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Proton transfer equilibrium in the intramolecular hydrogen bridge in sterically hindered *Schiff* bases[☆]

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Dedicated to the memory of Professors J. Kroon, P. Huyskens and N.D. Sokolov

Abstract

Six *Schiff* bases (4-chloro-2-(1-ethylimino-ethyl)-5-methyl-phenol (**I**), 2,4-dichloro-6-(1-ethylamino-ethylidene)-cyclohexa-2,4-dienone (**II**), 4-chloro-2-nitro-6-(1-ethylamino-ethylidene)-cyclohexa-2,4-dienone (**III**), 2-nitro-4-methyl-6-(1-ethyl-amino-ethylidene)-cyclohexa-2,4-dienone (**IV**), 2-(1-phenylimino-iso-propyl)-phenol (**V**) and 4-chloro-2-(1-phenylimino-ethyl)-5-methyl-phenol (**VI**)) were synthesised with replacement of the H atom in the C–C(H)=N group by either methyl, or phenyl substituent. The data were collected at 293 K temperature. Additionally in order to study the temperature influence on proton transfer two crystal structures were obtained at 100 K temperature. The influence of different substitution in phenol ring on the position of hydrogen in hydrogen bridge was discussed. © 2002 Elsevier Science B.V. All rights reserved.

Keywords: *Schiff* bases; Proton transfer; Hydrogen bond; Steric repulsion

1. Introduction

This paper presents the steps taken to study proton transfer mechanism in *Schiff* bases characterized by extremely short OHN intramolecular hydrogen bonds. Related to this study, six crystallographic structures were determined at room temperature (see Scheme 1), and additionally two of them—at liquid nitrogen temperature. It is widely known that the temperature decrease of solutions with the compounds forming intramolecular hydrogen bond leads to proton transfer forms [1].

Alike the other compounds having π-conjugated intramolecular hydrogen bridge, *Schiff* bases are notable for the proton transfer form acting as resonance of two structures—keto and zwitterionic ones (see Scheme 2). Structural and spectroscopic evidences show, that the enol tautomer should also be considered as resulting from resonance between the molecular and *o*-quinoid forms [2].

So far a few papers have been published investigating X-ray structures data on the study of *Schiff* bases properties in solid state as a function of temperature [3–9].

In the pioneer Ref. [3] Schmidt et al. investigated the influence of low temperature on the *N-5-chlorosalicylideneaniline* structure. The authors observed elongation of C–C bond between phenol ring and imine group, and shortening of C=N double
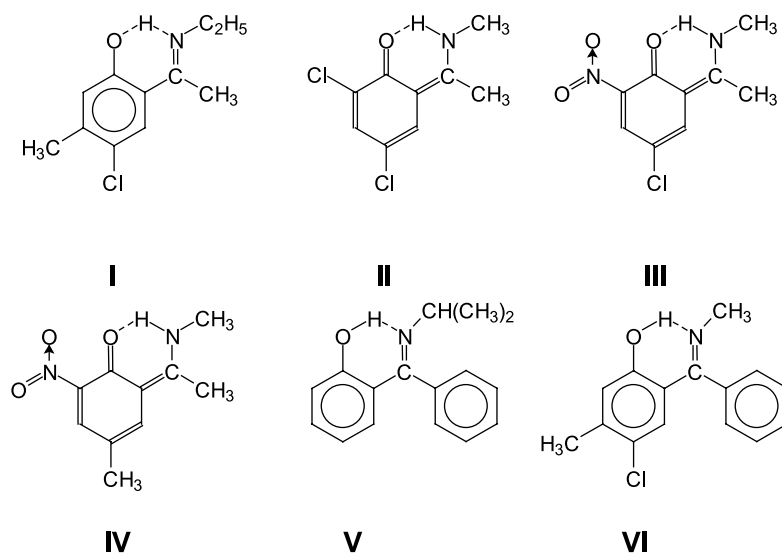
Scheme 1.

bond with temperature decreasing. These facts confirm the balance shift from enol form to keto form. Recently, more precise measurements [4] revealed also the shortening of C–O bond with temperature decreasing.

Ogawa et al. [4–6] made a research of *N-(5-chloro-2-hydroxybenzylidene)-4-hydroxyaniline* where step-by-step transition from enol form to proton transfer form is observed on condition of temperature decreasing. However, intramolecular hydrogen bridge OHN in *N-(5-chloro-2-hydroxybenzylidene)-4-hydroxyaniline* was influenced by OHO intermolecular hydrogen bond, which promoted proton transfer form with temperature decreasing. The substituents in the phenyl rings of the compounds studied in this work

(cf. Scheme 1) are surely not forming a strong intermolecular hydrogen bonding.

The studied *Schiff* bases form very short hydrogen bonds resulting from steric squeezing of chelate hydrogen bridge caused by substituent (R_1) attached to carbon atom of imine group (see Scheme 3).

The structural effects of such interaction can be visualized by increase of valence angles external to the chelate ring and decrease of internal ones, that leads to shortening of O···N distance [10]. These compounds make new class of sterically hindered *Schiff* bases with considerably strengthened intramolecular hydrogen bonds.

