

Journal of Molecular Structure 484 (1999) 75-89

Journal of MOLECULAR STRUCTURE

# Strengthening of the intramolecular O···H···N hydrogen bonds in Schiff bases as a result of steric repulsion

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Received 28 September 1998; accepted 25 October 1998

#### Abstract

Three ortho hydroxy Schiff bases 2-(*N*-methyl- $\alpha$ -iminoethyl)-phenol (**I**), 2-(*N*-benzyl- $\alpha$ -iminoethyl)-phenol (**II**) and 2-(*N*-benzyl- $\alpha$ -iminopropyl)-phenol (**III**) were synthesised in which the hydrogen atoms in C–C(H)=N group were replaced by an alkyl substituent. The crystal structures were determined and ab initio calculations at the B3LYP/6-31G\*\* basis set were performed. One of the shortest known O–H…N hydrogen bonds were found with O…N distance equal to 2.459(3), 2.497(3) and 2.494(3) Å, respectively in **I**, **II** and **III**. Steric repulsion of substituted alkyl results in this unusual strengthening of the hydrogen bonds. FT-IR spectra in solution and in the solid state in function of the temperature were determined. Strong influence of the temperature on the character of the hydrogen bond was observed. © 1999 Elsevier Science B.V. All rights reserved.

Keywords: Schiff bases; Crystal structure; Ab initio; Steric repulsion; Hydrogen bonds

## 1. Introduction

The ortho-hydroxy Schiff bases form the intramolecular hydrogen bonds, which reveal very interesting properties like thermochromism [1], attributed to the intramolecular proton transfer reaction. It suggests that the proton transfer state is comparatively easy accessible-the energy of keto and enol forms should not be very different.

A large group of Schiff bases show photochromism that is explained by photo-induced proton transfer. Such behaviour suggests the possibility of using these compounds as elements for constructing the optical switches or optical memory devices [2]. This

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behaviour is strongly related to the double fluorescence observed in salicyl anilides [3].

It was shown that double fluorescence is not limited only to aromatic–aromatic (condensation products of salicyl aldehydes and anilines) systems, but is also observed in aromatic–aliphatic ortho-hydroxy Schiff bases. Grabowska et al. [4,5] have performed the luminescence studies with the aim to establish the structure of the basic molecular units responsible for double fluorescence. They have found that 2-(*N*methyliminophenyl)-phenol is such a unit. More specific question arises–what is the structure of the state after the proton transfer? Does it contain more zwitterionic or keto form? (Scheme 1).

In our previous studies on the structure of two chloro derivatives the 2-(*N*-methyliminomethyl)-4-Cl-phenol and 2-(*N*-methyliminomethyl)-2,4-di-Clphenol the strong coupling of C=N double bond

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with the phenol ring was demonstrated [6]. In the structure with  $O-H\cdots N$  intramolecular hydrogen bond about 20% of keto resonance form was found, while in the proton transfer (PT)  $O\cdots H-N$  form the amount of keto resonance form was estimated to be about 50%. Strong coupling between chelate and phenol rings leads to the increase in the strength of hydrogen bond and to lowering of the energy of PT

Table 1

Summary of data collection and processing parameters (w =  $1/[\sigma^2(F_0^2) + (a \cdot P)^2 + b \cdot P]$  where  $P = [f \cdot Max. of (0 \text{ or } F_0^2) + (1 - f) \times F_c^2]$ 

Compound	Ι	II	III
Formula	C <sub>9</sub> H <sub>11</sub> NO	C <sub>15</sub> H <sub>15</sub> NO	C <sub>16</sub> H <sub>17</sub> NO
Color	Yellow	Yellow	Yellow
Molecular weight	149.19	225.28	239.31
Space group	P1	P <sub>ccn</sub>	$P2_1/n$
Temperature,°C	293(2) K	293(2) K	293(2) K
Cell constants	50 ref., $20.6 < 2\theta < 33.5$	25 ref., $25.0 < 2\theta < 38.0$	50 ref., $21.2 < 2\theta < 38.3$
Crystal system	Triclinic	Orthorhombic	Monoclinic
a (Å)	7.548(2)	21.838(2)	10.187(3)
b (Å)	7.560(2)	15.745(3)	6.847(2)
<i>c</i> (Å)	16.379(3)	7.020(4)	18.850(4)
$\alpha$ (°)	94.78(3)		
β(°)	100.95(3)		93.50(3)
γ (°)	113.94(3)		
Cell volume ( $Å^{-3}$ )	825.2 (3)	2414(2)	1312.3(4)
Formula units/unit cell	4	8	4
$D_{cal}(Mg \times m^{-3})$	1.201	1.240	1.211
Difractometer/Scan		Kuma KM4/ $\omega$ -2 $\theta$	
Radiation (Å), graph	ΜοΚα	CuKα	ΜοΚα
monochromator			
Max. crystal dimensions (mm)	$0.35 \times 0.40 \times 0.60$	$0.20 \times 0.25 \times 0.25$	$0.45 \times 0.45 \times 0.55$
Scan width (deg)	Variable	Variable	Variable
No. of stand. Ref. and int.	3 (100 ref.)	3 (100 ref.)	3(100 ref.)
Reflections measured	2667	2401	2730
$2\theta$ range (deg)	5.1-50.1	6.0-160.4	4.3-52.1
Range of h, k, l	- 8/8, - 8/8, 0/19	0/27, 0/20, - 8/0	0/12, 0/8, -23/23
Reflections observed $[F_0 > 4 - (F_0)]$	1490	1333	1427
$4\sigma(r_0)$		Lorentz and polarization offects	
Computer programs		Shalva 86 [10] Shalvi 02 [11]	
Computer programs		Brogroms	
Source of structure factors used		Piograms Diverse weatherd	
Structure solution		Direct method	
Treatment of hydrogen atoms	212	Refined parameters: $x, y, z, U_{iso}$	1.00
No of parameters varied	212		109
Weights $(a, b, f)$	0.0801, 0.0316, 1/3	0., 0., 1/3	0.0503, 0.2022, 1/3
	1.034	0.957	1.029
$R_1 = \sum_{i=1}^{n} ( F_0  - F_c ) / \sum_{i=1}^{n} ( F_0 )$	0.0428	0.0435	0.0334
$WR_2 = \{ [WF_0^2 - F_0^2]^2 \}$	0.1200	0.1210	0.0900
$\sum [w(r_0)]$		$\sum w(F^2)^2$	
Largest feature final diff. Mer	0.200  and  - 0.102	$\sum w(r)$ 0.154 and $-0.107$	0.159  and  -0.119
$(e A^{-3})$	0.200  and  = 0.195	0.134  and  = 0.197	0.136 anu = 0.118

Table 2 Final atomic coordinates and equivalent thermal parameters with esd's in parentheses for 2-(*N*-methyl- $\alpha$ -iminoethyl)-phenol (I)

	x/a	y/b	z/c	$U_{eq}\!/U_{iso}$
011	0.7665(2)	0.2959(2)	0.61779(11)	0.0891(5)
O21	0.1787(3)	0.1488(2)	0.88210(11)	0.0884(5)
N11	0.6776(3)	0.2684(2)	0.46336(11)	0.0767(5)
N21	0.3052(3)	0.2146(3)	1.03659(11)	0.0769(5)
C11	0.5833(3)	0.2750(3)	0.61790(12)	0.0641(5)
C12	0.4430(3)	0.2473(2)	0.54181(12)	0.0591(5)
C13	0.2539(3)	0.2265(3)	0.5478(2)	0.0805(6)
C14	0.2047(4)	0.2323(3)	0.6245(2)	0.0951(8)
C15	0.3455(5)	0.2598(3)	0.6973(2)	0.0924(8)
C16	0.5299(4)	0.2800(3)	0.69387(14)	0.0814(7)
C17	0.4983(4)	0.2427(2)	0.46066(12)	0.0660(5)
C18	0.3485(4)	0.2091(4)	0.37992(15)	0.1025(9)
C19	0.7560(5)	0.2691(4)	0.3887(2)	0.1083(9)
C21	0.1571(3)	-0.0345(3)	0.88217(12)	0.0647(5)
C22	0.2056(3)	-0.0993(3)	0.95825(12)	0.0603(5)
C23	0.1779(3)	-0.2941(3)	0.9520(2)	0.0818(7)
C24	0.1072(4)	-0.4196(3)	0.8753(2)	0.0949(8)
C25	0.0623(3)	-0.3513(4)	0.8025(2)	0.0918(8)
C26	0.0868(3)	-0.1642(4)	0.80616(14)	0.0810(6)
C27	0.2821(3)	0.0379(3)	1.03939(12)	0.0661(5)
C28	0.3294(4)	-0.0323(4)	1.12012(15)	0.1034(9)
C29	0.3800(4)	0.3671(4)	1.1111(2)	0.1097(9)

