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Proton Transfer Equilibria in Schiff Bases with Steric Repulsion

I. Król-Starzomska, A. Filarowski, M. Rospenk, and A. Koll*

Faculty of Chemistry, University of Wrocław, 14 F. Joliot-Curie str., 50-383 Wrocław, Poland

S. Melikova

Institute of Physics, St. Petersburg State University, 198-904 St. Petersburg, Russia

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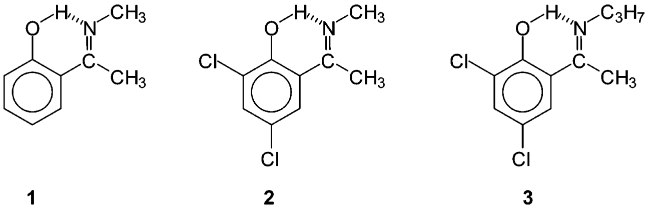
The proton transfer equilibria in CH_2Cl_2 solutions of 2-(α-(*N*-methylimino)ethyl)phenol (**1**), 2-(α-(*N*-methylimino)ethyl)-4,6-dichlorophenol (**2**) and 2-(α-(*N*-propylimino)ethyl)-4,6-dichlorophenol (**3**) are studied by UV−vis, ^{1}H NMR, and FT-IR spectra as a function of temperature. Thermodynamic parameters of the proton transfer reaction have been determined. It has been demonstrated that introducing of the methyl substituent into the C−C(H)═N moiety of the Schiff bases alters the tautomeric equilibrium in favor of the proton transfer forms in comparison with Schiff bases deprived of such substituent and related Mannich bases. Solvatochromy of electronic absorption in Schiff bases is evidence that the proton transfer state is neither zwitterionic nor orthoquinoid in their character but has to be taken as a resonance hybrid of these forms. According to this, a scheme of proton transfer equilibria specific for Schiff bases is proposed, which is in agreement with numerous structural evidences. The B3LYP/6-31G(d,p) frequency calculations performed for both the molecular and proton transfer forms precisely reproduce the experimental spectra measured as a function of temperature. The calculations show that the ν(C═N) band assignment, widely discussed in the literature, is ambiguous because of the strong dependence of normal coordinates content on the character and conformation of particular forms of molecules. The calculations definitely show that the protonation of the C═N−R group decreases the force constants of the C═N bonds, in spite of numerous opposite suggestions in the literature.

1. Introduction

The nature of hydrogen bonding is an open question partly due to a large variety of different systems forming hydrogen bonds. This problem, being of a great theoretical and practical significance,[1−3] has been studied with the use of model systems, among which those with intramolecular hydrogen bonds are of large importance because of their thermodynamic and structural stability.[4,5] The *o*-hydroxy Schiff bases, which are able to form the intramolecular, resonance-stabilized hydrogen bonds take a very special position here.[6] Their specificity results from the existence of comparatively easily accessible intramolecular proton transfer forms.[7] The proton transfer reaction is responsible for thermochromic and photochromic properties of these systems.[8,9] It makes them potential molecular memory devices, optical switches,[10] and photodetectors in biological systems.[11] The structure of the species responsible for double fluorescence is still an open question in the literature.[12−14] In this paper we aim to study the equilibrium of intramolecular proton transfer reaction in three Schiff bases (cf. Chart 1) 2-(α-(*N*-methylimino)ethyl)phenol (**1**), 2-(α-(*N*-methylimino)ethyl)-4,6-dichlorophenol (**2**) and 2-(α-(*N*-propylimino)ethyl)-4,6-dichlorophenol (**3**), which have very specific properties.

The replacement of the hydrogen atom by the methyl, ethyl,[15] or phenyl[16] substituents in the C−C(H)═N moiety in *o*-hydroxy Schiff bases shortens the intramolecular hydrogen bonds. It was found that compound **1** forms the shortest OHN hydrogen bond (2.459(3) Å) known in the literature.[15] IR spectra of **1** in the solid state show continuous absorption, which shifts to lower wavenumbers on a decrease of temperature. However, its spectra in CCl_4 solution indicate much weaker hydrogen bonding, with the maximum of absorption at about 2600 cm^{-1}. The calculations give, obviously, spectra more resembling those in CCl_4 solution than in the solid state. We intend to compare these systems with both Schiff bases without such a substitution[17] and the related Mannich bases[5] to explain the influence of the electronic coupling and steric strain on the proton transfer equilibria.

CHART 1



Thermodynamic characteristics of the intramolecular proton transfer process in salicylidenealkylamines were studied by UV−vis spectroscopy.[18] ΔH°_{PT} values were within the range of −5 to −14 kJ/mol, when ΔS°_{PT} values were between −30 and −50 J/(mol·K). However, a combination of these thermodynamic parameters for the particular compounds leads to positive values of ΔG°_{PT} at room temperature with a comparatively low concentration of NH (proton transfer) forms.

It was shown[18] that, to observe the proton transfer equilibria in salicylidenealkylamines in CH_2Cl_2, some limit of acidity of

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* To whom correspondence should be addressed. E-mail: akoll@wchuwr.chem.uni.wroc.pl.

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the phenolic part should be exceeded; at least two chloro substituents in the phenol ring are necessary. For the compound with one chloro substituent, no evidence of the PT state was found down to 190 K (cf. ref 7).