Having been studied in Ref. [11], simultaneous steric squeezing of chlorine atoms on the hydroxy and
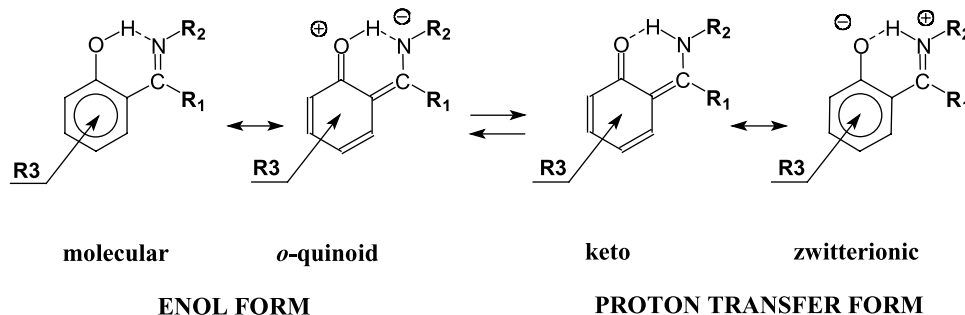
Scheme 2.
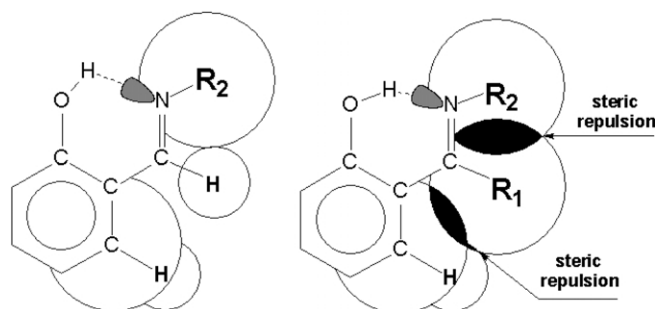
Scheme 3.

imino groups is the reason of the hydrogen bridge shortening in *Schiff* bases.

Sterically hindered *Schiff* bases are a group of compounds where the potential for proton movement within the hydrogen bridge is easily modified [12]. This can be a basis for selection of the compounds of desired properties from the point of view of potential applications of these compounds as photo- and thermochromic materials [13–16] and electronically functional materials [17–19].

2. Experimental

Standard procedure was used to perform synthesis of compounds **I–VI** from stoichiometric mixtures of the corresponding ketone and aliphatic amine in methanol [20]. Solid products obtained from methanol after recrystallization were afterwards studied by X-ray diffraction. Summary of the data collected is given in Table 1. The structure was solved by direct methods using SHELXS97 [21] and refined by the full matrix, the least squares method on all F^2 data using SHELXL97 [22]. Anisotropic thermal displacement parameters were used for all non-hydrogen atoms. The hydrogen atoms were located from difference *Fourier* maps and refined with thermal parameters. The oxygen atoms of nitro group in compound **VI** were refined in two equally populated positions.

Final atomic coordinates have been deposited as supplementary data (BLLD) SUP 26682 (10 pages).

3. Results

Molecular structures and atoms labelling the system are demonstrated in Figs. 1–6. Tables 2–8 present selected bond distances and valence angles.
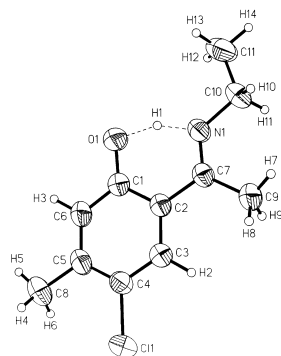

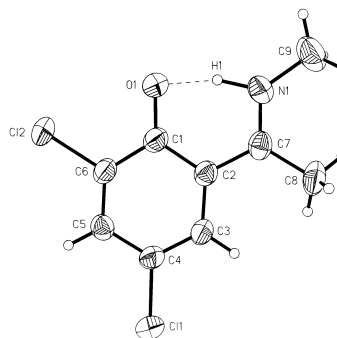Fig. 1. ORTEPII [23] drawing of **I** showing the atom numbering scheme.

Fig. 2. ORTEPII [23] drawing of **II** showing the atom numbering scheme.

