7.54 (t)	δ 7.28 *J* 8.48 (t)	δ 7.41 *J* 7.32 (t)
H_7	δ 7.51 *J* 6.99 (t)	δ 7.49 *J* 7.64 (t)	δ 7.56 *J* 7.70 (t)	δ 7.56 *J* 8.47 (t)	δ 7.49 *J* 7.51 (t)	δ 7.59 *J* 8.27 (t)
H_8	δ 8.49 *J* 8.57 (d)	δ 8.40 *J* 8.28 (d)	δ 8.55 *J* 8.27 (d)	δ 8.52 *J* 8.39 (d)	δ 8.47 *J* 8.40 (d)	δ 8.58 *J* 8.39 (d)

[a] In brackets: multiplicity of signals denoted as: (s) singlet, (d) doublet, (t) triplet.

Anal. Calcd. for $C_{34}H_{22}N_2O_4Zn_2$ (M_r = 653.30): C 62.50, H 3.39, N 4.29 %; found: C 62.34, H 3.71, N 4.18 %.

*2-Hydroxy-α-naphthylidene-3-chloroaniline (**3**):*

M.p. 112–113 °C (116–117 °C);[40] 70 % yield; R_f = 0.25 (petrolether, TS-S). Recrystallization from toluene gave a single crystal of good diffraction quality and crystallographic structure was X-ray determined.

Cu^{II} complex was dark yellow and obtained in 98 % yield.

*2-Hydroxy-α-naphthylidene-4-chloroaniline (**4**):*

M.p. 153–154 °C (158–159 °C);[40] 71.7 % yield; R_f = 0.32 (petrolether, TS-S).

Dark yellow coloured Cu^{II} complex was prepared in 69.8 % yield.

*2-Hydroxy-α-naphthylidene-2-hydroxy-5-chloroaniline (**5**):*

M.p. 248–250 °C; 84 % yield; R_f = 0.45 (chloroform, TS-S).

Anal. Calcd. for $C_{17}H_{12}NO_2Cl$ (M_r = 297.73): C 68.58, H 4.05, N 4.74 %; found: C 68.61, H 4.21, N 4.67 %.

Cu^{II} complex, olive green, 85.5 % yield.

Anal. Calcd. for $C_{34}H_{20}N_2O_4Cl_2Cu_2$ (M_r = 718.52): C 56,83, H 2.81, N 3.90 %, found: C 56.91, H 3.05, N 3.46 %.

Preparation with Cu^I salt gave the product with the same analysis (found C 56.82, H 3.07, N 3.79 %).

*2-Hydroxy-α-naphthylidene-2,4-dichloroaniline (**6**):*

M.p. 168–169 °C; 93.6 % yield; R_f = 0.5 (chloroform, TS–S).

Anal. Calcd. for $C_{17}H_{11}NOCl_2$ (M_r = 316.17): C 64.58, H 3.51, N 4.43 %; found: C 64.68, H 3.72, N 4.28 %.

TABLE II. ^{13}C chemical shifts, δ/ppm, of Schiff bases **1**–**6**

C atom	^{13}C δ/ppm					
	1	**2**	**3**	**4**	**5**	**6**
C_α	155.31	149.49	157.16	156.68	150.30	158.26
C_1	108.49	107.76	108.86	108.80	108.26	109.36
C_2	171.26	177.62	169.58	169.48	177.11	167.51
C_3	120.48	125.14	121.71	121,74	124.72	120.87
C_4	137.11	137.96	137.12	136,94	138.25	137.06
C_5	129.09	129.03	129.04	129.07	129.06	129.31
C_6	123.57	123.09	123.73	123.67	123.40	123.92
C_7	128.21	128.15	128.18	128.17	128.18	128.48
C_8	120.38	119.79	120.74	120.57	120.27	120.87
C_9	126.68	128.64	126.89	126.88	123.71	127.14
C_{10}	133.31	133.98	133.12	133.10	133.86	132.87
$C_{1'}$	143.70	125.89	146.13	143.46	130.34	141.49
$C_{2'}$	122.49	148.49	120.08	122.54	147.55	128.24
$C_{3'}$	129.73	119.88	134.21	129.51	117.17	129.09
$C_{4'}$	126.59	126.79	126.19	130.73	126.07	131.05
$C_{5'}$	129.73	116.01	131.11	129.51	126.20	128.24
$C_{6'}$	122.49	117.65	120.20	122.54	117.37	121.26

Cu^{II} complex, red-brown, was prepared in 47.3 % yield. *Anal. Calcd.* for $C_{34}H_{20}N_2O_2Cl_4Cu$ (M_r = 693.87): C 58.84, H 2.91, N 4.06 %; found: C 58.51, H 3.10, N 3.91 %.

RESULTS AND DISCUSSION

As shown in Figure 3, Schiff bases **1**–**6** can exist in two tautomeric forms, OH form (a) and *cis* NH form (b). Measurements of NMR and IR spectra revealed the tautomeric forms of **1**–**6**, under defined conditions.

^1H-NMR and ^{13}C NMR spectra were measured in DMSO-d_6 solutions and the chemical shifts and coupling constants are presented in Tables I and II. Enumeration of atoms is shown in Figure 4. Combination of COSY, NOESY and HETCOR spectra enabled assignment of hydrogen atoms and determination of the tautomeric forms and conformation of investigated molecules.

