

Strengthening of the intramolecular O...H...N hydrogen bond in 2-(N-benzyl- α -iminoethyl)-naphthol as a result of steric repulsion

A Mandal, A Koll¹, A Filarowski¹ & S Mukherjee*[†]

Department of Physical Chemistry, Indian Association for the Cultivation of Science, Calcutta 700 032, India

¹Faculty of Chemistry, University of Wroclaw, Poland

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One new *ortho*-hydroxy Schiff base, 2-(N-benzyl- α -iminoethyl)-naphthol (BEIN) in which the hydrogen atom in the C(H)=N group is replaced by a methyl substituent, is synthesized. The crystal structure is determined and *ab initio* calculations with B3LYP/6-31G** basis sets are performed. The O...N distance found in the O-H...N hydrogen bond turns out to be quite short and is equal to 2.499 Å. This shortening is due to the steric repulsion of methyl substituent group and results in strengthening of the hydrogen bond.

Large number of Schiff bases form intramolecular hydrogen bonds. They reveal some interesting properties like thermochromism and photochromism¹ which can be explained by photoinduced proton transfer reaction. Such behaviour suggests the possibility of using these compounds as elements for constructing optical switches or optical memory devices². This behaviour is strongly related to the double fluorescence in salicylanilide³. Grabowska *et al.*^{4,5} have studied the emission properties of Schiff bases with the aim of establishing the structure of the basic molecular units responsible for double fluorescence. They have found that 2-(N-methyliminophenyl) phenol is such a unit. However, some questions like what will be the structure of the state after proton transfer, whether it is zwitterionic or keto form remain open. In some earlier studies on the structure of Schiff bases with O-H...N intramolecular hydrogen bond about 20% keto resonance form was found while in the proton transferred (O...H-N) form the amount of keto resonance form was estimated to be about 50%. Strong coupling between chelate and phenyl ring leads to an increase in the strength of hydrogen bond and lowering of the energy of proton transferred state^{6,7}. Crystallographic structures of numerous derivatives for the condensation products of salicylaldehyde and anilines have been determined and analyzed⁸. Double fluorescence is observed in such compounds. In this work we focuss on X-ray studies and *ab initio* calculations on a newly synthesized Schiff

base, 2-(N-benzyl- α -iminoethyl)-naphthol (BEIN). The *ab initio* calculations for the gas phase at the level of B3LYP/6-31G** predicted that the proton transferred state is located 4.7 kcal mol⁻¹ above the molecular O-H...N state in BEIN. However, in the condensed phase this value could be different. In this Schiff base BEIN, the H-atom in the C-C(H)=N group is replaced by methyl group which introduces perturbations to intramolecular hydrogen bonds and modifies the potential of the proton transfer. Some strengthening of the hydrogen bond by this substituent is expected due to the inductive influence on the basic centre of the hydrogen bond. The steric interaction of methyl group, which pushes the centre of basicity in the direction of OH group, decreases the O...N distance⁹. Opposite effect can also be expected if the alkyl group makes the chelate ring less planar due to the steric repulsion.

The molecular structure of BEIN is determined by X-ray crystallography and *ab initio* B3LYP/6-31G** calculations.

Materials and Methods

Schiff base, BEIN was synthesized from a stoichiometric mixture of the corresponding salicylaldehyde and methylamine in methanol with standard procedure^{10,11}. The salicylaldehyde and methylamine are liquids which undergo self-condensation to the solid product. The solid product was then recrystallized from methanol, dried before use and then studied by X-ray diffraction at room temperature (293K). Summaries of the collected data are shown in Table 1.

[†]Fax (91)33473-2805; E-mail: pscm@mahendra.iacs.res.in

Table 1—Crystal data and structure refinement for BEIN

Compound	BEIN
Empirical formula	C ₁₉ H ₁₇ NO
Formula weight	275.34
Temperature	293 K
Wavelength	1.54180
Crystal system	Monoclinic
Space group	p2(1)/n
Unit cell dimensions	a=10.238 (2) Å b=8.162 (2) Å c=17.837 (4) Å β=103.78° (3)
Volume	1447.6 (6) Å ³
Cell measurement ref. number	25
Cell measurement 2theta range	26.0≤38.0 deg.
Density	1.263 mg/m ³
Absorption coefficient	6.07 cm ⁻¹
F (0 0 0)	584
Crystal size	0.20X0.20X0.20 mm
Data collection method	Omega/2theta scan
2theta range for data collection	8.0 to 161.0 deg.
No. of standard ref. and interval	3 (100 ref)
Index ranges	-13≤h≤12, 0≤k≤9, 0≤l≤22
Reflections collected	2661
Refinement method	Full-matrix least-square on F ²
Data [I>2sigma (I)]/parameters	1542/196
Goodness of fit on F ²	1.009
Final R indices [I.2sigma (I)]	R1=0.0447, wR2=0.1397
R indices (all data)	R1=0.0843, wR2=0.1532
Extinction coefficient	0.0068 (8)
Largest diff. Peak and hole	0.188 and -0.158 e Å ⁻³

Anisotropic thermal parameters for non-hydrogen atoms are applied¹². By means of gas chromatography HP 5890 II combined with mass spectrometer HP 5971 A, BEIN was shown to be 99% pure. Atomic coordinates, isotropic and anisotropic displacement parameters are displayed in Tables 2-4.