Table 1

Summary of data collection and processing parameters

| Compound	I	I	II	II	III	IV	V	VI
Formula	$C_{11}H_{14}NOCl$	$C_{11}H_{14}NOCl$	$C_9H_9N_2O_3Cl_2$	$C_9H_9N_2O_3Cl_2$	$C_9H_9N_2O_3Cl$	$C_{10}H_{12}N_2O_3$	$C_{16}H_{17}NO$	$C_{15}H_{14}NOCl$
Color	Yellow	Yellow	Yellow	Yellow	Yellow	Yellow	Yellow	Yellow
Molecular weight	211.68	211.68	218.07	218.07	228.63	208.22	239.31	259.72
Space group	$P1$	$P1$	$P2_1/n$	$P2_1/n$	$Pna2_1$	$Pbn2_1$	$P2_12_12_1$	$C2/c$
Temperature., K	100(2)	293(2)	100(2)	293(2)	293(2)	293(2)	293(2)	293(2)
Cell constants				25 ref.,	25 ref.,	25 ref.,	25 ref.,	25 ref.,
				$22.3 < 2\theta < 45.8$	$23.6 < 2\theta < 48.6$	$22.6 < 2\theta < 43.8$	$25.3 < 2\theta < 49.6$	$28.6 < 2\theta < 46.8$
Crystal system	Triclinic	Triclinic	Monoclinic	Monoclinic	Orthorhombic	Orthorhombic	Orthorhombic	Monoclinic
a (Å)	6.923(1)	6.984(1)	7.811(2)	7.886(2)	7.323(2)	12.987(3)	8.945(2)	24.557(5)
b (Å)	7.318(1)	7.515(2)	12.474(2)	12.546(3)	13.003(3)	10.994(3)	9.922(2)	11.896(2)
c (Å)	11.211(2)	11.298(2)	9.610(2)	9.799(3)	10.490(3)	7.024(2)	15.231(3)	9.585(2)
α (deg)	74.84(3)	75.26(3)						
β (deg)	79.63(3)	79.65(3)	101.73(3)	102.90(1)				107.97(3)
γ (deg)	73.99(3)	72.89(3)						
Cell volume (Å^3)	523.4(1)	544.5(1)	916.8(3)	945.0(4)	998.9(4)	1002.9	1351.8(5)	2663.5(9)
Formula units/unit cell	2	2	4	4	4	4	4	8
D_{cal} (Mg m^{-3})	1.343	1.291	1.580	1.533	1.520	1.379	1.176	1.295
Difractometer/Scan	KUMA KM4CCD	KUMA KM4CCD	KUMA KM4CCD	KUMA KM4/$\omega-2\theta$	KUMA KM4/$\omega-2\theta$	KUMA KM4/$\omega-2\theta$	KUMA KM4/$\omega-2\theta$	KUMA KM4/$\omega-2\theta$
Radiation (Å), graphite monochromator	Mo Kα	Mo Kα	Mo Kα	Cu Kα	Cu Kα	Cu Kα	Cu Kα	Cu Kα
Max. crystal dimensions (mm)	$0.15 \times 0.15 \times 0.20$	$0.15 \times 0.15 \times 0.20$	$0.20 \times 0.20 \times 0.25$	$0.20 \times 0.20 \times 0.20$	$0.20 \times 0.20 \times 0.25$	$0.20 \times 0.20 \times 0.35$	$0.15 \times 0.20 \times 0.20$	$0.25 \times 0.25 \times 0.35$
No.of stand. ref. and int.				3 (100 ref.)	3 (100 ref.)	3 (100 ref.)	3 (100 ref.)	3 (100 ref.)
Reflections measured/independent	3680/2347	3946/2506	4410/1776	3984/1964	2025/1089	2052/2052	3310/2962	8252/2938
2θ range (deg)	3.69–28.56	3.90–28.94	3.12–25.98	10.6–160.4	10.2–160.4	8.2–160.5	10.6–160.2	7.6–162.0
Range of h, k, l	$-8/9, -9/8,$ $-14/14$	$-9/5, -10/9,$ $-14/14$	$-9/9, -15/12,$ $-11/10$	$-10/9, -15/16,$ $-12/12$	$-8/8, -16/0, 0/13$	0/16, 0/14, $-8/8$	$-11/0, -12/0,$ $-19/19$	0/31, $-15/15,$ $-12/11$
Reflections observed [$F_0 > 4\sigma(F_0)$]	2182	2081	1766	1578	955	1491	2286	2145
Corrections applied	Lorentz and polarization effects							
Structure solution	Direct method—SHELXS-97 [21]							
Structure refinement	SHELXL97 [22]							
Treatment of hydrogen atoms	Refined parameters: x, y, z, U_{iso}							
No. of parameters varied	183	184	154	155	150	203	232	220
GOF	1.086	1.107	1.064	1.027	1.092	1.067	1.031	1.028
$R_1 = \sum(|F_0| - |F_c|)/\sum(|F_0|)$	0.0302	0.0537	0.0507	0.0552	0.0395	0.0410	0.0327	0.0495
$WR_2 = \{\sum[w(F_0^2 - F_0^2)^2]/\sum[w(F_0^2)^2]\}^{1/2}$	0.0835	0.1543	0.1354	0.1476	0.1057	0.1153	0.0847	0.1306
Function minimized	$\sum w(\Delta F^2)^2$							
Largest feature final diff. map (e Å^{-3})	0.311 and -0.227	0.302 and -0.483	0.573 and -0.351	0.408 and -0.369	0.273 and -0.378	0.220 and -0.178	0.084 and -0.088	0.273 and -0.326
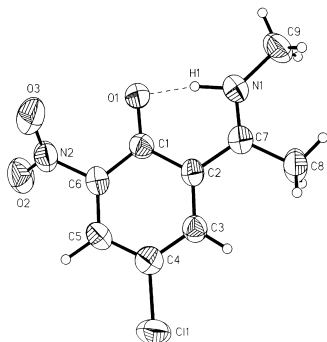
Fig. 3. ORTEPII [23] drawing of **III** showing the atom numbering scheme.

4. Discussion

4.1. Structural aspects

In solid state at room temperature the first compound (**I**) forms a very short OHN hydrogen bond, where the proton is located almost in the center. Under condition of temperature decreasing the hydrogen bond is undergoing certain changes. The crystal structure obtained at 100 K presents equilibrium shifted in direction to proton transfer form. The hydrogen is located definitely closer to nitrogen atom, while O···H distance pronouncedly increases. A weak decrease of the C1–O1 bond length (1.317(1) Å) can be mentioned. The calculated amount of keto form is also slightly increased (Table 8), but both values for the room and low temperatures are in the same range of data. The increase of the C7=N1 double bond length also speaks in favour of stronger intramolecular coupling within the molecule. However, the
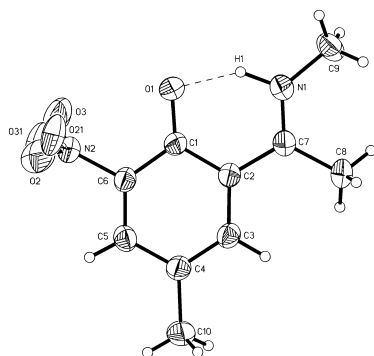

Fig. 4. ORTEPII [23] drawing of **IV** showing the atom numbering scheme.
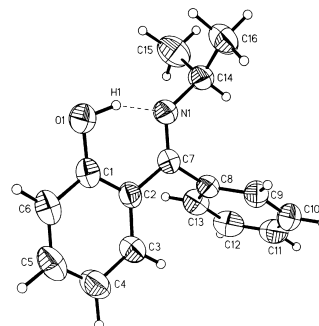
C2–C7 bond length does not show this effect; the differences in distances are within the experimental uncertainty of the bond length.