For Mannich bases, in which the $-CH_2-$ bridge radically decreases the electron coupling between the phenol and amine parts of the system, the proton transfer equilibrium was observed at low temperatures for polychloro-substituted compounds, starting from tetrachloro derivatives[19] in nonpolar solvents and trichloro derivatives in alcohols.[5] For the systems showing such an equilibrium, the thermodynamic characteristics of the intramolecular proton transfer reaction were within a similar range as in the above-mentioned Schiff bases: $15 > -\Delta H^{\circ}_{PT} > 6$ kJ/mol, $65 > -\Delta S^{\circ}_{PT} > 30$ J/(mol·K).[4] Evidence for solvent participation in the intramolecular proton transfer reaction can be anticipated from the comparatively large negative values of ΔS°_{PT}.[20]

The study of the equilibrium position in the intramolecular hydrogen bond in sterically modified Schiff bases **1**−**3** in low polar CH_2Cl_2 (CD_2Cl_2) solutions was performed by applying FT-IR, UV−vis, and NMR spectroscopy in a wide temperature range, from room to liquid nitrogen temperature. Especially interesting is the modification, in comparison to Mannich bases, of the character of species participating in proton transfer equilibrium, resulting from π-electron coupling. This modification is discussed in detail on the basis of spectral evidences as well as results of DFT (B3LYP/6-31G(d,p)) calculations. These calculations also allow us to estimate the force field in internal coordinates and make the ν(C═N) bands assignment as well as to discuss the force constants modification upon protonation, which is a topic of controversy in the literature.[21]

2. Experimental Section

Synthesis of Schiff bases from the stoichiometric mixtures of corresponding ketones and amines in methanol was made according to ref 22. The quantum mechanical calculations were performed with the use of the Gaussian 94 program.[23]

The UV spectra were recorded by using a Cary 1 UV−vis spectrophotometer with the homemade two-beam cryostat allowing measurements down to −130 °C in quartz cells. The IR spectra were measured on an Avatar 360 FTIR spectrophotometer with a resolution of 1 cm^{-1}. The ^1H NMR spectra were recorded on a Bruker AMX 300 spectrometer. The measurements were performed in CD_2Cl_2 solutions within the temperature range of 300−180 K.

3. Results and Discussion

3.1. UV−Vis Spectra. Figure 1a presents the evolution of the electronic absorption spectra of **1** upon solvent polarity increase. It shows that compound **1** in CCl_4 exists exclusively in molecular form (absorption band at ~320 nm), whereas in methanol a very strong predominance of absorption band at about ~385 nm can be taken as evidence of the prevailing of proton transfer forms. In CH_2Cl_2, one observes the equilibrium with a predominance of molecular forms at room temperature.

Figure 1b presents the effects of temperature on the spectra of **1** in CH_2Cl_2 solutions. At −90 °C the fraction of PT form reaches approximately 50%. The estimation was made using the extinction coefficient determined in methanol, where spectra suggest a complete proton transfer at low temperatures. The extinction coefficient value was extrapolated to desired temperatures with the help of the temperature dependence of the solvent density. Proton transfer equilibrium constants defined as $K_{PT} = C_{PT}/C_M$, where C_{PT} is the fraction of the form with absorption band at ~385 nm and C_M is the fraction of the molecular form, are presented in Table 1. These results clearly demonstrate that steric interaction of the methyl group substituted in the N═C(H)−C fragment strongly promotes the proton transfer. Such equilibria were not observed in Schiff bases without steric repulsion,[17] nor in Mannich bases[5] for compounds without substituents in the phenol ring.

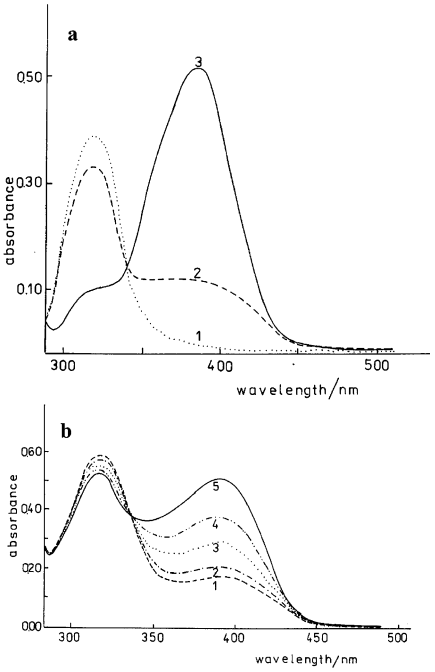


Figure 1. Dependence of electronic absorption spectra of 2-(α-(*N*-methylimino)ethyl)phenol (**1**) on (a) solvent [1, CCl_4; 2, CH_2Cl_2; 3, $HOCH_3$] and (b) temperature [1, 298 K; 2, 273 K; 3, 265 K; 4, 255 K; 5, 245 K].

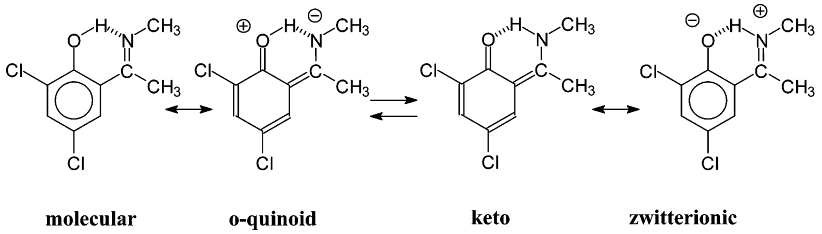
TABLE 1: Thermodynamic Characteristics of Proton Transfer Equilibrium (from UV−Vis Spectra) and ^{1}H NMR Data for 2-(α-(*N*-Methylimino)ethyl)phenol (1), 2-(α-(*N*-Methylimino)ethyl)-4,6-dichlorophenol (2), and 2-(α-(*N*-Propylimino)ethyl)-4,6-dichlorophenol (3) in CH_2Cl_2

compd	*T*, K	K_{PT}	ΔS°_{PT}, J/mol	ΔG°_{PT}, kJ/mol	ΔH°_{PT},[a] kJ/mol	*T*, K	*δ*(XH), ppm
1	298	0.14	−33.12	4.87		293	16.46
	274	0.20	−31.62	3.67		273	16.68
	256	0.25	−31.09	2.95		253	16.90
	237	0.29	31.38	2.44		233	17.13
	217	0.37	−31.29	1.80		213	17.34
	185	0.50	−32.77	1.07		203	17.44
	179	0.63	−31.75	0.69	−5.00	193	17.55
						183	17.62
2	298	1.55	−48.43	−1.09		300	17.76
	273	2.14	−50.52	−1.73		250	17.83
	252	4.39	−49.30	−3.10		220	17.73
	233	8.58	−48.90	−4.16	−15.50	200	17.62
						180	17.45
3	298	1.48	−42.08	−0.97		300	17.60
	273	2.03	−43.63	−1.60		250	17.65
	265	2.98	−41.90	−2.41		220	17.49
	255	3.64	−42.23	−2.74		200	17.43
	245	4.59	−42.47	−3.11	−13.50	180	17.32

[a] Average value for the studied range of temperatures.