Results and Discussion

The crystallographic studies of intramolecular hydrogen bond in *ortho*-hydroxy Schiff base i.e. anils of salicylaldehyde (BEIN) have been performed. Molecular structural parameters of BEIN determined by X-ray crystallography and *ab initio* (B3LYP/6-31G**) calculations are shown in Tables (1-5). Atoms

Table 2—Fractional atomic coordinates and equivalent isotropic displacement parameters for BEIN

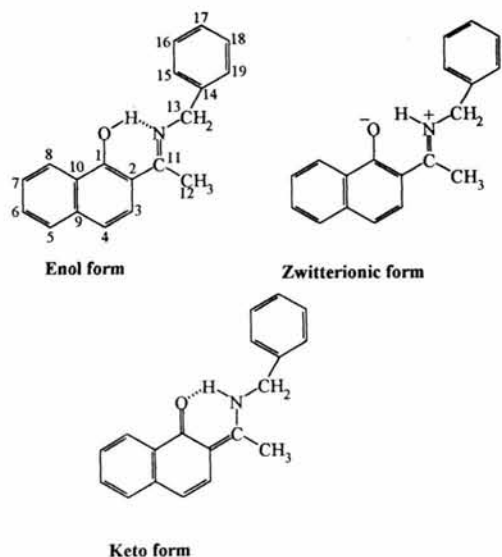
	X	Y	Z	U(eq)
O	0.5272(1)	0.2760(2)	0.1405(1)	0.0578(4)
N	0.3456(2)	0.1460(2)	0.0396(1)	0.0523(4)
C(1)	0.5836(2)	0.3181(2)	0.0868(1)	0.0466(4)
C(2)	0.5294(2)	0.2771(2)	0.0076(1)	0.0453(4)
C(3)	0.5985(2)	0.3322(3)	-0.0483(1)	0.0535(5)
C(4)	0.7135(2)	0.4178(3)	-0.0299(1)	0.0567(5)
C(5)	0.8925(2)	0.5515(3)	0.0707(2)	0.0645(6)
C(6)	0.9446(3)	0.5931(3)	0.1459(2)	0.0784(7)
C(7)	0.8805(2)	0.5440(3)	0.2027(1)	0.0716(7)
C(8)	0.7644(2)	0.4557(3)	0.1833(1)	0.0594(6)
C(9)	0.7727(2)	0.4597(2)	0.0485(1)	0.0521(5)
C(10)	0.7084(2)	0.4105(2)	0.1063(1)	0.0486(5)
C(11)	0.4077(2)	0.1847(2)	-0.0140(1)	0.0475(5)
C(12)	0.3504(2)	0.1311(3)	-0.0956(1)	0.0582(6)
C(13)	0.2196(2)	0.0555(3)	0.0280(1)	0.0583(5)
C(14)	0.1734(2)	0.0457(3)	0.1020(1)	0.0539(5)
C(15)	0.0566(2)	0.1216(3)	0.1084(2)	0.0676(6)
C(16)	0.0117(3)	0.1077(4)	0.1750(2)	0.0803(8)
C(17)	0.0828(3)	0.0182(3)	0.2362(2)	0.0777(8)
C(18)	0.2010(3)	-0.0562(3)	0.2307(1)	0.0757(7)
C(19)	0.2449(2)	-0.0428(3)	0.1641(1)	0.0684(6)

labeling system and molecular structure of BEIN are demonstrated in Fig. 1. Final atomic coordinates are given in Tables 2, 3 and 4. There are two non-equivalent molecules in the basic crystal unit of BEIN. Differences between related parameters are on average less than the experimental σ values and average parameter values for these two molecules. Analysis of the bond lengths indicates the presence of intramolecular hydrogen bonds in the normal enol form. Among all the bonds shown in keto resonance structure as double bonds (Fig. 1), shortening of the bonds is an indication of the presence of O-quinoid structure; C17-C12 (1.481 Å) and C13-C14 (1.36 Å). On the basis of the structural parameters of the naphthol ring, it is not possible to predict the strengthening of electronic coupling in the molecule or hydrogen bond, due to the resonance effects^{13,14}. For atom labelling (Fig. 1) it is also observed that double bonds are shorter in O-quinoid resonance structure compared to the single bonds. Thus, coupling is not very effective as it leads to mild differentiation of bond lengths. However, coupling increases the amount of keto form and gives complete equalization of all bonds in the benzene ring.