The increase of the acidity of phenolic part of compound **II** provides more definite proton transfer form at room temperature in comparison to compound **I**, despite of some decrease of the basicity of nitrogen atom. In compound **II** the temperature affect is very interesting and different from those in compound **I**. Despite of more definite localization of proton closer to nitrogen atom, the structural parameters changes as follows: the C1–O1 bond length is decreasing, meanwhile the C7=N1 double bond length is increasing, and so is the *A* value. These alterations suggest larger amount of keto form in the resonance. This unusual feature, appears to be typical for hydrogen bonding in *Schiff* bases according to detailed ab initio calculations [24].

Further increase of acidity of phenolic part is expected when the chlorine atom at *ortho*-position is replaced by nitro group in compound **III**. The content of keto form is increased; the C1–O1 bond is shorter,

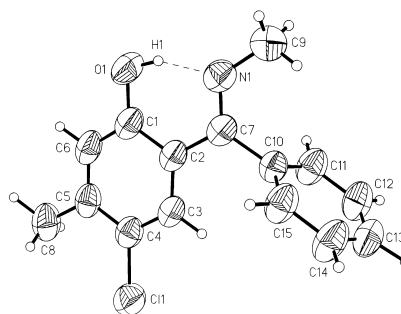Fig. 5. ORTEPII [23] drawing of **V** showing the atom numbering scheme.

Fig. 6. ORTEPII [23] drawing of **VI** showing the atom numbering scheme.

Table 2
Experimental bond lengths (Å) and angles (°) for **I** at 293 and 100 K (*esds* in parentheses)

Bond (Å)	$T = 293$ K	$T = 100$ K	Valence angles (°)	$T = 293$ K	$T = 100$ K
Cl1–C4	1.746(2)	1.750(1)	C7–N1–C10	123.8(2)	124.1(1)
O1–C1	1.319(2)	1.317(1)	O1–C1–C6	119.4(2)	119.5(1)
N1–C7	1.286(2)	1.299(2)	O1–C1–C2	122.3(2)	122.4(1)
N1–C10	1.463(2)	1.465(2)	C6–C1–C2	118.4(2)	118.1(1)
C1–C6	1.403(2)	1.412(2)	C3–C2–C1	118.2(2)	118.8(1)
C1–C2	1.423(2)	1.432(2)	C3–C2–C7	121.7(1)	121.5(1)
C2–C3	1.401(2)	1.409(2)	C1–C2–C7	120.0(2)	119.8(1)
C2–C7	1.464(2)	1.462(2)	C4–C3–C2	120.9(2)	120.5(1)
C3–C4	1.372(2)	1.377(2)	C3–C4–C5	122.3(2)	122.2(1)
C4–C5	1.396(3)	1.405(2)	C3–C4–Cl1	118.8(1)	119.2(1)
C5–C6	1.378(3)	1.384(2)	C5–C4–Cl1	118.9(1)	118.6(1)
C5–C8	1.503(3)	1.505(2)	C6–C5–C4	116.8(2)	117.3(1)
C7–C9	1.493(3)	1.499(2)	C6–C5–C8	121.1(2)	121.0(1)
C10–C11	1.504(3)	1.516(2)	C4–C5–C8	122.0(2)	121.7(1)
			C5–C6–C1	123.3(2)	123.0(1)
			N1–C7–C2	117.0(1)	116.8(1)
			N1–C7–C9	122.3(2)	121.9(1)
			C2–C7–C9	120.7(2)	121.3(1)
			N1–C10–C11	109.5(2)	109.3(1)

Table 3
Experimental bond lengths (Å) and angles (°) for **II** at 293 and 100 K (*esds* in parentheses)

Bond (Å)	$T = 293$ K	$T = 100$ K	Valence angles (°)	$T = 293$ K	$T = 100$ K
Cl1–C4	1.734(3)	1.741(2)	C7–N1–C9	125.1(3)	125.3(2)
Cl2–C6	1.734(2)	1.733(2)	O1–C1–C6	121.0(2)	121.1(2)
O1–C1	1.288(3)	1.280(3)	O1–C1–C2	122.9(2)	123.2(2)
N1–C7	1.296(4)	1.305(3)	C6–C1–C2	116.1(2)	115.7(2)
N1–C9	1.453(4)	1.445(3)	C3–C2–C1	119.3(2)	120.1(2)
C1–C6	1.421(3)	1.435(3)	C3–C2–C7	121.1(2)	120.6(2)
C1–C2	1.435(3)	1.437(3)	C1–C2–C7	119.5(2)	119.2(2)
C2–C3	1.410(3)	1.408(3)	C4–C3–C2	121.0(2)	120.3(2)
C2–C7	1.448(3)	1.445(3)	C3–C4–C5	121.6(2)	122.1(2)
C3–C4	1.364(4)	1.367(3)	C3–C4–Cl1	119.3(2)	118.9(2)
C4–C5	1.395(3)	1.398(3)	C5–C4–Cl1	119.1(2)	118.1(2)
C5–C6	1.368(3)	1.366(3)	C6–C5–C4	117.9(2)	118.1(2)
C7–C8	1.485(4)	1.497(3)	C5–C6–C1	124.0(2)	123.7(2)
			C5–C6–Cl2	119.5(2)	120.1(2)
			C1–C6–Cl2	116.5(2)	116.3(2)
			N1–C7–C2	117.7(2)	118.0(2)
			N1–C7–C8	120.6(3)	119.5(2)
			C2–C7–C8	121.8(3)	122.5(2)