For **2** and **3** one observes a stronger tendency to shift the equilibria in direction of proton transfer forms in CH_2Cl_2 than for **1**. Table 1 shows that the absolute values of the thermodynamic characteristics of the proton transfer process in **1** are much lower than in **2** and **3** at the same temperature. The ΔG°_{PT} values in **1** are positive, but a temperature decrease provokes

SCHEME 1



their reduction. For compounds **2** and **3**, ΔG°_{PT} becomes clearly negative. It is an interesting fact that the ^{1}H NMR signal of the hydroxy group in **1** shifts to lower field with temperature decrease, whereas in **2** and **3** the opposite tendency can be mentioned. This is an indication that in **2** and **3** the proton transfer forms predominate already at room temperature (cf. ref 24).

Increased acidity of the phenolic part of molecules **2** and **3** caused by the substitution of two chlorine atoms explains the observed trends. The substituents at 2- and 4-positions are not coupled to the imino group and pK_a values of the basic part of hydrogen bond weakly depend on substitution. In *N*-propyl derivative **3** all the thermodynamic characteristics are between those of **1** and **2**. This phenomenon can be explained by an increase of steric shielding of the acid−base center from the active solvent molecules, resulting from the elongation of the N-chain (cf. ref 25).

The formal similarity of the electronic spectra evolution of Mannich bases, Schiff bases, and Schiff bases with steric repulsion as well as the range of the determined ΔH°_{PT} and ΔG°_{PT} values could suggest a similar nature of the intramolecular proton transfer (PT) in all these three classes of compounds with an increasing ability to the PT reaction in the following sequence: Mannich bases < Schiff bases < Schiff bases with steric repulsion.

Nevertheless, one should mention a large difference in the electronic absorption band positions for both the molecular and proton transfer forms between Mannich and Schiff bases. In 2-((*N*-dimethylamino)methyl)-3,4,6-trichlorophenol (Mannich base) the molecular form absorbs at 282 nm, whereas the zwitterionic one absorbs at 325 nm.[4] In Schiff bases (cf., for example, Figure 1) molecular forms absorb at 320−330 nm, whereas proton transfer forms absorb at 385−430 nm. This effect shows that absorbing species in Schiff bases appear to be different from the phenol and phenolate ions, participating in tautomeric equilibrium in Mannich bases.[26]

3.2. Tautomeric Equilibria and Resonance. Structural studies and calculations at the B3LYP/6-31G(d,p) and MP2/6-31G(d,p) levels[7] demonstrate that in Schiff bases the C−O and $C_{aryl}-C_{alkyl}$ bonds are shortened in comparison with Mannich bases, whereas the C=N bonds are extended in comparison with standard bond lengths.[27] Also some bond distances in the phenol ring are extended, whereas others are shortened according to the orthoquinoid pattern[7] (cf. Scheme 1).

The proposed scheme describing the tautomeric equilibrium in Schiff bases is directly based on the structural and spectral behavior of these compounds. According to the observed structural evidences,[7] the resonance orthoquinoid structures participate both in the enol and in the proton transfer tautomers. These structures, however, differ in the proton locations.

The resonance of the keto and zwitterionic forms was used already[28,29] to explain the origin of electronic absorption bands ~400 nm in the polar solvent and anomalies in the kinetics of the hydrolysis of *o*- and *p*-hydroxy-2-(*N*-benzylideneamino)-propane in dependence on pH.[28−30] Weakening of the resonance[31] by stabilization of a phenolate state in strongly basic solutions led to a shift of the long-wave band back to ~320 nm. Protonation of Schiff bases also resulted in a blue shift of the long-wave absorption band. An additional evidence of resonance in the proton transfer tautomer is dependence of the UV band positions on the solvent polarity, as in a typical solvatochromy of organic dyes.[31] As an example, the results for compound **2** are shown in Figure 2. The negative solvatochromy suggests that a nearly equivalent amount of zwitterionic and keto forms participates already in resonance in nonpolar solvents. Polar solvents decrease the energy of the zwitterionic form and make the resonance less effective.

On the basis of structural data in solid state as well as DFT calculations,[7] we have estimated the amount of orthoquinoid structure in 2-((*N*-methylimino)methyl)-4-chlorophenol, crystallizing in the enol form, as 22%, whereas in 2-((*N*-methylimino)-methyl)-2,4-dichlorophenol as 47% in the PT form. It demonstrates that especially in the hydrogen bonded proton transfer state the resonance is very effective. A similar amount of the orthoquinoid form was found by Krygowski at al. for the solid 2-((*N*-methylimino)methyl)-4-nitrophenol.[32]

In ref 7 we used the average square of the ring bond length deviations (A) as a measure of the orthoquinoid type perturbation of the phenol ring: $A = 1/n\sum_i^n(d_i - \bar{d})^2 \times 10^6$. In molecular forms without the π-electron coupling (Mannich bases) A reaches values of 40−50 Å^2 [33,34] at the B3LYP/6-31(d,p) level. In Schiff bases it was 143 for the molecular form and 1376 for the proton transfer form.[7]

In this work the calculations performed at the same level gave A equal to 142 for **1** and 245/860 for molecular/proton transfer forms of **2**, respectively. These data demonstrate that for the proton transfer structures the participation of keto forms in resonance is substantial.

3.3. Theoretical Estimation of Energetic Features of the Proton Transfer. To estimate the energetic characteristics of

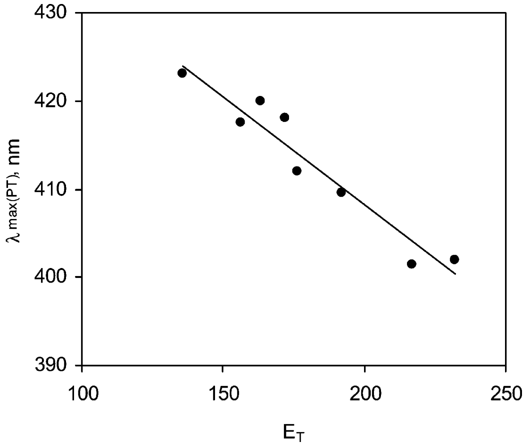


Figure 2. Dependence of the position of maximal absorption of long-wave absorption band ($\lambda_{max(PT)}$) of **2** on the parameter of solvent polarity (E_T). ($\lambda_{max(PT)} = -0.2449(\pm 0.0279)E_T + 457.35(\pm 5.16)$).