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Final	atomic	coordinates	and	equivalent	thermal	parameters	with
esd's	in parei	theses for 2	2-( <i>N</i> -ł	benzyl- $\alpha$ -ir	ninoethy	l)-phenol (II	)

	x/a	y/b	z/c	$U_{eq}\!/U_{iso}$
N	0.47671(7)	0.29171(9)	0.0521(3)	0.0503(4)
0	0.49437(6)	0.13502(9)	0.0555(2)	0.0577(4)
C1	0.43364(8)	0.12571(11)	0.0585(3)	0.0471(4)
C2	0.39373(8)	0.19641(11)	0.0571(3)	0.0464(5)
C3	0.33097(9)	0.17954(14)	0.0591(4)	0.0633(6)
C4	0.30814(10)	0.0989(2)	0.0630(4)	0.0726(7)
C5	0.34773(10)	0.03096(14)	0.0671(4)	0.0670(6)
C6	0.40961(10)	0.04378(12)	0.0629(3)	0.0574(5)
C7	0.41815(8)	0.28348(11)	0.0554(3)	0.0474(5)
C8	0.37509(10)	0.35762(12)	0.0565(4)	0.0605(6)
C9	0.50569(9)	0.37527(12)	0.0507(4)	0.0551(5)
C10	0.57425(9)	0.36744(11)	0.0490(3)	0.0503(5)
C11	0.60864(10)	0.41167(13)	-0.0840(3)	0.0606(6)
C12	0.67175(11)	0.40851(15)	-0.0817(4)	0.0705(7)
C13	0.70148(11)	0.35958(15)	0.0517(4)	0.0719(7)
C14	0.66774(11)	0.31427(15)	0.1820(4)	0.0690(7)
C15	0.60504(10)	0.31838(13)	0.1816(3)	0.0604(6)

state. The ab initio calculations at the level of B3LYP/  $6-31G^{**}$  predicted that the PT state is located 4.5 kcal/mol above the molecular O–H···N (HB) state in 2-(*N*-methyliminomethyl)-4-Cl-phenol and 3.1 kcal/mol in 2-(*N*-methyliminomethyl)-2,4-di-Cl-phenol. However, the ab initio calculations were performed for the gas phase. In condensed phases these differences could be remarkably lower. Supposition about the thermal activation of the intra molecular proton transfer appears to be realistic.

In this work we have performed studies of a new class of ortho hydroxy Schiff bases. Replacement of the H atom in the C-C(H)=N group by methyl or ethyl substituent introduces perturbations to intramolecular hydrogen bonds and modifies the potential for the intramolecular proton transfer.

One can expect some strengthening of the hydrogen bond by these substituents owing to inductive influence on the basicity centre and the opposite effect owing to lowering the acidity of phenol. An average electronic effect will be diminished owing to mutual compensation.

The steric interaction of alkyl substituent, which by pushing the centre of basicity in direction of OH group decreases the O···N distance. Similar effect was shown earlier in the case of 2-(N,N-dimethylaminomethyl)-3,4,6-tri-CH<sub>3</sub>-phenol [7]. Steric shortening of the hydrogen bridge led to the increase of the spectroscopic consequences of the hydrogen bond formation [7]. Opposite effect can also be anticipated if the alkyl groups make the chelate rings less planar as a result of steric repulsion. (Scheme 2).

Three Schiff bases with methyl and ethyl substituents in C–C=N group were synthesized: 2-(*N*-methyl- $\alpha$ -iminoethyl)-phenol (**I**), 2-(*N*-benzyl- $\alpha$ -imino-propyl)-phenol (**II**) and 2-(*N*-benzyl- $\alpha$ -imino-propyl)-phenol (**III**). The molecular structures were determined by X-ray crystallography and ab initio-B3LYP/6-31G\*\* calculations. Performed studies indicate that the steric effects lead to strong strengthening of intramolecular hydrogen bonds. In all the systems studied here the intramolecular hydrogen O–H…N bonds belong to the shortest reported in literature so far.

#### 2. Experimental

Synthesis of a Schiff base from stoichiometric



Fig. 1. Molecular structure and atoms labelling system of 2-(N-methyl- $\alpha$ -iminoethyl)- phenol(I).

mixtures of particular salicylaldehyde and methylamine in methanol was performed with the standard procedure [8]. After recrystallization of the solid products from methanol they were studied by X-ray diffraction. Summary of the data collected is given in Table 1. Anisotropic thermal parameters for non-H atoms were applied [9]. Final atomic coordinates are given in Tables 2–4.

Vibrational spectra were measured by FT-IR Nicolet-205 spectrophotometer, at the resolution of  $2 \text{ cm}^{-1}$ , in CCl<sub>4</sub> solutions, in cells with KBr windows. Low temperature measurement was performed on the specimens melted between KBr windows.

Table 4

Final atomic coordinates and equivalent thermal parameters with esd's in parentheses for  $2-(N-\text{benzyl}-\alpha-\text{iminopropyl})-\text{phenol (III)}$ 

	x/a	y/b	z/c	$U_{eq}\!/U_{iso}$
0	0.58989(13)	0.0760(2)	0.71937(7)	0.0587(4)
Ν	0.71804(13)	-0.1552(2)	0.64831(7)	0.0471(3)
C1	0.5269(2)	-0.0786(2)	0.74375(8)	0.0460(4)
C2	0.55769(15)	-0.2709(2)	0.72280(7)	0.0405(4)
C3	0.4855(2)	-0.4230(2)	0.75048(9)	0.0532(4)
C4	0.3881(2)	-0.3907(3)	0.79611(10)	0.0654(5)
C5	0.3602(2)	-0.2026(3)	0.81654(11)	0.0690(5)
C6	0.4289(2)	-0.0488(3)	0.79074(10)	0.0617(5)
C7	0.65950(15)	-0.3062(2)	0.67220(8)	0.0414(4)
C8	0.6848(2)	-0.5124(2)	0.64948(9)	0.0493(4)
C9	0.5840(2)	-0.5786(3)	0.59118(10)	0.0641(5)
C10	0.8199(2)	-0.1633(3)	0.59696(10)	0.0592(5)
C11	0.79025(15)	-0.0220(2)	0.53692(8)	0.0463(4)
C12	0.8660(2)	0.1411(3)	0.52833(11)	0.0621(5)
C13	0.8367(2)	0.2679(3)	0.47153(13)	0.0771(6)
C14	0.7318(2)	0.2305(4)	0.42474(11)	0.0751(6)
C15	0.6564(2)	0.0715(4)	0.43324(10)	0.0741(6)
C16	0.6857(2)	-0.0534(3)	0.48868(9)	0.0627(5)

## 3. Results

Molecular structures and atoms labelling system are demonstrated in Figs. 1–3. In **I** two non-equivalent molecules in basic crystal unit were found. Table 5 presents selected bond distances and valence angles. Selected torsional angles are presented in Table 6.

## 4. Discussion

## 4.1. Molecular structure

There are two non-equivalent molecules in the



Fig. 2. Molecular structure and atoms labelling system of  $2-(N-benzyl-\alpha-iminoethyl)$ - phenol(**II**).



Fig. 3. Molecular structure and atoms labelling system of  $2-(N-\text{benzyl}-\alpha-\text{iminopropyl})$ - phenol(III).

crystal unit cell of **I**. Differences between related parameters are in average, less than the experimental  $\sigma$ values and average parameter values for these two molecules are used for discussion. One such exclusion is the geometry of hydrogen bonds, where two structures will be distinguished.