Table 4
Experimental bond lengths (Å) and angles (°) for **III** at 293 K (*esds* in parentheses)

Bond (Å)		Valence angles (°)	
Cl1–C4	1.737(4)	C7–N1–C9	127.6(3)
O1–C1	1.280(5)	O2–N2–O3	123.8(4)
O2–N2	1.222(5)	O2–N2–C6	118.1(4)
O3–N2	1.229(5)	O3–N2–C6	118.1(3)
N1–C7	1.282(5)	O1–C1–C6	122.4(3)
N1–C9	1.455(5)	O1–C1–C2	122.9(3)
N2–C6	1.457(4)	C6–C1–C2	114.7(3)
C1–C6	1.407(5)	C3–C2–C7	121.3(3)
C1–C2	1.452(5)	C3–C2–C1	119.8(3)
C2–C3	1.387(6)	C7–C2–C1	118.9(3)
C2–C7	1.445(5)	C4–C3–C2	121.6(3)
C3–C4	1.375(6)	C3–C4–C5	120.7(4)
C4–C5	1.391(6)	C3–C4–Cl1	119.9(3)
C5–C6	1.365(5)	C5–C4–Cl1	119.4(3)
C7–C8	1.501(4)	C6–C5–C4	117.8(3)
		C5–C6–C1	125.4(3)
		C5–C6–N2	117.5(3)
		C1–C6–N2	117.1(3)
		N1–C7–C2	118.4(3)
		N1–C7–C8	121.0(3)
		C2–C7–C8	120.6(3)

Table 5
Experimental bond lengths (Å) and angles (°) for **IV** at 293 K (*esds* in parentheses)

Bond (Å)		Valence angles (°)	
O1–C1	1.282(2)	C7–N1–C9	127.3(1)
O2–N2	1.178(11)	O2–N2–O31	106.5(6)
O3–N2	1.246(11)	O31–N2–O21	122.0(6)
O21–N2	1.234(10)	O2–N2–O3	123.3(7)
O31–N2	1.179(9)	O21–N2–O3	118.0(5)
N1–C7	1.296(2)	O2–N2–C6	122.0(7)
N1–C9	1.451(2)	O31–N2–C6	120.8(6)
N2–C6	1.462(2)	O21–N2–C6	116.9(6)
C1–C6	1.418(2)	O3–N2–C6	114.6(6)
C1–C2	1.438(2)	O1–C1–C6	122.0(1)
C2–C3	1.402(2)	O1–C1–C2	124.2(1)
C2–C7	1.457(2)	C6–C1–C2	113.8(1)
C3–C4	1.374(2)	C3–C2–C1	119.9(1)
C4–C5	1.405(2)	C3–C2–C7	120.8(1)
C4–C10	1.511(2)	C1–C2–C7	119.3(1)
C5–C6	1.365(2)	C4–C3–C2	123.7(1)
C7–C8	1.493(2)	C3–C4–C5	117.5(1)
		C3–C4–C10	121.0(1)
		C5–C4–C10	121.4(2)
		C6–C5–C4	119.4(1)
		C5–C6–C1	125.7(1)
		C5–C6–N2	118.5(1)
		C1–C6–N2	115.9(1)
		N1–C7–C2	117.6(1)
		N1–C7–C8	120.6(2)
		C2–C7–C8	121.6(1)

both the *A* value and the fraction of keto form-X_k are larger. However, the C7=N1 bond length shortening suggests some kind of change of π-electron coupling. The nitro group is turned out from the plane of the ring on 50°, thus indicating repulsion between the nitro and hydroxy groups.

The difference between compounds **IV** and **III** lays in the replacement of the chlorine atom by methyl group in the former compound, weakening the ability of proton transfer. The most unexpected thing about compound **IV** is disorder in position of nitro group. Coplanar and perpendicular orientations of nitro group with respect to phenol ring were determined. The repulsion between negatively charged oxygen atoms of phenolate and nitro group overpasses the coupling forces, which act in favour of coplanar form, and makes two above mentioned structures energetically equivalent. Average C6–N2 distance in compound **IV** is slightly longer than in compound **III**. Rather large non-equivalence of the N2–O2 and N2–O3 bonds of nitro group features compound **IV**, meanwhile in compound **III** these bonds are practically equal. It is hardly to assume that the reason for appearance of perpendicular form is a little bit higher

unit cell volume in compound **IV** than in compound **III**.

Compounds **V** and **VI** contain the phenyl substituent at the carbon atom of imine group. Substitution by a phenyl ring (R_1) in –C(R_1)=N– moiety in **V** and **VI** reduces the basicity of the nitrogen atom, thus making hydrogen bond in **V** and **VI** weaker. Nevertheless, mostly due to steric repulsion, compounds **V** and **VI** form rather short OHN hydrogen bonds, which are slightly weaker than in compounds with methyl substituent.