CHART 2

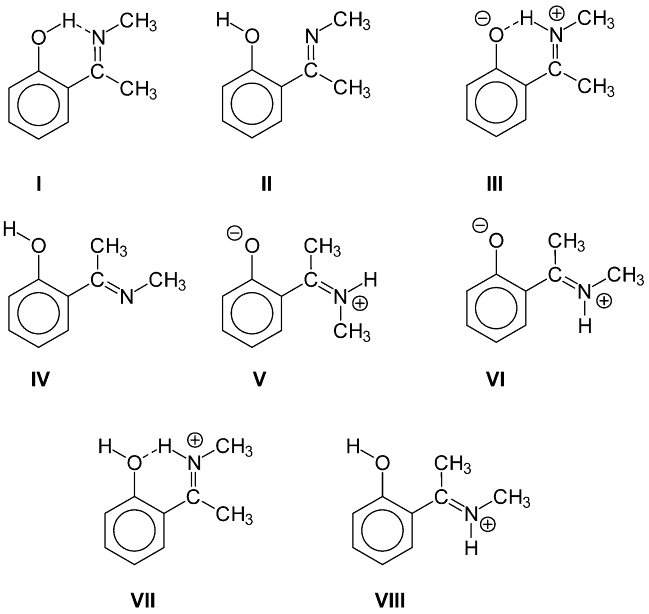


TABLE 2: Values of the Potential Energy[a] (kcal/mol) of Different Conformers of 2-(α-(*N*-Methylimino)ethyl)phenol (1) and 2-(α-(*N*-Methylimino)ethyl)-4,6-dichlorophenol (2) Calculated at the B3LYP/6-31G(d,p) Level

	conformer[b]							
compd	I	II	III	IV	V	VI	VII[c]	VIII[c]
1	0	16.38	3.20	12.73	18.49	16.48	0	4.73
2	0	13.72	2.30	10.11	16.28	14.30	0	4.62

[a] Related to energy of conformer I. [b] Definition of conformers as in Scheme 3. [c] Calculated for the protonated forms of Schiff bases.

the proton transfer process and hydrogen bonding, one should take into consideration a great variety of conformational equilibria of both tautomers. The calculated values of the energy of different conformers (II−VIII; Chart 2) of **1** and **2** in relation to the energy of the most stable conformers I with intramolecular hydrogen bonding (see Chart 2) are presented in Table 2. The values given there demonstrate that the proton transfer forms III are energetically the nearest to conformer I ($\Delta E = 3.2$ kcal/mol for **1** and $\Delta E = 2.3$ kcal/mol for **2**) of all the discussed states. The obtained values are smaller in comparison to Mannich bases (>15 kcal/mol[35]) or nonhindered Schiff bases (∼5 kcal/mol[7]), as for the gas phase calculations. A similar procedure of discussing the energy and geometry of different conformers was applied in studies of intramolecular hydrogen bond in *o*-hydroxybenzaldehyde. It is interesting that for this compound the results are different than obtained for the Schiff base; internal rotation was found there energetically much easier than intramolecular proton transfer.[36,37] It demonstrates once more very specific character of proton transfer process in Schiff bases.

The negative values of order (−5 to −15 kcal/mol) were obtained experimentally (cf. Table 1). This additional stabilization originates from interaction with solvent.

The energy of the intramolecular hydrogen bond can be established in relation to II or IV. It is a matter of a definition of the reference state.[17] Nevertheless, it appears to be rather large, 12.7−16.4 kcal/mol.

Comparison of the energy of III with the energy of V and VI allows estimation of the energy of the intramolecular $O^{-}\cdots H{-}N^{+}$ hydrogen bonding, which is similar (13.3−15.3 kcal/mol) to the hydrogen bond strength in the molecular form. The stabilization of the intramolecular hydrogen bonding in protonated Schiff bases (VII in relation to VIII state) appears to be about 5 kcal/mol, which suggests that intramolecular hydrogen bonding in compounds **1** and **2** exists even in acidic media. The calculations for the states with the $N{-}H^{+}$ group were performed mainly with the aim to discuss the IR spectra of these forms in relation to extensive literature discussions on the ν(C═N) absorption bands, especially in protonated forms.[38−40]

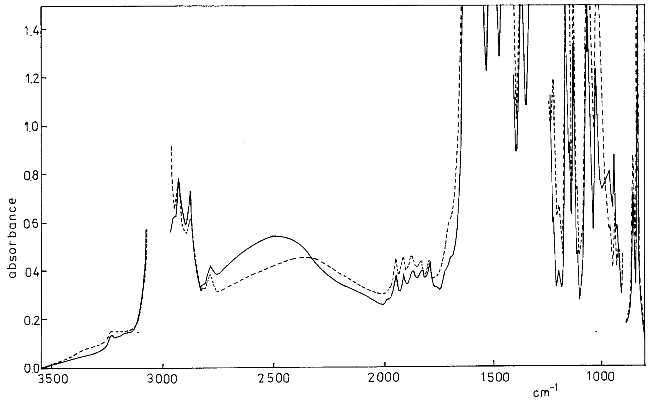


Figure 3. IR absorption spectra of **1** in the range of ν(O···H···N) absorption in CH_2Cl_2: full line, 298 K; dashed line, 193 K.

3.4. FT-IR Spectra. The most characteristic features of the formation of a hydrogen bond are the shift of the ν(OH) absorption band and its intensity increase.