Analysis of the bond lengths in I shows, that intramolecular hydrogen bonds exist in the molecular (HB) form. Lesser amount of the ortho quinoic resonance structure was found in the structure of phenyl ring of I than in 2-(N-methyliminomethyl)-4-Clphenol (V), which presents the experimentally known structure of 2-(*N*-methyliminomethyl)-phenols [6]. Of all the bonds shown in keto resonance structure as double bonds (see Scheme 1), shortening of the bonds is an indication of participation of o-quinoic structure, two are longer than in V; C17-C12 (1.47 Å in I besides of 1.448 (in V) and C13-C14 (1.378 Å besides of 1.355 Å in V). Calculations for the ionic form (about 50% of keto form was found 2-(N-methyliminomethyl)-2,4-Clpreviously in phenol [6]) show these bonds to be much shorter

(Table 5). The third, C15–C16 was of the same length in **I** and in **V**. For atom labelling see Fig. 1.

On the basis of the structural parameters of the phenol ring one should neither predict a strong electronic coupling in the molecule, nor strong strengthening of hydrogen bond, owing to resonance effects [12,13].

In other (II, III) compounds the phenyl ring situation seem to be similar. The bonds which are double in o-quinoic resonance structure are shortened (3-4, 5-6) in comparison to those which are formally single ones (1-2, 6-1, 5-4, 2-3). Especially elongated are 1-2 bonds, characteristic for collective effect of both substituents, and extended by the formation of the chelate ring. Like in I all those effects are less pronounced than in V, and in comparison to the calculated structure of ortho hydroxy Schiff base without substituents (IV) (Table 5). Thus coupling is not very effective as it leads to mild differentiation of bond lengths. As it was shown earlier [6] such a coupling increases the content of keto form and leads to bond differentiation in opposite to general resonance



Scheme 2.

Table 5

Experimental and calculated (B3LYP/6-31G\*\*) bond lengths (Å) and angles (°) with esd's in parentheses for 2-(*N*-methyl- $\alpha$ -iminoethyl)-phenol (I) <sup>b</sup>, 2-(*N*-benzyl- $\alpha$ -iminoethyl)-phenol (II) and 2-(*N*-benzyl- $\alpha$ -iminopropyl)-phenol (III)