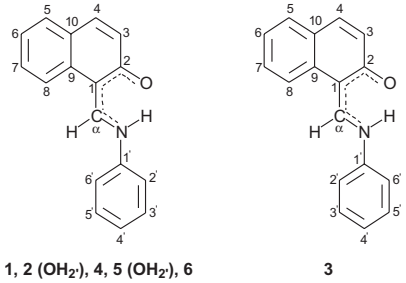


Figure 4. Enumeration of atoms in Schiff bases **1**–**6**.

Based on the analysis of NMR data we have established that Schiff bases **1**–**6** exist as NH tautomers in the DMSO solution. The NH group orientation is *cis* in relation to the carbonyl group on the naphthalene ring. The analysis also revealed the orientation of the substituents at the aniline moiety towards the naphthylidene moiety (Figure 5).

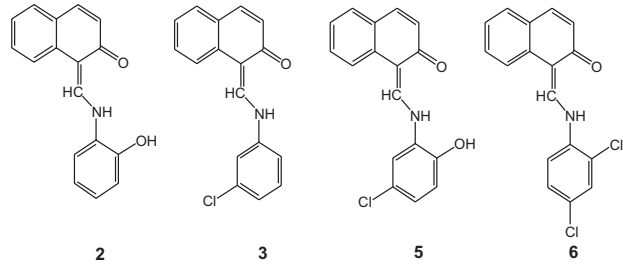


Figure 5. Structures of Schiff bases **2**, **3**, **5** and **6** in DMSO-d_6 solution.

On the other hand, the IR spectra of solid samples (KBr pellets) do not show the presence of the carbonyl group. Absorption bands attributed to imine ν(C=N) and phenolic ν(C–O) groups[33,38] suggested that Schiff bases **1–6** exist in the solid state as OH tautomers (Table III).

In our previous work,[25] it was found by X-ray single crystal diffraction that compound **3** in the crystalline

TABLE III. The ν(C=N) and ν(C–O) absorption bands in IR spectra of Schiff bases **1**–**6**

	Absorption bands ν/cm^{-1}					
	1	**2**	**3**	**4**	**5**	**6**
C=N	1623.6	1625.8	1619.3	1613.3	1621.3	1621.4
	1591.4		1568.6	1565.3		1606.4
C–O	1347.2	1353.6	1317.7	1320.6	1344.4	1326.2
		1318.8			1300.3	

state exists as OH tautomer, which is in agreement with the presented IR spectral data.

Comparison of NMR and IR spectra results indicated a significant influence of solvent on the tautomerization process. The polar solvent dimethylsulfoxide caused the proton transfer reversible process, *i.e.*, tautomer changing from the OH to NH form. Polarity of the solvent as well as the parent aromatic aldehyde obviously plays a more important role in equilibria between tautomers than the polarity of substituents at the aniline ring (nonpolar as chloro atom in compound **3** or polar as hydroxyl group in compound **2**).[42]

However, the position of substituents at the aniline ring, especially the polar ones, influences stabilization of the corresponding tautomer. A polar substituent, such as the carboxylate group at the *meta*-position on the aniline ring in 3-[(2-hydroxy-1-naphthyl)methyleneamino]benzoic acid, homologous to **1**–**6** structure in this work, participates in stabilization of the NH tautomer by strong intermolecular hydrogen bond formation in the crystal, as we recently published.[21] The question is why a polar substituent, such as the hydroxy group on the aniline ring in compound **2,** does not prefer formation of the NH tautomer in the solid state. The reason is that the position of the polar substituent on the aniline ring has to be taken into account. In compound **2,** the hydroxyl group in *ortho*-position on the aniline ring obviously prefers intramolecular to intermolecular hydrogen bond formation.

NH tautomers are, by reason of the presence of intermolecular hydrogen bond formation, accompanied by molecules planarity much more than OH tautomers. The molecule of a Schiff base with a *meta*-carboxylate group on the aniline ring, as NH tautomer, is planar in the crystalline state, as it was established by single X-ray diffractrometry.[18] In contrast, compound **3**, with *meta*-chloro substituent on the aniline ring, as OH tautomer, is nonplanar and there are no intermolecular hydrogen bonds between molecules.[25] However, the dependence of molecular planarity on intermolecular hydrogen bond formation for the NH form has not been strictly determined.[14,36]

The relation between conformation and the type of tautomer obviously includes all dynamic aspects of hydrogen bond formation considering physicochemical mechanisms based on the proton transfer equilibrium, including redistribution of electron density, resonance and delocalization energy.

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SAŽETAK

NMR spektroskopija 2-hidroksi-1-naftiliden Schiffovih baza s kloro i hidroksi supstituiranim anilinom

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Schiffove baze kao produkti reakcija primarnih amina i karbonilnih spojeva uključene su u mnoge metaboličke procese. Fizikalno-kemijske studije Schiffovih baza kao modelnih spojeva mogu stoga pridonijeti boljem poznavanju bioloških sustava. Utjecaj supstituenata na kemijske pomake te spin-spin interakcije Schiffovih baza 2-hidroksi-1-naftilidena s kloro i hidroksi supstituiranim anilinima, proučavani su na osnovu jedno- i dvodimenzijskih homo- i heteronuklearnih ^{1}H i ^{13}C NMR spektara. Utvrđeno je da istraživane Schiffove baze postoje kao NH tautomeri u otopini DMSO-d_6 s *cis* orijentacijom NH skupine u odnosu na karbonilnu skupinu naftalenskog prstena. Položaj supstituenata na anilinskom prstenu u skladu je s rasporedom intra- i intermolekulskih vodikovih veza. Planarnost ili neplanarnost molekule Schiffove baze ovisi o utjecaju tautomernog oblika, te vrsti i položaju supstituenta.