A comparison of intramolecular hydrogen bonds shows that the ν(OH) band shift in Schiff bases is larger than in Mannich bases at the same ΔpK_a,[41,42] whereas the intensity of ν(OH) absorption is considerably lower in Schiff bases. Due to π-electron coupling, the charge distribution in Schiff bases is more uniform, leading to a decrease of the $\partial\mu/\partial q_{OH}$ parameter, which is related to a lower value of the dipole moment increase ($\Delta\mu$) upon proton transfer (PT)[17] than in Mannich bases.[5] This leads to decrease of the relative energy of the PT state.

An additional increase of the hydrogen bond strength due to steric influence of the methyl group substituted in the C(H)═N−R moiety results in the shift of the ν(OH) absorption band to 2500 cm^{-1} (cf. Figure 3), whereas the Schiff bases free from steric squeezing reveals the absorption band at 2760 cm^{-1}.[42]

Figure 3 also shows the effect of temperature decrease on the ν(O···H···N) absorption bands of **1**. According to the results of the electronic absorption studies discussed above, this effect is connected with achieving an approximately 50% transfer of the proton at −80 °C. An increase of the intensity absorption in the lower frequency part of the 3000−1700 cm^{-1} range and also, most probably, below 1700 cm^{-1} is observed. Separate absorption bands of the OH and HN forms cannot be distinguished,[43] particularly because they are very broad.

An independent analysis of the influence of temperature on tautomeric equilibrium in Schiff bases can be done on the basis of the spectra within the range of 1400−1700 cm^{-1}, where the ν(C═N) stretching absorption is located (Figure 4).

The IR spectra of Schiff bases in this range are widely discussed in the literature. They are interesting in the context of explaining the mechanism of the functioning of the bacteriorhodopsin chromophore,[40,44,45] but also in understanding of the nature of the PT state after irradiation.[38] The ν(C═N) band located in the range of 1620 cm^{-1} in compounds of the type studied here shows an increase of frequency on protonation and deuteration.[38−40]

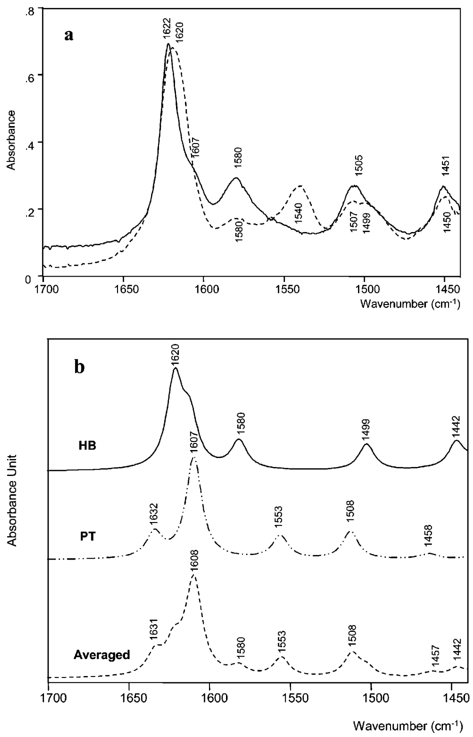
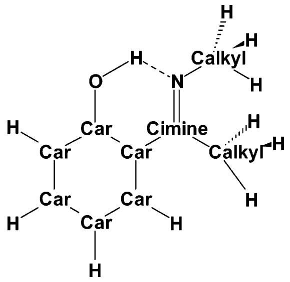


Figure 4. IR absorption spectra of **1** in the range of ν(C═N) absorption in CH_2Cl_2: (a) experimental spectra in CH_2Cl_2 [full line, 298 K; dashed line, 193 K]; (b) calculated spectra [average obtained by assuming a 1:1 composition of HB and PT].

CHART 3: Definition of Internal Coordinates Used in Potential Energy Distribution (PED) Analysis



To facilitate the discussion on the assignment of particular bands, we have performed the B3LYP/6-31G(d,p) calculations for eight different structures, presented in Chart 2.

Chart 3 shows the atom labeling and the definition of the internal spectroscopic coordinates. The results of the frequency calculations are presented in Table 3, after multiplication by the factor 0.96 (suggested in the literature[46]) to simplify direct graphical comparison of the calculated and experimental spectra in this range.

Figure 4 shows that temperature lowering leads to the intensity decrease of the 1580 cm^{-1} band, which belongs to the OH form. The 1620 cm^{-1} band is broad and is not resolved into bands of the enol and PT forms; nevertheless, an increase of the lower frequency component, connected with the shift of equilibrium in direction of the PT form, is observed. The splitting of the band at 1505 cm^{-1} into two subbands demonstrates the existence of equilibrium at −80 °C. The increase of the integral intensity of the band at 1540 cm^{-1} appears to be very characteristic and can be attributed to the calculated band of PT form at 1553 cm^{-1}.

In the bottom part of Figure 4 the calculated spectra of **1** in the enol and proton transfer forms are shown. It is seen that the combination of 50% of calculated spectra of the enol and PT forms can quite adequately reproduce the experimental spectrum. This can be taken as a proof of the quality of the performed DFT calculations.

The results of B3LYP/6-31G(d,p) calculations presented in Table 3, concerning the 1400−1700 cm^{-1} spectral range, can be compared with literature data.[30,39,40,44,45,47−55] A blue shift upon protonation of the strongest band in this range, assigned to ν(C═N) vibration was connected to an increase of the force constant of this bond. This dependence was explained by rehybridization leading to an increase of the s character of the C═N bond upon protonation.[47] An alternative explanation was made on the basis of mixing of the C═N stretching and the N−H in-plane bending vibrations.[48,49]

The results shown in Table 3 demonstrate that the character of normal vibrations is seriously affected by the proton transfer process, so the spectral modifications cannot be understood properly without PED analysis. For example, the R(CN) internal coordinate is almost equally distributed among the 1632, 1607, and 1553 cm^{-1} bands in the PT form of **1** (III), whereas in the molecular structure (I) this coordinate is located mainly in the 1621 cm^{-1} mode (56%). The results of the PED calculations show that none of observed bands can be completely assigned to ν(C═N) mode. The largest content of this internal coordinate in vibrational modes was calculated as about 60% for the structures with intramolecular hydrogen bonding of **1** and **2**.