$ \begin{array}{ c c c c c c c c c c c c c c c c c c c$	Bond lengths	/Å				Valence angles/°			
$\begin{array}{c c c c c c c c c c c c c c c c c c c $	_	X-ray	Calculated		IV <sup>a</sup>		X-ray	Calculated	
021-021   1.328(2)   -   -   -   C77-N21-C29   123.5(2)   1.23.9   1.27.9     0.11-021   1.327(2)   1.3358   1.2759   1.3403   C17-N11-C19   123.5(2)   123.49   127.9     N11-021   1.280(3)   -   -   -   021-C21-C22   121.3(2)   -   -     N11-C17   1.278(3)   1.2448   1.2447   011-C11-C12   119.4(2)   -   -     N11-C19   1.456(3)   1.4449   1.4488   C16-C11-C12   119.4(2)   -   -     C11-C16   1.384(3)   -   -   -   C23-C22-C1   117.2(2)   -   -     C11-C16   1.384(3)   -   -   -   C23-C22-C1   119.0(2)   12.29   12.29     C12-C27   1.4114   1.4263   1.4039   C11-C12-C17   122.4(2)   12.19     C12-C17   1.456(3)   1.4114   1.4263   1.4039   C11-C12-C17   12.9(2)   12.11     C12-C12   1.457(3)	Bonds	HB	HB	PT	HB	Angles	HB	HB	РТ
011-C11 1.327(2) 1.338 1.279 1.3403 C17-N11-C19 122.5(2) 122.49 127.91   N21-C27 1.280(3) - - - 011-C11-C12 121.0(2) - -   N11-C19 1.454(3) - - - C26-C21-C22 119.4(2) - -   N11-C19 1.456(3) 1.4489 1.4488 C16-C11-C12 119.8(2) 119.89 116.89   C21-C26 1.384(3) - - - C23-C22-C21 117.2(2) - -   C11-C16 1.381(3) 1.4066 1.4389 1.4033 C12-C27 119.9(2) - -   C12-C21 1.414(3) - - - C21-C22-C27 119.9(2) - -   C12-C13 1.395(3) 1.414 1.4263 1.4039 C11-C12-C17 12.04(2) 122.131 12.19   C22-C27 1.476(3) 1.479 1.4303 1.4703 1.4024 C13-C12-C17 12.04(2) - - - C12-C17 1.46(3) 1.49 - - -<	O21-C21	1.328(2)	_	_	_	C27-N21-C29	123.5(2)	_	_
N21-C27   1280(3)   -   -   -   O21-C21-C22   121.212   12.52   122.52   122.52   122.52     N21-C29   1.454(3)   1.248   1.2487   0.11-C11-C12   119.420   -   -   -   C26-C21-C22   119.420   -   -   -   -   -   C26-C21-C22   119.420   -   -   -   -   -   C26-C21-C22   119.430   119.89   116.89     C11-C16   1.381(3)   1.4408   1.4438   C13-C12-C11   117.2(2)   -   -   -   -   C21-C21   117.34   118.94     C21-C21   1.414(3)   -   -   -   C21-C21   120.4(2)   122.53   122.93   122.93   122.93   122.93   122.93   122.93   122.93   122.93   122.93   122.93   122.93   122.93   121.99   123.93   121.99   123.93   121.99   124.93   122.91   121.93   121.99   124.93   124.93   124.93   124.93   124.93	O11-C11	1.327(2)	1.3358	1.2759	1.3403	C17-N11-C19	123.5(2)	123.49	127.91
$\begin{split} & \text{N11-C17} & 1.278(3) & 1.2948 & 1.2263 & 1.2847 & \text{O11-C11-C12} & 121.0(2) & 12.252 & 122.21 \\ & \text{N21-C29} & 1.456(3) & 1.4489 & 1.4481 & 1.4488 & \text{C16-C11-C12} & 119.8(2) & 119.89 & 116.89 \\ & \text{C21-C26} & 1.384(3) & - & - & - & \text{C23-C22-C21} & 117.2(2) & - & - \\ & \text{C21-C22} & 1.414(3) & - & - & - & \text{C23-C22-C71} & 117.3(2) & - & - \\ & \text{C21-C12} & 1.414(3) & - & - & - & \text{C23-C22-C71} & 123.0(2) & - & - \\ & \text{C11-C12} & 1.414(3) & 1.4315 & 1.4673 & 1.4224 & \text{C13-C12-C17} & 122.4(2) & 122.53 & 122.29 \\ & \text{C22-C23} & 1.393(3) & - & - & - & \text{C21-C22-C27} & 119.9(2) & - & - \\ & \text{C12-C13} & 1.395(3) & 1.4114 & 1.4263 & 1.4039 & \text{C11-C12-C17} & 120.4(2) & 120.14 & 118.94 \\ & \text{C22-C27} & 1.473(3) & - & - & - & \text{C21-C22-C27} & 119.9(2) & - & - \\ & \text{C12-C17} & 1.468(3) & 1.4790 & 1.4300 & 1.4484 & \text{C14-C13-C12} & 121.8(2) & 122.31 & 121.99 \\ & \text{C23-C24} & 1.378(4) & 1.3869 & 1.3726 & 1.3871 & \text{C15-C14-C13} & 119.4(2) & 119.89 & 119.45 \\ & \text{C24-C25} & 1.376(4) & - & - & - & \text{C25-C24-C22} & 120.4(2) & - & - \\ & \text{C14-C15} & 1.375(4) & 1.4013 & 1.4202 & 1.4029 & \text{C16-C15-C14} & 120.5(2) & 120.29 & 121.17 \\ & \text{C25-C26} & 1.345(3) & - & - & - & \text{C25-C26-C21} & 120.4(2) & - & - \\ & \text{C14-C15} & 1.375(4) & 1.5202 & 1.3705 & 1.3890 & \text{C15-C16-C11} & 121.4(2) & 120.77 \\ & \text{C28} & 1.500(3) & - & - & - & \text{N21-C27-C22} & 170.0(2) & - & - \\ & \text{N11-C17-C18} & 1.29.0(3) & - & - \\ & \text{N11-C17-C18} & 122.90 & 126.6 \\ & \text{N-C9} & 1.260(2) & 1.294 & 1.329 & \text{C7-N-C9} & 121.5(2) & 122.9 & 126.6 \\ & \text{N-C9} & 1.260(2) & 1.294 & 1.329 & \text{C7-N-C9} & 121.5(2) & 122.9 & 126.6 \\ & \text{N-C9} & 1.260(2) & 1.294 & 1.329 & \text{C7-N-C9} & 121.5(2) & 122.9 & 126.6 \\ & \text{N-C9} & 1.460(2) & 1.478 & \text{N-C7} & \text{C2} & 121.7(2) & 117.4 & 117.89 \\ & \text{N-C9} & 1.260(3) & 1.385 & 1.570 & \text{C7-N-C9} & 121.5(2) & 122.9 & 126.6 \\ & \text{N-C7} & 1.280(2) & 1.294 & 1.329 & \text{C7-N-C9} & 121.5(2) & 122.9 & 126.6 \\ & \text{N-C9} & 1.460(2) & 1.471 & \text{C3-C3-C2} & 124.0 & 100.0 & 112.1 \\ & \text{C3-C6} & 1.357(3) & 1.386 & 1.571 & \text{C3-C3-C2} & 1$	N21-C27	1.280(3)	_	_	_	O21-C21-C22	121.3(2)	_	_
N21-C29 1.456(3) 1.4489 1.4481 1.4488 C16-C11-C12 119.4(2) - -   N11-C19 1.456(3) 1.4489 1.4488 C16-C11-C12 119.4(2) - -   C11-C16 1.381(3) 1.4066 1.4389 1.4033 C13-C12-C11 117.2(2) 117.3(2) - -   C11-C12 1.414(3) 1.415 1.4673 1.4224 C13-C12-C17 123.4(2) 120.14 118.94   C22-C23 1.393(3) 1.4114 1.4263 1.4039 C11-C12-C17 120.4(2) 120.14 118.94   C22-C27 1.473(3) - - - C24-C23-C22 120.9(2) - -   C12-C17 1.468(3) 1.4790 1.4300 1.4548 C14-C13-C17 120.4(2) 120.14 118.94   C12-C17 1.468(3) 1.4790 1.4300 1.4548 C14-C13-C12 121.8(2) 120.91 121.99   C3-C24 1.378(4) - - - C25-C26-C24 120.4(2) - - - C13-C16 120.4(2) 120.91<	N11-C17	1.278(3)	1.2948	1.3263	1.2847	O11-C11-C12	121.0(2)	122.52	122.71
$\begin{split} & \text{N11-C19} & 1.456(3) & 1.4489 & 1.4481 & 1.4488 & \text{C16-C11-C12} & 119.8(2) & 119.89 & 116.89 \\ & \text{C21-C26} & 1.384(3) & - & - & & \text{C23-C22-C21} & 117.2(2) & - & - \\ & \text{C23-C22-C21} & 117.2(2) & - & - \\ & \text{C23-C22-C21} & 117.2(2) & - & - \\ & \text{C23-C22-C21} & 123.0(2) & - & - \\ & \text{C23-C22-C21} & 123.0(2) & - & - \\ & \text{C23-C22-C21} & 123.0(2) & - & - \\ & \text{C22-C23} & 1.393(3) & - & - & - \\ & \text{C21-C12} & 1.442(3) & 1.4315 & 1.4673 & 1.4224 & (C13-C12-C17 & 122.4(2) & 122.53 & 122.29 \\ & \text{C22-C23} & 1.395(3) & 1.4114 & 1.4263 & 1.4039 & \text{C11-C12-C17} & 120.4(2) & 120.14 & 118.94 \\ & \text{C22-C21} & 1.473(3) & - & - & - & - & \text{C21-C22-C22} & 120.0(2) & - & - \\ & \text{C12-C17} & 1.468(3) & 1.4790 & 1.4300 & 1.4548 & \text{C14-C13-C12} & 121.8(2) & 122.31 & 121.99 \\ & \text{C23-C24} & 1.378(4) & 1.3869 & 1.3726 & 1.3871 & \text{C15-C14-C13} & 119.4(2) & 119.89 & 119.45 \\ & \text{C24-C25} & 1.376(4) & - & - & - & & \text{C25-C24-C21} & 120.4(2) & - & - \\ & \text{C13-C14} & 1.378(4) & 1.4038 & 1.4202 & 1.4029 & \text{C16-C15-C14} & 120.5(2) & 120.29 & 121.17 \\ & \text{C25-C26} & 1.345(3) & - & - & - & & \text{C25-C24-C21} & 120.4(2) & - & - \\ & \text{C17-C18} & 1.350(3) & - & - & - & & \text{C25-C24-C21} & 121.8(2) & - & - \\ & \text{C17-C18} & 1.350(3) & - & - & - & & \text{C25-C24-C21} & 121.8(2) & - & - \\ & \text{C17-C18} & 1.495(3) & 1.502 & 1.5094 & - & & \text{N11-C17-C12} & 116.7(2) & 117.41 & 117.89 \\ & \text{C27-C28} & 1.500(3) & - & - & - & & & \text{N21-C27-C22} & 117.0(2) & - & - \\ & \text{N11-C17-C18} & 122.9(2) & 121.98 & 118.47 \\ & \text{C-C7} & 1.286(2) & 1.494 & 1.329 & & \text{C7-N-C9} & 121.5(2) & 122.9 & 126.6 \\ & \text{N-C9} & 1.406(2) & 1.458 & 1.454 & & \text{O-C1-C6} & 118.8(2) & 117.9 & 120.6 \\ & \text{N-C9} & 1.406(2) & 1.458 & 1.454 & & \text{O-C1-C6} & 119.8(2) & 117.9 & 116.8 \\ & \text{C2-C3} & 1.396(2) & 1.411 & 1.427 & & \text{C3-C2-C7} & 122.9(2) & 121.4 & 122.0 \\ & \text{C2-C4} & 1.378(3) & 1.406 & 1.439 & & \text{C6-C1-C2} & 117.1(2) & 117.8 & 118.0 \\ & \text{C1-C2} & 1.396(3) & 1.395 & 1.396 & & \text{C1-C1-C6} & 119.8(2) & 119.3 & 119.4 \\ & \text{C2-C3} & 1.396(2) & 1.411 & 1.427 & & \text{C3-C2} & 12$	N21-C29	1.454(3)	_	_	_	C26-C21-C22	119.4(2)	_	_
