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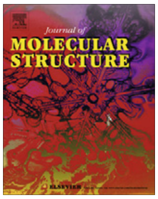

Tautomeric Schiff bases: Iono-, solvato-, thermo- and photochromism

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ABSTRACT

The review article summarizes the recent data about novel tautomeric iono-, solvato-, thermo- and photochromic Schiff bases. This contribution focuses on the factors determining tautomeric equilibrium and on the investigations into the proton transfer mechanisms.

1. Introduction

Due to their synthetic accessibility and readiness to coordinate main group and transition metal ions Schiff bases represent one of the most extensively used class of mono-, bi- and polydentate ligands in coordination chemistry [1–6]. The metal cation complexes based on Schiff base ligands serve as good building blocks for molecular magnets and catalytic reagents [7]. Schiff bases have wide applications in medicine [8–11], chemosensor chemistry [12–14] and in biological processes [15–18]. Many of these compounds exhibit tautomeric rearrangements because of intramolecular proton transfer between the enolimine (OH) and the ketoenamine (NH) forms possessing different electronic absorption spectra. Tautomeric Schiff bases can serve as the specific type of molecular switches in optical recording technology, molecular electronics, and computing [19–21]. The bistable tautomeric Schiff bases constitute two-level systems which can be manipulated by light, heat or electric current. The advantage of such systems consists in their high stability due to the absence of significant structural rearrangements in the molecule under reversible switching.

The tautomerism of Schiff bases received renewed interest due to application of improved experimental and theoretical methods. Most of these studies were focused on estimation of tautomeric preferences, investigation of the role of substituents on the position of the tautomeric equilibria, solvato-, iono-, thermo- and photochromic effects [20–34].

2. Tautomerism of Schiff bases: generalities

The prototropic enolimine–ketoenamine equilibrium is the most studied tautomeric process inherent in Shiff bases (Scheme 1). In the recent years this interconversion was amply studied for hydroxy-substituted Schiff bases in vapor [35], solutions [22], solid state [36] and Langmuir–Blodgett films [37]. Other examples of tautomeric equilibria related to Schiff bases (excluding prototropy [22,38–43]), such as ring-chain tautomerism [44–48], metallotropy [49] will be out of the scope of this review.

Tautomer stability as described by the equilibrium constant values K_T or other thermodynamic parameters (ΔG, ΔH, ΔS), can be evaluated directly from spectroscopic measurements (UV, IR, NMR, mass-spectroscopy, etc.) in such cases when tautomers exhibit separate nonoverlapping spectroscopic signals. NMR spectroscopy is the most frequently used experimental method for the investigation of prototropic equilibria of Schiff bases [50].

The coupling constant of OH···N proton (^3J(HN, CH)) is an important NMR parameter that allows to estimate mole fraction of the NH tautomeric form [51,52]. One of the first quantitative studies based on the measurement of coupling constants was undertaken by Brown and Nonhebel determined 12.5 Hz value of ^3J(HN, CH) for a pure ketoenamine form [53]. The Eq. (1) can be used for the estimation of mole fraction (χ) of the NH tautomer in solution.

$$^3J(\mathrm{NH,CH}) = 12.5 \times \chi\ [\mathrm{Hz}] \tag{1}$$

The main problem of the NMR method is line broadening and coalescence of signals of the tautomers when their lifetimes are very short and the NH tautomer is present in a small amount.

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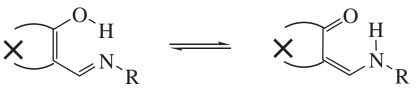


X = Alk, Ar, Het; R = Alk, Ar

Scheme 1.

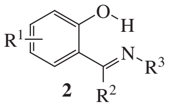
The $^1J(^{15}N–^1H)$ coupling constant of the NH tautomeric form is another very sensitive parameter to characterize tautomeric equilibria of Schiff bases [50,51]. Mole fraction of NH tautomer can be estimated assuming a value of 89 Hz for $^1J(^{15}N–^1H)$ in the NH form and 0 Hz in the OH form [54,55]:

$$^1J(^{15}N{-}^1H) = 89 \times \chi \ [\mathrm{Hz}] \tag{2}$$

However this parameter is not perfectly constant and depends on the structure of a molecule. The ^{13}C and ^{15}N NMR methods for investigation of tautomeric equilibrium of Schiff bases in solutions and solid state are widely represented in the literature [51,52,56–66]. Alarcon and co-workers [60] measured chemical shifts of carbons C2 and used Eq. (3) to determinate the K_T values (Scheme 2).

$$K_T = [\mathbf{b}]/[\mathbf{a}] = (\delta_{(C2)} - 155\,\mathrm{ppm})/(180\,\mathrm{ppm} - \delta_{(C2)}) \tag{3}$$

Isotope effect method using ^{13}C chemical shifts ($^n\Delta C(XD)$) was also adopted to establish the presence and position of the prototropic equilibria in Schiff bases **2–5** [51,52,56,59].