One can compare compound **V** with the *2-(methylimino-phenyl-methyl)-phenol* [25] which differs only in the substituent at nitrogen atom of imine group. *Iso*-propyl *N*-chain was replaced in above mentioned compound by *N*-methyl group. Substantial strengthening of the hydrogen bond in the last compound can be observed. It demonstrates that *iso*-propyl group in compound **V** is shielding the reaction

Table 6
Experimental bond lengths (Å) and angles (°) for **V** at 293 K (*esds* in parentheses)

Bond (Å)		Valence angles (°)	
O1–C1	1.346(2)	C7–N1–C14	122.6(1)
N1–C7	1.285(2)	O1–C1–C6	118.3(2)
N1–C14	1.467(2)	O1–C1–C2	121.8(1)
C1–C6	1.395(2)	C6–C1–C2	119.9(2)
C1–C2	1.405(2)	C3–C2–C1	118.1(1)
C2–C3	1.392(2)	C3–C2–C7	120.9(1)
C2–C7	1.470(2)	C1–C2–C7	121.0(1)
C3–C4	1.384(2)	C4–C3–C2	121.8(2)
C4–C5	1.383(3)	C5–C4–C3	118.9(2)
C5–C6	1.367(3)	C6–C5–C4	121.1(2)
C7–C8	1.494(2)	C5–C6–C1	120.2(2)
C8–C9	1.380(2)	N1–C7–C2	118.5(1)
C8–C13	1.382(2)	N1–C7–C8	123.5(1)
C9–C10	1.383(2)	C2–C7–C8	118.1(1)
C10–C11	1.364(3)	C9–C8–C13	118.7(2)
C11–C12	1.367(3)	C9–C8–C7	120.9(1)
C12–C13	1.382(3)	C13–C8–C7	120.5(1)
C14–C16	1.512(3)	C8–C9–C10	120.3(2)
C14–C15	1.513(3)	C11–C10–C9	120.6(2)
		C10–C11–C12	119.8(2)
		C11–C12–C13	120.3(2)
		C12–C13–C8	120.5(2)
		N1–C14–C16	107.7(2)
		N1–C14–C15	108.7(2)
		C16–C14–C15	111.5(2)

Table 7
Experimental bond lengths (Å) and angles (°) for **VI** at 293 K (*esds* in parentheses)

Bond (Å)		Valence angles (°)	
Cl1–C4	1.741(2)	C7–N1–C9	122.0(2)
O1–C1	1.340(3)	O1–C1–C6	118.8(2)
N1–C7	1.287(2)	O1–C1–C2	121.6(2)
N1–C9	1.446(3)	C6–C1–C2	119.7(2)
C1–C6	1.387(3)	C3–C2–C1	117.5(2)
C1–C2	1.417(2)	C3–C2–C7	121.5(2)
C2–C3	1.391(3)	C1–C2–C7	121.1(2)
C2–C7	1.469(3)	C4–C3–C2	121.3(2)
C3–C4	1.373(3)	C3–C4–C5	122.1(2)
C4–C5	1.399(3)	C3–C4–Cl1	118.6(1)
C5–C6	1.377(3)	C5–C4–Cl1	119.4(2)
C5–C8	1.506(3)	C6–C5–C4	116.6(2)
C7–C10	1.500(2)	C6–C5–C8	121.0(2)
C10–C15	1.376(3)	C4–C5–C8	122.4(2)
C10–C11	1.381(3)	C5–C6–C1	123.0(2)
C11–C12	1.381(3)	N1–C7–C2	117.6(2)
C12–C13	1.361(3)	N1–C7–C10	123.9(2)
C13–C14	1.362(3)	C2–C7–C10	118.5(2)
C14–C15	1.383(3)	C15–C10–C11	119.2(2)
		C15–C10–C7	121.3(2)
		C11–C10–C7	119.5(2)
		C10–C11–C12	120.0(2)
		C13–C12–C11	120.6(2)
		C12–C13–C14	119.7(2)
		C13–C14–C15	120.7(2)
		C10–C15–C14	119.8(2)

center from surroundings, that strongly affects the tautomeric equilibrium.

Presented compounds can be treated as poly substituted phenols. Internal angles of the aromatic ring are the combined results of the position and the character of substitutes (cf. [26]). Decreasing of the C6–C1–C2 angle in relation to regular hexagonal ring structure as well as shortening of the C1–O1 bond length for compounds **I–IV** reveal the presence of keto form (cf. [27]).

Practically in all compounds investigated in this paper we steadily observe decreasing of the C1–C2–C3 angle, except for compounds **III** and **IV**, where there is a strong influence of nitro group. This group is responsible for increasing of the C1–C2–C3 angle, meanwhile imine substitution acts in opposite direction making this angle decrease.

The C2–C3–C4 angle tends to increase in all investigated compounds, the influence of imine group is likely to blame here.

The C3–C4–C5 angle for compounds with chlorine substitution at *para*-position is obviously increased (cf. [26]), though in the rest of the compounds this angle is close to 120°. However, compound **IV** is an exception due to methyl group attached, which leads to the C3–C4–C5 angle diminishing. The methyl group in *meta*-position participates in decreasing of the C4–C5–C6 angle in compounds **I** and **VI**.

In compounds **II–IV** nitro group or chlorine substitution at *ortho*-position makes the C1–C6–C5 angle increase; the similar influence of nitro group on benzene ring was observed in Ref. [28].