C21-C26 1.384(3) C23-C22-C21 117.2() C11-C16 1.381(3) 1.4066 1.4389 1.4038 C13-C12-C11 117.2() C11-C12 1.414(3) C23-C22-C27 123.0(2) C12-C12 1.414(3) C23-C22-C27 119.9(2) C12-C13 1.395(3) 1.4114 1.4263 1.4039 C11-C12-C17 120.4(2) 120.14 118.94 C22-C27 1.473(3) C24-C23-C22 122.0(2) C12-C17 1.468(3) 1.4790 1.4300 1.4548 C14-C13-C12 121.8(2) 122.31 121.99 C23-C24 1.378(4) C25-C24-C23 119.4(2) 120.14 118.94 C24-C25 1.375(4) 1.3869 1.3726 1.3871 C15-C14-C13 119.4(2) 120.37 121.37 C24-C25 1.375(4) 1.4013 1.4202 1.4029 C16-C15-C14 120.4(2) C15-C16 1.350(3) 1.8852 1.3705 1.3890 C15-C16-C11 121.8(2) C15-C16 1.350(3) 1.8852 1.3705 1.3890 C15-C16-C11 121.8(2) C17-C18 1.495(3) 1.5202 1.5094 - N11-C17-C12 116.7(2) 117.0(2) C17-C18 1.495(3) 1.5202 1.5094 - N11-C17-C12 116.7(2) 117.0(1) C17-C18 1.495(3) 1.5202 1.5094 - N11-C17-C12 117.0(2) 117.0 117.9 118.9 C1-C6 1.339(3) 1.406 1.439 C6-C1-C2 119.8(2) 119.7 116.8 C1-C2 1.444(2) 1.428 1.468 C3-C2-C1 117.1(2) 117.8 118.0 C1-C6 1.339(3) 1.406 1.439 C6-C1-C2 119.8(2) 119.3 119.4 C1-C6 1.336(3) 1.386 1.371 C6-C5-C4 120.0(2) 120.5 121.3 C1-C10 1.538(4) 1.400 1.401 N-C7-C2 117.1(2) 117.8 118.0 C1-C10 1.538(4) 1.400 1.401 N-C7-C2 119.9(2) 120.5 1	N11-C19	1.456(3)	1.4489	1.4481	1.4488	C16-C11-C12	119.8(2)	119.89	116.89
$\begin{array}{cccccccccccccccccccccccccccccccccccc$	C21-C26	1.384(3)	_	_	_	C23-C22-C21	117.2(2)	_	-
C21-C22   1.41(3)   -   -   -   C32-C27   123.0(2)   -   -     C11-C12   1.412(3)   1.4315   1.4673   1.4224   C13-C12-C17   123.0(2)   122.53   122.39     C22-C23   1.393(3)   1.4114   1.4263   1.4039   C11-C12-C17   120.4(2)   120.14   118.94     C22-C27   1.468(3)   1.4790   1.4300   1.4548   C14-C13-C12   121.8(2)   122.31   121.99     C23-C24   1.378(4)   -   -   -   C25-C24-C13   119.4(2)   119.89   119.45     C24-C25   1.376(4)   1.4013   1.4202   1.4029   C15-C14-C13   119.4(2)   -   -     C15-C16   1.350(3)   1.3812   1.3705   1.3890   C15-C16-C11   121.4(2)   120.29   121.17     C25-C26   1.350(3)   1.3822   1.3705   1.3890   C15-C16-C11   121.4(2)   120.77   121.73     C27-C28   1.5003   -   -   N11-C17-C12   11	C11-C16	1.381(3)	1.4066	1.4389	1.4038	C13-C12-C11	117.2(2)	117.34	118.77
$\begin{array}{cccccccccccccccccccccccccccccccccccc$	C21-C22	1.414(3)	_	_	_	C23-C22-C27	123.0(2)	_	_
$\begin{array}{cccccccccccccccccccccccccccccccccccc$	C11-C12	1.412(3)	1.4315	1.4673	1.4224	C13-C12-C17	122.4(2)	122.53	122.29
$\begin{array}{cccccccccccccccccccccccccccccccccccc$	C22-C23	1.393(3)	_	_	_	C21-C22-C27	119.9(2)	_	_
$\begin{array}{cccccccccccccccccccccccccccccccccccc$	C12-C13	1.395(3)	1.4114	1.4263	1.4039	C11-C12-C17	120.4(2)	120.14	118.94
$\begin{array}{cccccccccccccccccccccccccccccccccccc$	C22-C27	1.473(3)	_	_	_	C24-C23-C22	122.0(2)	_	_
$\begin{array}{cccccccccccccccccccccccccccccccccccc$	C12-C17	1.468(3)	1.4790	1.4300	1.4548	C14-C13-C12	121.8(2)	122.31	121.99
$\begin{array}{cccccccccccccccccccccccccccccccccccc$	C23-C24	1.378(4)	_	_	_	C25-C24-C23	119.3(2)	_	_
$\begin{array}{cccccccccccccccccccccccccccccccccccc$	C13-C14	1.378(4)	1.3869	1.3726	1.3871	C15-C14-C13	119.4(2)	119.89	119.45
$\begin{array}{cccccccccccccccccccccccccccccccccccc$	C24-C25	1.376(4)	_	_	_	C26-C25-C24	120.4(2)	_	_
$\begin{array}{cccccccccccccccccccccccccccccccccccc$	C14-C15	1.375(4)	1.4013	1.4202	1.4029	C16-C15-C14	120.5(2)	120.29	121.17
$\begin{array}{cccccccccccccccccccccccccccccccccccc$	C25-C26	1.345(3)	_	_	_	C25-C26-C21	121.8(2)	_	_
$\begin{array}{cccccccccccccccccccccccccccccccccccc$	C15-C16	1.350(3)	1.3852	1.3705	1.3890	C15-C16-C11	121.4(2)	120.77	121.73
$\begin{array}{cccccccccccccccccccccccccccccccccccc$	C27-C28	1.500(3)	_	_	_	N21-C27-C22	117.0(2)	_	_
$\begin{array}{cccccccccccccccccccccccccccccccccccc$	C17-C18	1.495(3)	1.5202	1.5094	_	N11-C17-C12	116.7(2)	117.41	117.89
$\begin{array}{c c c c c c c c c c c c c c c c c c c $						N21-C27-C28	123.3(2)	_	_
$\begin{array}{c ccccccccccccccccccccccccccccccccccc$						N11-C17-C18	122.9(2)	121.98	118.74
$ \begin{array}{cccccccccccccccccccccccccccccccccccc$	2-(N-benzyl-a	<i>x</i> -iminoethyl)-ph	enol (II)						
$\begin{array}{cccccccccccccccccccccccccccccccccccc$	N–C7	1.286(2)	1.294	1.329		C7-N-C9	121.5(2)	122.9	126.6
$\begin{array}{cccccccccccccccccccccccccccccccccccc$	N-C9	1.460(2)	1.458	1.454		O-C1-C6	118.5(2)	117.9	120.6
$\begin{array}{cccccccccccccccccccccccccccccccccccc$	O-C1	1.335(2)	1.338	1.276		O-C1-C2	121.7(2)	122.4	122.8
$\begin{array}{cccccccccccccccccccccccccccccccccccc$	C1-C6	1.393(3)	1.406	1.439		C6-C1-C2	119.8(2)	119.7	116.8
$\begin{array}{cccccccccccccccccccccccccccccccccccc$	C1-C2	1.414(2)	1.428	1.468		C3-C2-C1	117.1(2)	117.9	118.9
$\begin{array}{cccccccccccccccccccccccccccccccccccc$	C2-C3	1.396(2)	1.411	1.427		C3-C2-C7	122.2(2)	121.4	122.0
$\begin{array}{cccccccccccccccccccccccccccccccccccc$	C2-C7	1.471(2)	1.476	1.427		C1-C2-C7	120.7(2)	120.7	119.0
$\begin{array}{cccccccccccccccccccccccccccccccccccc$	C3-C4	1.365(3)	1.387	1.372		C4-C3-C2	122.4(2)	120.0	121.9
$\begin{array}{cccccccccccccccccccccccccccccccccccc$	C4-C5	1.375(3)	1.402	1.421		C3-C4-C5	119.6(2)	119.3	119.4
$\begin{array}{cccccccccccccccccccccccccccccccccccc$	C5-C6	1.367(3)	1.386	1.371		C6-C5-C4	120.4(2)	120.5	121.3
$\begin{array}{cccccccccccccccccccccccccccccccccccc$	C7–C8	1.499(2)	1.516	1.507		C5-C6-C1	120.7(2)	120.7	121.7
$\begin{array}{cccccccccccccccccccccccccccccccccccc$	C9-C10	1.502(3)	1.518	1.524		N-C7-C2	117.1(2)	117.8	118.0
$\begin{array}{cccccccccccccccccccccccccccccccccccc$	C10-C15	1.384(3)	1.400	1.401		N-C7-C8	123.1(2)	123.9	118.2
$\begin{array}{cccccccccccccccccccccccccccccccccccc$	C10-C11	1.386(3)	1.399	1.399		C2-C7-C8	119.9(2)	118.3	123.8
$\begin{array}{cccccccccccccccccccccccccccccccccccc$	C11-C12	1.379(3)	1.395	1.395		N-C9-C10	111.0(2)	112.1	114.0
$\begin{array}{cccccccccccccccccccccccccccccccccccc$	C12-C13	1.376(3)	1.395	1.396		C15-C10-C11	118.1(2)	118.8	119.1
$\begin{array}{cccccccccccccccccccccccccccccccccccc$	C13-C14	1.374(3)	1.396	1.395		C15-C10-C9	121.7(2)	121.3	120.8
C12-C11-C10 121.0(2) 120.8 120.3 C13-C12-C11 120.0(2) 120.0 120.3 C14-C13-C12 119.4(2) 119.6 119.7 C15-C14-C13 120.7(2) 120.3 120.0 C14-C15-C10 120.9(2) 120.5 120.6	C14-C15	1.371(3)	1.395	1.396		C11-C10-C9	120.3(2)	119.9	120.0
C13-C12-C11 120.0(2) 120.0 120.3 C14-C13-C12 119.4(2) 119.6 119.7 C15-C14-C13 120.7(2) 120.3 120.0 C14-C15-C10 120.9(2) 120.5 120.6						C12-C11-C10	121.0(2)	120.8	120.3
C14-C13-C12 119.4(2) 119.6 119.7 C15-C14-C13 120.7(2) 120.3 120.0 C14-C15-C10 120.9(2) 120.5 120.6						C13-C12-C11	120.0(2)	120.0	120.3
C15-C14-C13 120.7(2) 120.3 120.0 C14-C15-C10 120.9(2) 120.5 120.6						C14-C13-C12	119.4(2)	119.6	119.7
C14–C15–C10 120.9(2) 120.5 120.6						C15-C14-C13	120.7(2)	120.3	120.0
						C14-C15-C10	120.9(2)	120.5	120.6