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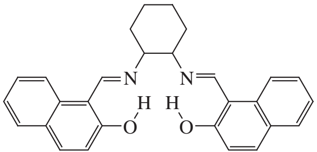
R^1 = H, CH_3, OCH_3, Cl, Br, F, NO_2, di-Cl, di-Br, di-F, di-OCH_3, di-CH_3;
R^2 = H, CH_3, Ph;
R^3 = CH_3, C_2H_5, C_3H_7, t-C_4H_9, CH_2Ph



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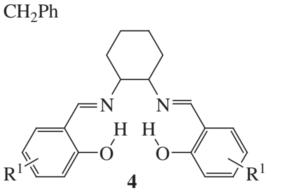

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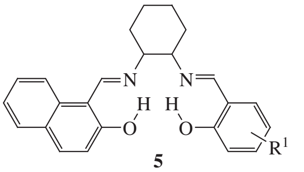

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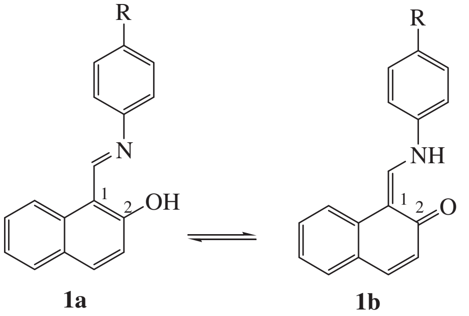
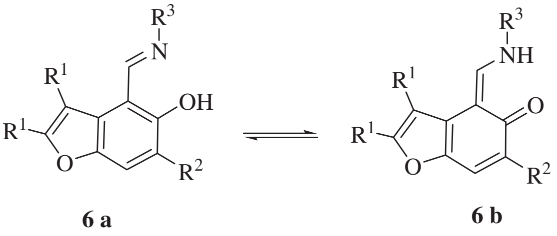
Deuterium isotope effects on ^{13}C chemical shifts caused by deuterium substitution of the OH···N proton were measured as the difference between the chemical shifts of ^{13}C signals in partially deuterated compounds: $^n\Delta C(XD) = \Delta C(XH) - \delta C(XD)$, where *n* is the number of bonds between the deuterium and the carbon. The $^n\Delta C(XD)$ value depends on the position of the tautomeric equilibrium and is a sensitive non-monotonic function (S-shape) of the mole fractions of the tautomers.



Scheme 2.



R^1+R^1 = Ph,-$(CH_2)_4$-; R^2 = H, Br, I, t-Bu, NO_2; R^3 = Alk, Ar

Scheme 3.

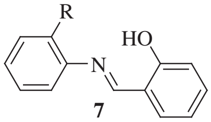
Recent studies [57] showed that ^{15}N cross-polarization magic angle spinning CPMAS nuclear magnetic resonance is a useful method for investigation of the tautomerism of Schiff bases due to the large difference in the nitrogen chemical shifts of OH and NH tautomers. It was found that the values between −85 ppm and −110 ppm in the solid state ^{15}N NMR spectra are typical for the OH tautomers of Schiff bases, while signals within the range −192 to −239 ppm indicate NH tautomers.

^{15}N NMR spectra of a series of N-(R-salicylidene)alkylamines in $CDCl_3$ revealed correlation between the chemical shifts ^{15}N and spin–spin coupling constants $^1J(^{15}N-^1H)$, but a separate plot for each compound was found [64]. The values of the ^{15}N chemical shift are influenced not only by the content of the ketoenamine form but also by electronic and steric effects of substituents in the aromatic ring and alkyl groups linked to the nitrogen atom.

The NMR results combined with those obtained by absorption spectrophotometry allowed to determine the equilibrium constants of Schiff bases **6** derived from 5-hydroxy-2,3-tetramethylene- and 5-hydroxy-2,3-diphenylbenzo[*b*]furan-4-carbaldehydes [67,68] (see Scheme 3).

Form **a** is colorless or slightly yellow with an absorption band in the near UV region, whereas the form **b** is of red color and exhibits an additional nonoverlapping absorption band with wavelength longer than 430 nm (Fig. 1). The molar extinction coefficients of ketoenamine form of model compounds obtained through measurement of its mole fraction using ^1H NMR method were employed for estimation of content of the tautomer **b** in different solvents.

Diffuse reflectance spectra were measured to obtain the absorption spectra of powdered materials [69]. Temperature-dependent UV–vis Kubelka–Munk spectra of crystalline powders of salicylideneanilines **7** were reported. However the intensity of the corresponding absorption band in the Kubelka–Munk spectra is very weak. Traces of the *cis*-keto form with λ_{max} different from that of the *trans*-keto form exists in the crystals at room temperature but these almost disappear at low temperatures.



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R = H, Cl

The IR spectroscopy is also a very important tool to study the hydrogen bond in Schiff bases [70–72] but strong coupling of vibrations and complexity of the spectra in many cases have made reliable assignments of the spectra impossible. Dziembowska and co-workers carried out theoretical analysis of vibrational spectra of the simplest di-Schiff base – trans-N,N′-bis-salicylidene-1′,2′-cyclohexanediamine and assigned its vibrations by comparison of the calculated and experimental IR spectra [73]. In contrast to