4.2. Crystal data correlation

In order to characterize the steric and electronic interactions influencing hydrogen bond in the studied compounds in the solid state one can use a few semiquantitative descriptors based on experimental parameters of the molecular structure. It can be *A*

Table 8
Hydrogen bond parameters and selected bond lengths and angle in pseudoaromatic chelate rings (*esds* in parentheses)

|	Form of HB	T (K)	d(OH) (Å)	d(ON) (Å)	d(HN) (Å)	α(OHN) (°)	d(CO) (Å)	d(CN) (Å)	Q (Å)	A (Å^2)	X_k (%)
I	O···H···N	293	1.22(5)	2.488(2)	1.30(5)	160(4)	1.319(1)	1.286(2)	0.074	284	32
	O···H···N	100	1.36(3)	2.481(1)	1.17(3)	156(3)	1.317(1)	1.299(2)	0.048	333	35
II	O···H–N	293	1.42(7)	2.493(3)	1.14(7)	154(5)	1.288(3)	1.296(4)	0.005	683	41
	O···H–N	100	1.62(4)	2.496(3)	0.95(4)	151(3)	1.280(3)	1.305(3)	0.005	817	41
III	O···H–N	293	1.49(5)	2.501(4)	1.03(5)	167(5)	1.280(5)	1.282(5)	−0.009	794	43
IV	O···H–N	293	1.63(2)	2.523(2)	1.02(2)	144(2)	1.282(2)	1.296(2)	0.005	616	41
V	O–H···N	293	1.05(3)	2.534(2)	1.54(3)	155(2)	1.346(2)	1.285(2)	0.126	139	24
VI	O–H···N	293	0.91(3)	2.524(2)	1.67(4)	156(3)	1.340(3)	1.287(2)	0.105	213	27

parameter

$$A = \frac{\sum\limits_{i}^{n} (d_i - \bar{d})^2}{n} \times 10^6$$

reflecting aromaticity of phenol ring [29–31] so as Q [$Q = (d(C1O1) - d(C7N1)) + (d(C2C7) - d(C1C2)]$ parameter, characterizing the chelate ring structure [32]. Both parameters use separate sets of crystal data and describe the amount of keto forms independently.

The situation can be related to some determinants influencing the proton position in intramolecular hydrogen bridge. These determinants are basicity of nitrogen atom and acidity of oxygen atom bridged with chelate ring, and strong π-electron interaction between these centers, which provides the formation of the Resonance Assisted Hydrogen Bonds (RAHB) [33,34].

One more determinant affecting intramolecular hydrogen bridge is the mentioned above steric interaction, which evokes significant shortening of O···N distance [10,12].

These determinants can act in accordance with each other, but in some cases act contrary one to another. Compounds **V** and **VI** can serve as an example, where phenyl ring substituted to the carbon
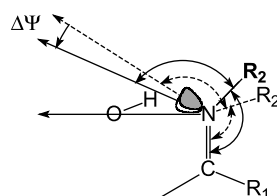
atom of imine group decreases basicity of the nitrogen atom thus making hydrogen bond weaker, from one side. However, steric squeezing of phenyl ring makes hydrogen bridge shorter, from the other side.

A number of papers [35,36] proves that direction of lone electron pair of nitrogen strongly influences the strength of intramolecular hydrogen bond. The direction of lone electron pair can be related to geometry of C(R$_1$)=NR$_2$ fragment (see Scheme 4).

Scheme 4 demonstrates the decrease of the angle ($\Delta\Psi$) between the direction of lone electron pair (drawn along the bisector of R$_2$–N–C angle) and the ON line caused by steric squeezing. The shift of the lone electron pair in direction to oxygen makes the hydrogen bridge more linear. This appears to be an additional factor involving in shortening of the O···N distance in sterically hindered *Schiff* bases.

The fraction of keto form X_K was calculated according to equation $Q = Q_M(1 - X_K) - Q_K X_K$, where Q_M and Q_K are values of Q parameter

Scheme 4.

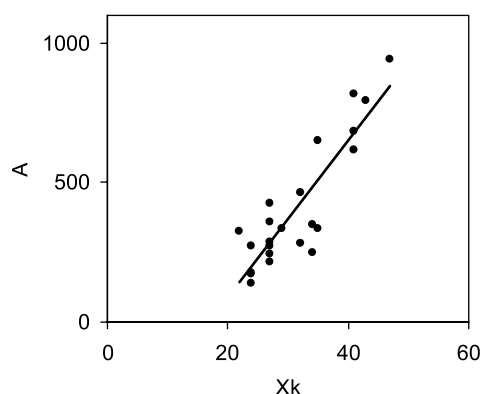
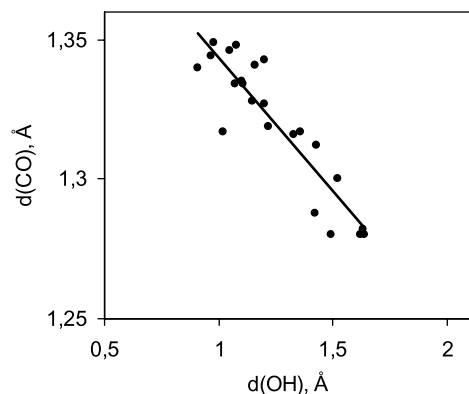Fig. 7. The A parameter vs. the fraction of keto form X_k (%); $A = 28.09 X_k - 474.94$, $R = 0.90$.