Table 5 (continued)

Bond lengths /Å					Valence angles/°			
C	X-ray	Calculated		$IV^a$	C	X-ray	Calculated	
Bonds	HB	HB	PT	HB	Angles	HB	HB	РТ
2-(N-benzyl- $\alpha$ -in	ninopropyl)-phe	enol (III)						
O-C1	1.334(2)	1.338	1.276		C7-N-C10	124.3(2)	124.7	127.3
N-C7	1.288(2)	1.296	1.329		O-C1-C6	118.8(2)	117.8	120.6
N-C10	1.463(2)	1.452	1455		O-C1-C2	121.5(1)	122.3	122.7
C1-C6	1.390(2)	1.406	1.439		C6-C1-C2	119.7(2)	119.9	116.7
C1-C2	1.415(2)	1.430	1.466		C3-C2-C1	117.4(2)	117.5	119.1
C2-C3	1.395(2)	1.411	1.426		C3-C2-C7	121.9(1)	122.0	121.7
C2-C7	1.471(2)	1.479	1.427		C1-C2-C7	120.7(1)	120.5	119.3
C3-C4	1.371(3)	1.387	1.373		C4-C3-C2	122.2(2)	122.2	121.8
C4-C5	1.379(3)	1.402	1.421		C3-C4-C5	119.7(2)	119.4	119.4
C5-C6	1.370(3)	1.386	1.371		C6-C5-C4	120.0(2)	120.4	121.3
C7-C8	1.503(2)	1.521	1.513		C5-C6-C1	121.0(2)	120.7	121.7
C8–C9	1.526(2)	1.541	1.541		N-C7-C2	117.0(1)	117.1	117.8
C10-C11	1.506(2)	1.526	1.524		N-C7-C8	124.3(1)	123.9	119.4
C11-C12	1.372(2)	1.400	1.399		C2-C7-C8	118.6(1)	119.1	122.8
C11-C16	1.374(2)	1.401	1.400		C7-C8-C9	111.4(1)	112.3	112.5
C13-C14	1.368(3)	1.395	1.395		N-C10-C11	110.8(1)	112.6	114.0
C13-C12	1.396(3)	1.396	1.396		C12-C11-C16	117.9(2)	118.8	119.1
C14-C15	1.348(3)	1.396	1.396		C12-C11-C10	121.5(2)	121.8	120.0
C15-C16	1.369(3)	1.395	1.395		C16-C11-C10	120.6(2)	119.3	120.9
					C14-C13-C12	120.0(2)	120.4	120.0
					C11-C12-C13	120.1(2)	120.4	120.9
					C15-C14-C13	120.2(2)	119.5	119.7
					C14-C15-C16	119.7(2)	120.1	120.3
					C15-C16-C11	122.1(2)	120.8	120.3

<sup>b</sup> Calculated at the same basis set for 2-(N-methylimino)-phenol (IV).

<sup>a</sup> Parameters for atoms directly involved into hydrogen bond formation are given in Table 7.

effects, which for example gives complete equalization of all bonds in benzene ring.

Despite this, an analysis of the geometry of the chelate ring shows existence of very strong intramolecular hydrogen bond, with predominance of molecular form (Table 7).

Chelate rings are planar (Table 6) and coplanar with the phenol ring; torsion angles characterizing deviations from the last plane are less than  $2^{\circ}$ . The C8 atom is also practically located in the phenol ring plane (torsion angle  $< 3^{\circ}$ ).

#### 4.2. Analysis of steric effects

Detailed analysis of the structure of **I** compounds shows that the intramolecular steric repulsions are the main factor, which is responsible for shortening of the hydrogen bridge.

These repulsions can be characterized by

shortening of non-bonded distances with respect to appropriate sum of the van der Waals radii. Following van der Waals radii were applied, after Bondi [14]:  $R_{\rm C} = 1.70$  Å,  $R_{\rm N} = 1.55$  Å,  $R_{\rm H} = 1.20$  Å,  $R_{\rm O} =$ 1.52 Å. Such an analysis cannot be performed for atoms 1...3 forming the 1-2-3 angle, called geminal interactions. The angle between 1...3 axis and 1-2, 2-3 bonds are less than  $90^{\circ}$  and because of non-spheric atom-atom potentials a special van der Waals radii should be established for such directions. However, this type of procedure would be very arbitrary. Among non-geminal interactions the C18-C13 and C18-C19 distances equal to 2.975 and 2.895 Å, respectively shortened by 0.425 and 0.505 Å with respect to an appropriate sum of the van der Waals radii (3.4 Å) were found.

Other distances between C18 atom (and hydrogen atoms attached to it) and C13 and C19 atoms (and hydrogen atoms attached to it) are shortened. It A. Filarowski et al. / Journal of Molecular Structure 484 (1999) 75-89



Fig. 4. Molecular conformers of 2-(*N*-methyl- $\alpha$ -iminoethyl)-phenol (I) obtained in ab initio B3LYP/6-31G\*\* calculations.

generates a strong strain within the molecules, which is partially released by change of some valence angles. The situation is illustrated in Scheme 3, where valence angles in **I**, **II** and **III** are compared with related angles in compounds (IV-VI) with C– C(H)=N moiety.

Compound **IV** is a liquid and its calculated structure (not experimental) (ab initio B3LYP/6-31 G\*\* level) is shown.

The structural data for **VI** are taken from [15]. Compound **I** can be compared with **IV** and **V** while **II** and **III** with **VI** as all the last compounds contain the *N*-benzyl group, while the **I**, **IV** and **V** contain the *N*-methyl group.

One can observe that within the group of compounds containing *N*-methyl substituent as well as in the group with *N*-benzyl substituent the angles  $C(H_3)-C-C$  are lager than related H-C-C angles in **IV**-VI compounds. The steric repulsion also leads to a strong increase of  $C(H_3)-C=N$  and C=N-C angles in **I**-III compounds. Decrease of  $H\cdots N-CH_3$  angle and especially pronounced decrease of N=C-C angle.

Despite this strong deformation of valence angles, pronounced shortening of distances between CH<sub>3</sub> group and neighbour C and H atoms were observed in experimental structures of **I**, **II** and **III** compounds.

Total steric interaction between substituents can be characterized by the energy of non-bonded (but not geminal) interactions of C-substituted methyl (or ethyl) groups with C3 and C9 atoms as well as H atoms attached to C3 and C9 atoms (labelling as in Fig. 2). Such calculations were also performed for V and VI compounds, which can be assumed as reference structures. Parameters of the potential from MM3 force field were applied [16].

Calculated values of strain energy are 3.982 kJ/mol in **I**, 4.147 kJ/mol in **II** and 4.821 kJ/mol in **III**, which can be compared with the results of analogous calculations for **V** and **VI** compounds; 1.737 and 1.483 kJ/ mol, respectively. The results clearly distinguish between compounds **I**–**III** type, and **IV**–**VI** type. (On deciding appears the introducing of a substituent at  $C(sp^2)$  atom in C–C(H)=N group.) Neither did the replacement of *N*-methyl by *N*-benzyl group nor the replacement of methyl substituent by the ethyl (Scheme 3) give any radical increase of steric repulsion.