Calculations show 100% of OH or NH^+ stretching in corresponding normal modes in all “open” conformations (II, IV, V, VI, VII, VIII). Formation of an intramolecular hydrogen bond does not seriously decrease this amount. The smallest content obtained in the calculations is 93% of R(NH^+) in III.

In open conformers (II, IV), the internal coordinates are more “localized”, in the particular normal vibrations. The R(CN) content in the first high-frequency bands (in the range 1400−1700 cm^{-1}) is 78% and 73%, respectively, for conformers II and IV. A similar pattern is found for **2**. In nonprotonated conformers (I, II, IV), R(CN) is accompanied by δ(CCN) vibration. In the zwitterionic forms (III, V, VI), the content of the δ(CCN) internal coordinate rapidly decreases and it is replaced by δ(CNH), which becomes the main component of the intensive band at about 1630−1640 cm^{-1} in the zwitterionic form with an intramolecular bond (III). In the zwitterionic conformers V and VI, δ(CNH) is a main component of the bands located at 1520−1540 cm^{-1}, where it is accompanied by a contribution from the R(CN) coordinate. This demonstrates that attributing the R(CN) character to a particular absorption band is highly arbitrary, especially if it concerns the band shifts upon protonation. Nevertheless, calculations demonstrate that the predictions of a large role of the δ(CNH) coordinate were proper. It is interesting to stress that only for the intramolecularly hydrogen bonded enol form there is observed a substantial contribution of the δ(COH) mode to the bands of the region being discussed. It is not traced in II, IV, VII, and VIII, which contain free hydroxy groups.

Stretching of the CO bond is not observed in normal modes showing absorption in the 1400−1700 cm^{-1} range, i.e., in the forms I, II, IV, VII, and VIII. It appears in forms with the $C-O^-$ bond (III, V, VI), but it is more evident when it does not participate in an intramolecular hydrogen bond (V and VI): ∼30% in conformer V in **1** and ∼60% in **2**. Nevertheless, one cannot use any “R(CO)” band for the identification of proton transfer forms. Despite general agreement in the tendencies found in **1** and **2**, it should be mentioned that 2,4-dichloro substituents influence the content of normal vibrations.

TABLE 3: Vibrational Frequencies ν (cm^{-1}) and Intensities A (km mol^{-1}), Calculated at the B3LYP/6−31 G(d,p) Level, with Assignment (PED, %) [Range: $1750 > \nu > 1400$, $A > 10$] for 2-(α-(*N*-Methylimino)ethyl)phenol (1) and 2-(α-(*N*-Methylimino)ethyl)-4,6-dichlorophenol (2)[a]