Fig. 8. The d(CO) (Å) distance vs. the d(OH) (Å) distance; d(CO) = $-0.102d$(OH) + 1.448, $R = 0.94$.

Fig. 10. The d(OH) (Å) distance vs. the fraction of keto form X_k (%); d(OH) = $0.028X_k + 0.356$, $R = 0.90$.

calculated for the molecular and proton transfer forms respectively, when using standard bond lengths [37], according to procedure described somewhere else [38]. It is seen (cf. Table 8) that when going from molecular form to proton transfer form of hydrogen bond A parameter increases, and Q parameter decreases.

Fig. 7 shows a correlation between the A and X_k parameters, which independently represent the amount of keto form in 22 crystal structures determined by us [10,12,25,38,39].

Fig. 8 presents the correlation between two of structural parameters, strongly dependent on the strength of hydrogen bonding. The correlation factor $R = 0.94$ implies that both these parameters can be characteristics of the strength of intramolecular
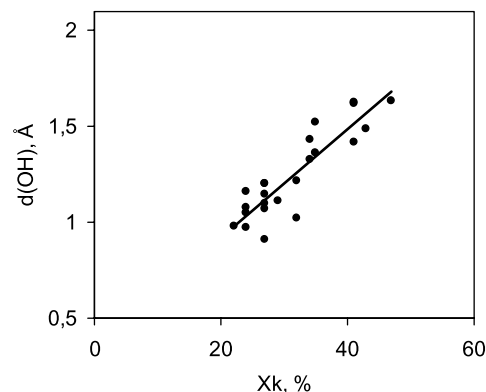
hydrogen bond in *Schiff* bases. It is clear that d(OH) increases, when d(CO) decreases.

Figs. 9 and 10 show that the local characteristics of intramolecular interactions (d(CO) and d(OH)) correlate with 'global' ones (A and X_K). It means that the strength of hydrogen bond can be correlated with the amount of keto form. The increasing fraction of keto form is positively correlated with the strength of hydrogen bond.

Figs. 10 and 11 demonstrate that the position of proton within the hydrogen bond is correlated with the amount of keto forms in *Schiff* bases.

The correlations depicted in this paper can serve to explain the nature of intramolecular hydrogen bond in *Schiff* bases as well as physical–chemical reactions taking place in molecule.
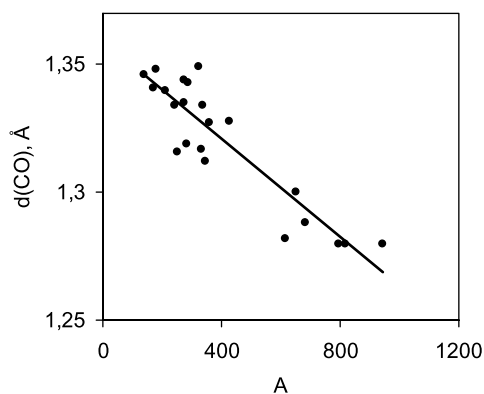

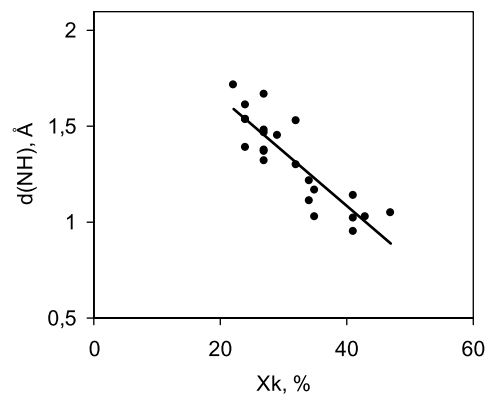Fig. 9. The d(CO) (Å) distance vs. the A parameter; d(CO) = $-0.96 \times 10^{-4}A + 1.36$, $R = 0.91$.

Fig. 11. The d(NH) (Å) distance vs. the fraction keto form X_k (%); d(NH) = $-0.028X_k + 2.205$, $R = 0.88$.

5. Conclusions

The crystal structures of six *Schiff* bases with steric interaction of the R_1 substituent in $-C(R_1)=N-$ moiety were measured. In all studied compounds the short intramolecular OHN hydrogen bond is formed. Nevertheless, the character of hydrogen bond in these compounds seriously depends on substitution.

The way the temperature decrease influences the character of the intramolecular hydrogen bond was studied in compounds **I** and **II**. In compound **I** some increase of proton transfer was found out, accompanied with strengthening of the hydrogen bond due to enhanced coupling and increase of the amount of keto resonance form. Such behaviour appears to be characteristic for hydrogen bond of enol type. For hydrogen bond with prevailing character of proton transfer, decrease of temperature leads to weakening of the hydrogen bond and supports the increase of keto character of the structure. So, hydrogen bond makes the resonance interactions increase in both enol and proton transfer tautomers. However, the structural consequences of that are opposite for enol and proton transfer states. In the enol form the hydrogen bonding strengthens due to the increased fraction of *o*-quinoid form. After the proton transfer, the strengthening of the hydrogen bond is accompanied with enhanced resonance interactions, that increases the amount of zwitterionic resonance form and decreases the alternation of bond lengths in the phenyl ring.

The obtained structural evidences are consistent with the model of proton transfer equilibrium in *Schiff* bases (cf. Scheme 2), where the quintessence of each of the tautomers is a result of resonance interaction, content of which is dependent on steric and electronic interactions.

Acknowledgments

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