The above mentioned effects cause a decrease in the O····N distance and "external" strengthening of the hydrogen bonds where some adaptation of lone electron pair direction also takes place (see Scheme 4).

In order to estimate this effect one can calculate values of angles  $(\vartheta, \psi)$  which makes the lone pair direction (assumed to lay on bisector of C=N-C angle) with the N···O line, which is an "ideal" direction of lone electron pair in linear complexes. Calculated values of  $\psi$  are 24.8°, 25.9° and 24.9°



![](_page_8_Figure_2.jpeg)

for **I**, **II** and **III**, respectively while for the compounds with less steric repulsions  $\varphi$  values are 32.3°, 32.2° and 31.5° for **IV**, **V** and **VI**, respectively. Such differences in direction of lone electron pair of N-atoms interacting with the hydrogen bond can be very important for the

properties of hydrogen bond as it was shown by Scheiner [17].

#### 4.3. Hydrogen bonding

Detailed description of the hydrogen bond studied

![](_page_8_Figure_7.jpeg)

Scheme 4.

Table 6

Selected torsion angles (°) for 2-(*N*-methyl- $\alpha$ -iminoethyl)-phenol (I), 2-(*N*-benzyl- $\alpha$ -iminoethyl)-phenol (II) and 2-(*N*-benzyl- $\alpha$ -iminopropyl)-phenol (III) with esd's in parentheses

I		II		III	
O11-C11-C12-C13	180.0(2)	0-C1-C2-C3	179.5(2)	0-C1-C2-C3	-179.30(14)
C16-C11-C12-C13	0.2(3)	C6-C1-C2-C3	-0.4(3)	C6-C1-C2-C3	0.7(2)
O11-C11-C12-C17	-0.5(3)	O-C1-C2-C7	-1.0(3)	O-C1-C2-C7	-1.0(2)
C16-C11-C12-C17	179.7(2)	C6-C1-C2-C7	179.1(2)	C6-C1-C2-C7	178.99(14)
C11-C12-C13-C14	-0.1(3)	C1-C2-C3-C4	0.2(4)	C1-C2-C3-C4	0.1(2)
C12-C13-C14-C15	0.2(3)	C7-C2-C3-C4	-179.2(2)	C7-C2-C3-C4	-178.2(2)
C13-C14-C15-C16	-0.3(3)	C2-C3-C4-C5	0.7(4)	C2-C3-C4-C5	-0.8(3)
C14-C15-C16-C11	0.4(3)	C3-C4-C5-C6	-1.5(4)	C3-C4-C5-C6	0.6(3)
C19-N11-C17-C12	-179.6(2)	C4-C5-C6-C1	1.4(4)	C10-N-C7-C2	-179.01(13)
C19-N11-C17-C18	0.5(3)	O-C1-C6-C5	179.7(2)	C10-N-C7-C8	-1.6(2)
C13-C12-C17-N11	178.3(2)	C9-N-C7-C2	-179.9(2)	C3-C2-C7-N	178.16(15)
C11-C12-C17-N11	-1.2(2)	C9-N-C7-C8	0.5(4)	C1-C2-C7-N	-0.1(2)
C13-C12-C17-C18	-1.8(3)	C3-C2-C7-N	-179.5(2)	C3-C2-C7-C8	0.6(2)
O21-C21-C22-C23	-180.0(2)	C1-C2-C7-N	1.1(3)	C1-C2-C7-C8	-177.66(13)
C21-C22-C27-C28	178.8(2)	C1-C2-C7-C8	-179.2(2)	N-C7-C8-C9	-96.5(2)
		C7-N-C9-C10	179.4(2)	C2-C7-C8-C9	80.9(2)
		N-C9-C10 C15	-52.4(3)	C7-N-C10-C11	130.6(2)
		N-C9-C10 C11	129.4(2)	N-C10-C11-C12	111.2(2)
		C15-C10-C11-C12	-1.5(3)	N-C10-C11-C16	-69.0(2)
		C9-C10-C11-C12	176.8(2)	C16-C11-C12-C13	-0.7(3)
		C10-C11-C12-C13	1.3(4)	C10-C11-C12-C13	179.2(2)
		C11-C12-C13-C14	-0.1(4)	C14-C13-C12-C11	0.6(3)
		C12-C13-C14-C15	-0.9(4)	C12-C13-C14-C15	0.0(3)
		C13-C14-C15-C10	0.7(4)	C12-C11-C16-C15	0.3(3)
		C9-C10-C15-C14	-177.8(2)	C10-C11-C16-C15	-179.6(2)

in **I–III** compound in comparison to two structures with lower steric repulsion (**V** and **VI**) is given in Table 7.

In one of the two non-equivalent molecules in the unit cell of **I**, very short hydrogen bond was found  $(d_N \cdots_O = 2.459(3) \text{ Å})$ , shortest of all the known O–H···N hydrogen bonds in the literature.

The proton is localized near the central position  $d_0 \cdots_{\rm H} = 1.20$  Å,  $d_{\rm H} \cdots_{\rm N} = 1.32(3)$  Å. The OHN angle is 153° larger than in V (142.5°). The COH angle strongly diminished from 111° in V to 102° in compound I. This hydrogen bond can be compared only with intramolecular O–H…N hydrogen bond in imazaryl [18], where O…H-1.16(2) Å, H…N-1.32(2) Å and O…N-2.465(2) Å distances were found. It was almost linear ( $\alpha$ (OHN) = 170(1)°) hydrogen bond forming seven membered ring, where <sup>1</sup>H NMR shift was found [18] to be 19 ppm, independent of concentration, solvent and temperature.

In the second molecule more asymmetric proton

localization was found to be  $d_{\rm O-H} = 1.15(4)$  Å,  $d_{\rm H} \cdots_{\rm N} = 1.38(2)$  Å while the length of the hydrogen bond is almost the same as 2.460(3) Å. The 2.46–2.47 Å distance seems to be the critical one (the shortest) in O–H…N type of hydrogen bridges.

Position of proton in **II** and **III** is more on the side of oxygen and lengths of hydrogen bond are higher than in **I**, which results from the decrease of basicity while one replaces the *N*-methyl group with *N*-benzyl.

Nevertheless the hydrogen bonds in **II** and **III** with N···O distances less than 2.5 Å, belong to the shortest known hydrogen bonds of O–H···N type. In compounds **V** and **VI** the hydrogen bonds are evidently longer, OH bonds are shorter than 1 Å and H···N distances are larger than 1.7 Å, while in **I**–**III** they are less than 1.5 Å. Hydrogen bond becomes more linear; the  $\alpha$ (OHN) angle is 10° larger in **I**–**III** than in **V**, **VI**. The strengthening of the hydrogen bond also gives a very characteristic [19] decrease of COH angle-from 110.5(3)° in **V**, **VI** to 103(1)° in **I**–**III**.