	compd **1**		compd **2**	
I	2785 (617)	r(OH) 99%	2661 (747)	r(OH) 99%
	1621 (203)	R(CN) 56%, α$_{\mathrm{im}}$(CCC) 9%, δ(CCN) 8%	1623 (164)	R(CN) 61%, α$_{\mathrm{im}}$(CCC) 9%, δ(CCN) 8%
	1611 (109)	τ(CC) 42%, δ(COH) 18%, α(CCC) 7%, β(CCH) 5%	1594 (67)	τ(CC) 36%, δ(COH) 29%, δ(CCO) 7%
	1580 (65)	τ(CC) 41%, δ(COH) 25%, β(CCH) 8%, R(CN) 7%	1469 (174)	τ(CC) 35%, δ(COH) 29%, β(CCH) 6%, α(CCC) 5%
	1499 (60)	τ(CC) 44%, δ(COH) 23%, β(CCH) 21%	1436 (13)	β(CCH$_3$) 75%, δ(NCH$_3$) 14%
	1462 (2)	δ(NCH$_3$) 82%, β(CCH$_3$) 5%		
II	3664 (37)	R(OH) 100%	3602 (88)	r(OH) 100%
	1663 (84)	R(CN) 78%, δ(CCN) 5%	1668 (77)	R(CN) 78%, δ(CCN) 5%
	1594 (34)	τ(CC) 60%, β(CCH)13% α(CCC) 9%	1553 (17)	τ(CC) 57%, α(CCC) 10%, β(CCH) 7%
	1576 (14)	τ(CC) 66%, α(CCC) 9%, β(CCH) 9%	1462 (18)	δ(NCH$_3$) 47%, β(CCH$_3$) 43%
	1487 (19)	β(CCH) 44%, τ(CC) 26%, R(CO) 5%	1447 (10)	δ(NCH$_3$) 65%,β(CCH$_3$) 27%
	1454 (18)	β(NCH$_3$) 60%, β(CCH$_3$) 27%	1444 (156)	τ(CC) 41%, β(CCH) 20%, R(CO) 19%
III	2490 (252)	R(NH) 93%	2508 (276)	r(NH) 93%
	1632 (149)	δ(CNH) 35%, R(CN) 13%, τ(CC) 20%, R(CO) 7%	1643 (362)	δ(CNH) 44%, R(CN) 23%
	1607 (604)	τ(CC) 12%, R(CN) 17%, R(CC) 11%, δ(CNH) 10%	1594 (314)	τ(CC) 34%, R(CO) 15%, R(CN) 12%, R(CC) 6%, α$_{\mathrm{im}}$(CCC) 6%
	1553 (137)	τ(CC) 22%, R(CO) 22%, R(CN) 12%, R$_{\mathrm{im}}$(CC) 11%, δ(CNH) 8%	1555 (163)	τ(CC) 28%, R(CO) 16%, R(CN) 10%, δ(CNH) 8%, β(CCH) 7%, α$_{\mathrm{im}}$(CCC) 7%
	1509 (165)	τ(CC) 53%, β(CCH) 13%, R(CO) 7%	1492 (157)	τ(CC) 54%, β(CCH) 10%, R(CO) 7%
	1464 (8)	β(NCH$_3$) 35%, β(CCH) 11%, R(CC) 10%, τ(CC) 6%	1464 (15)	δ(NCH$_3$) 50%, β(CCH$_3$) 15%
	1458 (27)	β(NCH$_3$) 36%, β(CCH$_3$) 30%, β(CCH) 13%, τ(CC) 5%	1439 (13)	δ(NCH$_3$) 66%, β(CCH$_3$) 29%
IV	3668 (47)	r(OH) 100%	3599 (106)	r(OH) 100%
	1640 (93)	R(CN) 73%, δ(CCN) 7%	1643 (80)	R(CN) 75%, α$_{\mathrm{alk}}$(CCC) and δ(CCN) 6%
	1593 (43)	τ(CC) 60%, β(CCH) 12%	1555 (15)	τ(CC) 65%, α(CCC) 9%, β(CCH) 7%
	1575 (12)	τ(CC) 66%, β(CCH) 9%, α(CCC) 7%	1448 (18)	β(CCH$_3$) 53%, δ(NCH$_3$) 25%
	1479 (11)	β(CCH) 43%, τ(CC) 31%		
V	3484 (58)	r(NH) 100%	3481 (73)	r(NH) 100%
	1635 (248)	R(CO) 32%, τ(CC) 32%, α(CCC) 5%	1630 (235)	R(CO) 60%, τ(CC) 5%
	1586 (70)	τ(CC) 38%, R(CO) 36%, β(CCH) 6%	1578 (114)	τ(CC) 65%, R(CO) 12%, β(CCH) 8%
	1520 (54)	τ(CC) 48%, R(CN) 16%, R(CC) 6%	1525 (219)	δ(CNH) 45%, R(CN) 27%
	1519 (99)	δ(CNH) 47%, τ(CC) 11%, R(CN) 10%	1510 (80)	τ(CC) 50%, R(CC) 15%, δ(CNH) 7%, R(CN) 6%
	1492 (484)	τ(CC) 42%, R(CN) 7%, δ(NCH$_3$) 7%, R(CO) 6%	1484 (265)	τ(CC) 32%, R(CC) 15%, δ(NCH$_3$) 7%, δ(CNH) 6%
	1461 (32)	δ(NCH$_3$) 72%, R(CN) 7%	1460 (31)	δ(NCH$_3$) 73%, R(CN) 6%
	1439 (23)	δ(CCH$_3$) 33%, δ(NCH$_3$) 23%, β(CCH) 12%, τ(CC) 6%	1442 (18)	δ(NCH$_3$) 88%
			1495 (29)	δ(CCH$_3$) 75%, R(CC) 5%
VI	3511 (27)	r(NH) 100%	3504 (32)	r(NH) 100%
	1631 (238)	τ(CC) 34%, R(CO) 28%, α(CCC) 5%	1626 (241)	R(CO) 59%, τ(CC) 5%
	1586 (78)	R(CO) 35%, τ(CC) 33%, β(CCH) 5%	1579 (96)	τ(CC) 57%, β(CCH) 15%, R(CO) 11%
	1541 (385)	δ(CNH) 26%, R(CN) 20%, R(CO) 11%, R(CC) 11%, τ(CC) 5%	1543 (582)	δ(CNH) 30%, R(CN) 25%, R(CC) 12%, R(CO) 6%
	1507 (370)	τ(CC) 60%	1495 (115)	τ(CC) 69%
VII	3649 (143)	r(OH) 100%	3534 (201)	r(OH) 100%
	3343 (136)	r(NH) 99%	3336 (140)	r(NH) 99%
	1621 (273)	R(CN) 43%, δ(CNH) 27%	1622 (407)	R(CN) 48%, δ(CNH) 26%, δ(CCN) 6%
	1596 (316)	τ(CC) 56%, β(CCH) 12%, α(CCC) 9%	1576 (59)	τ(CC) 62%, α(CCC) 11%, β(CCH) 11%
	1569 (80)	τ(CC) 48%, α(CCC) 8%, β(CCH) 8%, δ(CNH) 7%, α$_{\mathrm{im}}$(CCC) 5%	1550 (91)	τ(CC) 39%, δ(CNH) 12%, α(CCC) 8%, α$_{\mathrm{im}}$(CCC) 7%
	1510 (41)	δ(CNH) 22%, τ(CC) 16%, β(CCH) 16%, R(CN) 8%, R(CC) 6%	1501 (123)	τ(CC) 25%, δ(CNH) 24%, β(CCH) 9%, R(CN) 7%, R(CC) 5%
VIII	3649 (133)	r(OH) 100%	3558 (187)	r(OH) 100%
	3439 (58)	r(NH) 100%	3432 (60)	r(NH) 100%
	1599 (78)	τ(CC) 44%, R(CN) 20%, α(CCC) 6%, δ(CNH) 5%	1595 (303)	R(CN) 53%, δ(CNH) 16%, δ(CCN) 5%
	1582 (483)	R(CN) 32%, τ(CC) 17%, δ(CNH) 15%, R(CC) 7%	1571 (148)	τ(CC) 57%, α(CCC) 10%, β(CCH) 10%
	1562 (48)	τ(CC) 56%, α(CCC) 9%, β(CCH) 9%,	1541 (40)	τ(CC) 53%, δ(COH) 12%, α(CCC) 10%, δ(CCO) 6%, β(CCH) 5%
	1477 (28)	β(CCH) 40%, τ(CC) 26%, R(CC) 6%	1461 (101)	δ(NCH$_3$) 31%, δ(CNH) 24%, R(CC) 11%, β(CCH$_3$) 5%
	1466 (94)	δ(CNH) 16%, β(CCH) 10%, R(CC) 8%, R(CO) 7%, τ(CC) 7%, δ(NCH$_3$) 6%, α$_{\mathrm{im}}$(CCC) 6%	1453 (47)	δ(NCH$_3$) 60%, β(CCH$_3$) 22%
	1443 (24)	δ(NCH$_3$) 93%	1442 (56)	δ(NCH$_3$) 88%
			1441 (69)	δ(NCH$_3$) 27%, τ(CC) 22%, R(CO) 14%, β(CCH$_3$) 8%, β(CCH) 6%

[a] All calculated frequencies multiplied by factor equal to 0.96.

It seems clear that the calculations of the force constants in the internal coordinates should give more direct information on intramolecular interactions and the character of species participating in proton transfer tautomeric equilibria.

The results obtained are presented in Table 4.