	Form of HB	ОН	ON	HN	$\alpha$ (OHN)	$\beta$ (COH)	$\gamma$ (C7NH)	δ (C9NH)	
Meas	ured X-ray								
Ι	O…H−N	1.20(4)	2.459(3)	1.32(3)	153(1)	102(1)	106(1)	130(1)	
		1.15(4)	2.460(3)	1.38(2)	153(1)	103(2)	106(1)	131(1)	
II	O-H…N	1.10(3)	2.497(3)	1.47(3)	152(3)	103.1(12)	104.8(9)	133.7(9)	
III	$O-H\cdots N$	1.07(3)	2.494(3)	1.48(3)	155(1)	102(1)	104(1)	132(1)	
V	O-H…N	0.977	2.559	1.715	142.5	110.8	101.5	139.9	
VI	O-H···N	0.990	2.587	1.730	142.6	110.4	102.4	138.7	
Calcu	lated ab initio B3I	YP 6-31G**							$\Delta E^{\ a}$
Ι	O…H−N	1.503	2.484	1.074	148.7	101.5	110.3	121.8	2.77
	$O-H\cdots N$	1.014	2.526	1.595	150.2	105.3	104.4	132.1	0.00
II	O…H−N	1.521	2.490	1.067	147.8	101.5	110.5	122.2	2.76
	$O-H\cdots N$	1.009	2.548	1.627	149.4	105.7	103.8	133.3	0.00
III	O···H−N	1.520	2.492	1.068	148.2	101.4	110.4	121.9	2.29
	O-H…N	1.015	2.525	1.591	150.6	105.0	104.4	130.8	0.00
IV	O…H−N	1.636	2.551	1.053	142.1	103.7	110.7	124.1	5.00
	$O-H\cdots N$	1.000	2.617	1.713	148.4	107.0	99.6	141.1	0.00
V	O…H−N	1.647	2.664	1.051	141.7	103.6	111.0	123.8	4.57
	$O-H\cdots N$	1.000	2.377	1.712	148.17	107.0	99.9	140.7	0.00
VI	O…H−N	1.631	2.546	1.053	142.2	103.6	110.7	123.9	4.87
	$O-H\cdots N$	0.999	2.619	1.718	148.0	107.2	99.7	141.0	0.00

Hydrogen bond parameters and selected bond lengths (Å) and angles (°), with esd's in parentheses, in pseudoaromatic chelate rings

<sup>a</sup>  $\Delta E$  (kcal/mol)-relative energy of states for particular compounds. Energy of molecular forms was assumed as 0.

No real strengthening of the hydrogen bonding is observed in **III** in comparison to **II** resulting from the  $CH_3$  group replacement by  $C_2H_5$ , which should be the case if electronic and not steric effects decide about strengthening of hydrogen bond in **I–III**.

Table 7

Table 7 also contains the results of ab initio B3LYP-calculations for both molecular and zwitter ionic forms of intramolecular hydrogen bonding.

An interesting feature appears after calculations– two conformers resulting from the N–CH<sub>3</sub> group rotation were found (Fig. 4). One conformation is as in the experimental structure (Fig. 4a). The second one is characteristic of direct contact between four H atoms of both CH<sub>3</sub> groups (Fig. 4b). It appears that the **b** conformers are more stable, for example in **I**, by 0.435 kcal/mol in molecular form and 0.626 kcal/mol in zwitterionic one. It can be probably explained by very small shortening of the hydrogen bond while steric repulsion between methyl groups increases. Crystal packing conditions in the solid state are however in favour of conformers of **a** type.

In the last column of Table 7 are presented the differences in calculated energy of molecular (lower) and zwitterionic (PT) states. As discussed

earlier one can distinguish two classes of compounds. The first (**I–III** compounds) with large steric effects and short O···N distance reveal about two times lower difference in energy between molecular and PT state than in the second class (**IV–VI** compounds). Shortening of the hydrogen bridges strongly modifies the potential for the proton transfer making the PT form easily accessible. It can give pronounced consequences in thermochromic properties of these systems as well as its luminescence. The studies are in progress [20].

Stronger hydrogen bonds were observed in the experimental structures of **I–III** compounds than in the calculated structures. Crystal packing forces probably increase the intramolecular steric repulsion.

Strengthening of hydrogen bond in **I–III** compound give remarkable spectroscopic effects. Observed effects can be explained from the point of view of the steric interaction and the change of basicity upon replacement of *N*-methyl substituent by *N*-benzyl one;  $pK_a$  values of base part of these intramolecular complexes decrease more than 1 unit of  $pK_a$  ( $pK_a$  of methyl amine is 10.7 while benzylamine 9.4 [21]).

![](_page_11_Figure_1.jpeg)

Fig. 5. FT-IR spectra of 2-(N-methyl- $\alpha$ -iminoethyl)-phenol (I) and 2-(N-benzyl- $\alpha$ -iminoethyl)-phenol (II) in CCl<sub>4</sub> solutions.

The differences in IR spectra in the  $\nu$ (OH) absorption range between I and II (Fig. 5) demonstrate the last effect. No free  $\nu$ (OH) bands are observed. Intramolecular hydrogen bonds are stable in CCl<sub>4</sub> solutions and the spectra do not change upon dilution.

Fig. 6 shows the effect of increase of steric

repulsion in compounds with *N*-methyl substituent. In Fig. 7 are compared spectra of **VI**, **II** and **III**. All of these compounds contain the *N*-benzyl group.

As in Fig. 6 the effects of the increase of steric repulsion when going from compounds with N=C(H)-Cgroup through compounds with  $N=C(CH_3)-C$  group

![](_page_11_Figure_7.jpeg)

Fig. 6. FT-IR spectra of 2-(*N*-methyl- $\alpha$ -iminoethyl)-phenol (I), 2-(*N*-methylimino)-phenol (IV) and 2-(*N*-methyl- $\alpha$ -iminopropyl)-phenol (VII) in CCl4 solutions.

![](_page_12_Figure_1.jpeg)

Fig. 7. FT-IR spectra of  $2-(N-\text{benzyl}-\alpha-\text{iminoethyl})$ -phenol (II),  $2-(N-\text{benzyl}-\alpha-\text{iminopropyl})$ -phenol (III) and 2-(N-benzylimino)-phenol (VI) in CCl<sub>4</sub> solutions.

to compounds with  $N=C(C_2H_5)-C$  group are demonstrated.

A strong increase of  $\Delta \nu$ (OH) is observed between **VI** and **II** compounds, while an extension of steric repulsion by replacement of methyl group by the ethyl group is rather small. The same conclusions follow from comparison of compounds with N–CH<sub>3</sub> group (Fig. 6). Increase of steric repulsion is mostly pronounced when N=C(H)– C group is replaced by N=C(CH<sub>3</sub>)– C group.

It agrees with the structural effects, where a strong shortening of hydrogen bridge is observed upon introduction of methyl substituent and while passing from the compound with methyl to the compound with ethyl substituent do not modify the structure seriously.

Very special properties of I can be mentioned. In this compound with the strongest O–H…N hydrogen bridge, very labile potential for the proton transfer was detected. Decrease of the temperature causes a strong modification of IR spectra in  $\nu$ (OH) absorption range (Fig. 8).

Gradual decrease of the absorption above  $2500 \text{ cm}^{-1}$  and strong increase of the absorption below  $1700 \text{ cm}^{-1}$  is observed. Below 100 K spectrum it can be classified as a spectrum with continuous absorption, characteristic for very short hydrogen

bonds with large dynamics of proton movement within the  $O \cdots H \cdots N$  bridge.

Such strong temperature modifications of the potential for the proton transfer are interesting for further more extensive structural and spectroscopic studies.

#### 5. Conclusions

A group of three ortho hydroxy Schiff bases with methyl and ethyl substituents in the N=C(H)– C unit were synthesised and its molecular structure by crystallographic method and ab initio calculations was determined. Very strong strengthening of the intramolecular O–H···N hydrogen bridge was achieved owing to steric shortening of the hydrogen bridge. One of the compounds (I) contains the shortest O– H···N hydrogen bridge O···N distance equal to 2.46 Å known so far in the literature.

Two others also belong to the very short hydrogen bridges with O···N distance less than 2.5 Å. Detailed analysis of intramolecular steric interactions was performed and structure modifications resulting from these interactions were specified. Replacement of N– CH<sub>3</sub> group by *N*-benzyl moiety does not change pronouncedly the steric effects, but decreases the

![](_page_13_Figure_2.jpeg)

Absorbance

![](_page_13_Figure_3.jpeg)

hydrogen bond strength owing to change of  $pK_a$  of the basic part of the hydrogen bridge.

Very large liability of the potential for the proton movement within the hydrogen bridge was demonstrated in temperature studies of IR spectra. Radical decrease of the energy of PT forms of **I–III** compounds was stated in comparison to related compounds without alkyl substituents in the central part of a molecule. Steric modification of the potential for the proton movement discussed in this paper, can be a source of the compounds with desirable physicochemical properties, including potential practical applications resulting from thermochromic and photochromic properties of Schiff bases.

### Acknowledgements

Authors acknowledge the financial support of KBN grant No 3TO9A04210. We would also like to acknowledge Mr. Jerzy Jański for the help in performing quantum mechanical calculations.

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