Formation of an intramolecular hydrogen bond evokes decrease the ν(OH) and ν(NH$^+$) force constants. A strong increase of the δ(COH) force constant is observed. One can mention a substantial decrease of the R(C═N) force constant upon the formation of the hydrogen bond, by comparison of I

TABLE 4: Selected Values of Force Constants (mdyn/Å for Stretching and mdyn/rad for Bending), Calculated for 2-(α-(*N*-Methylimino)ethyl)phenol (1) and 2-(α-(*N*-Methylimino)ethyl)-4,6-dichlorophenol (2) with B3LYP/6-31G(d,p) Approximation

conformer	r(O—H) r(N—H)	R(C—O)	R(C═N)	R(C—N)	τ(CC)	R(CC)	δ(CNH)	δ(CCN)	δ(COH)
				2-(*N*-Methyl-α-iminoethyl)phenol					
I	4.577	7.569	10.201	5.294	7.246	5.459		1.487	1.470
II	8.154	6.566	11.152	4.979	6.717	4.677		0.795	0.826
III	3.312	9.222	8.905	5.329	5.951	7.172	1.038	1.540	
IV	8.171	6.313	10.873	4.951	6.790	4.808		1.232	0.811
V	7.309	11.005	7.521	5.286	4.782	7.158	1.038	1.712	
VI	7.425	10.929	7.554	5.385	4.919	7.167	1.030	1.699	
VII	8.082 6.708	6.482	9.465	4.921	6.730	5.896	1.056	1.562	0.798
VIII	8.081 7.118	6.908	9.220	4.917	6.535	5.646	0.950	1.254	0.806
				2-(*N*-Methyl-α-iminoethyl)—4,6-dichlorophenol					
I	4.128	7.915	10.303	5.031	7.335	5.415		1.538	1.526
II	7.879	6.972	11.234	5.006	6.674	4.609		1.107	0.883
III	3.412	9.555	9.096	5.272	6.029	6.940	1.207	1.665	
IV	7.866	6.719	10.948	4.954	6.763	4.731		1.199	0.871
V	7.293	11.410	7.720	5.223	4.899	6.988	1.057	1.712	
VI	7.397	11.340	7.730	5.332	5.023	7.001	1.039	1.693	
VII	7.578 6.682	6.758	9.580	4.888	6.820	5.774	1.054	1.584	0.856
VIII	7.686 5.598	7.187	9.364	4.869	6.636	5.511	0.961	1.234	0.854

and II structures. This is evidence of the increasing content of the orthoquinoid resonance structure in the enol tautomer (cf. Scheme 1). Proton transfer conformation III shows a further decrease of the ν(C═N) force constant. This force constant decreases even more largely in open zwitterionic conformations (V, VI). This is proof of the increasing content of the keto form in the resonance description of the proton transferred tautomer (see Scheme 1). In the open forms, resonance seems to be less effective, similarly to the enol tautomer, but with opposite consequences of the intramolecular hydrogen bond formation on ν(C═N) force constant.

Formation of a hydrogen bond increases the R(CO) force constants, which appears even higher in III, with further increase in V and VI, which speaks in favor of the resonance of keto and zwitterionic forms in the tautomer with intramolecular $O^{-}\cdots H-N^{+}$ hydrogen bonding. Similar conclusions were drawn from detailed calculations on the basic Schiff base in the aryl—alkyl series: the 2-hydroxy-*N*-methylbenzylidene amine.[56]

From the context of the literature discussions on the change of the ν(C═N) force constant, one can state that the protonation evidently decreases the R(C═N) force constant.

In the discussion of force constant modifications the situation is much more unambiguous than in direct comparisons of band positions or normal vibrations (Table 3), because substituents such as, for example, the chlorine atoms in **2** may greatly change the PED pattern. The force constants of r(OH) or r(NH) are generally lower for **2** than for **1**, whereas R(CO) force constants are larger in **2** than in **1**, according to the fact that hydrogen bonding is stronger in **2** than in **1**.

4. Conclusions

In this paper the role of steric interaction and resonance stabilization on the proton transfer equilibria in Schiff bases was investigated. The presented electronic and vibrational spectra demonstrate that the π-electronic coupling in Schiff bases increases the strength of intramolecular hydrogen bond and shifts the tautomeric equilibrium in the direction of the proton transfer form in comparison to the related Mannich bases, where such a coupling is very limited. Steric external squeezing of the chelate ring by the $-CH_3$ substituent in iminomethyl moiety shifts this equilibrium further in the direction of the proton transfer forms. Thermodynamic parameters of the proton transfer reaction appear to be within the same range for the three types of intramolecular hydrogen bonds compared here.

Both the experiment and performed B3LYP/6-31G(d,p) calculations demonstrate that the character of species in tautomeric equilibrium is different for Mannich and Schiff bases (cf. ref 56). The proposed scheme of the proton transfer process in Schiff bases stresses the role of resonance interaction in the description of particular tautomers.

Resonance stabilization follows from the long wave shift of the electronic absorption bands in Schiff bases, and from the force constant values, calculated at the B3LYP/6-31G(d,p) level in internal coordinates. It was shown that the force constants of the C—O and $C_{aryl}-C_{alkyl}$ bonds increase, whereas for the C═N bond the force constant decreases in the proton transfer tautomer. It was found that in calculated open proton transfer structures, the differentiation of the bonds is even stronger than in the forms with intramolecular hydrogen bonding. This is a result of the more effective resonance between the keto and zwitterionic resonance structures in the hydrogen bonded system.

The DFT calculations also allow the interpretation of the IR spectroscopic behavior of these systems, including the effect so widely discussed in the literature of the ν(C═N) band shift upon protonation.

The calculations demonstrate that the force constant of C═N bond stretching decreases and its content in the normal coordinate traditionally assigned as the ν(C═N) mode diminishes upon proton transfer. Simultaneously, the content of δ(C═N—H) vibration becomes considerable. It was shown that formation of the intramolecular hydrogen bonds leads to additional mixing of the internal coordinates in normal modes, except for the ν(OH) and ν(NH) normal coordinates.

Obtained results show that the discussion of the consequences of intramolecular hydrogen bond formation and proton transfer, based on direct comparison of IR bands positions and intensities, is less reliable than that based on the calculated, in internal coordinates, force constant values.

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