Total steric interaction between substituents can be characterized by the energy of non-bonded interaction of C-substituted methyl group with C3 and C13 atoms as well as H atoms attached to C3 and C13 atoms

Table 3—The anisotropic displacement factor exponent takes the form: $-2\pi^2 [h^2a^{*2}U11+....+2hka^*b^*U12]$

	U11	U22	U33	U23	U13	U12
O	0.0687 (9)	0.0691 (10)	0.0362 (6)	0.0017 (6)	0.0136 (6)	-0.0037 (7)
N	0.0572 (10)	0.0527 (11)	0.0454 (8)	-0.0007 (7)	0.0091 (8)	-0.0005 (8)
C(1)	0.0565 (11)	0.0447 (11)	0.0386 (9)	0.0046 (7)	0.0112 (8)	0.0099 (9)
C(2)	0.0562 (11)	0.0417 (11)	0.0373 (8)	0.0036 (7)	0.0098 (8)	0.0096 (8)
C(3)	0.0697 (13)	0.0542 (13)	0.0381 (9)	0.0004 (8)	0.0160 (9)	0.0130 (10)
C(4)	0.0697 (14)	0.0550 (13)	0.0515 (11)	0.0037 (9)	0.0268 (10)	0.0103 (10)
C(5)	0.0588 (12)	0.0581 (14)	0.081 (2)	0.0012 (11)	0.0247 (12)	0.0046 (11)
C(6)	0.0582 (14)	0.067 (2)	0.094 (2)	-0.0073 (13)	0.0072 (13)	-0.0015 (11)
C(7)	0.0689 (15)	0.071 (2)	0.0653 (14)	-0.0097 (12)	-0.0025 (12)	0.0023 (12)
C(8)	0.0643 (13)	0.0621 (14)	0.0478 (10)	-0.0001 (9)	0.0054 (9)	0.0050 (11)
C(9)	0.0562 (12)	0.0459 (12)	0.0566 (11)	0.0025 (9)	0.0184 (9)	0.0113 (9)
C(10)	0.0519 (11)	0.0490 (12)	0.0437 (9)	0.0025 (8)	0.0088 (8)	0.0080 (9)
C(11)	0.0584 (11)	0.0440 (11)	0.0381 (8)	0.0018 (7)	0.0080 (8)	0.0107 (9)
C(12)	0.0710 (14)	0.0555 (14)	0.0442 (10)	-0.0064 (9)	0.0061 (9)	0.0051 (10)
C(13)	0.0606 (12)	0.0548 (13)	0.0555 (11)	0.0005 (9)	0.0060 (10)	-0.0021 (10)
C(14)	0.0529 (11)	0.0476 (13)	0.0591 (12)	-0.0029 (9)	0.0091 (9)	-0.0034 (9)
C(15)	0.0561 (13)	0.0603 (15)	0.085 (2)	-0.0006 (12)	0.0151 (12)	0.0028 (11)
C(16)	0.0621 (15)	0.083 (2)	0.102 (2)	-0.009 (2)	0.0311 (15)	0.0042 (14)
C(17)	0.084 (2)	0.079 (2)	0.080 (2)	-0.0146 (14)	0.0397 (15)	-0.0190 (15)
C(18)	0.089 (2)	0.077 (2)	0.0621 (14)	0.0046 (12)	0.0202 (13)	0.0033 (14)
C(19)	0.0671 (14)	0.075 (2)	0.0637 (13)	0.0044 (12)	0.0166 (11)	0.0143 (12)

Fig. 1—Atomic labelling system of 2-(N-benzyl- α -iminoethyl)-naphthol (BEIN) and possible configurations of BEIN.

(Fig. 1). The calculated value of steric energy is 4.05 kJ/mol.

The position of proton in BEIN is more on the side of oxygen and the length of hydrogen bond is relatively higher compared to that observed in similar compounds like 2-(N-benzyl- α -iminoethyl)phenol (BIEP)¹⁵. This results from the decrease of basicity obtained by replacing the N-benzyl group with N-methyl group. The hydrogen bond in BEIN is less than 2.5 Å which is quite short compared to that in other similar compounds¹⁵. Moreover, the H...N distance is less than 1.6 Å.

Table 4—Hydrogen coordinates and isotropic displacement parameters (Å²) for BEIN

	X	Y	Z	U (eq)
H (1)	0.396 (3)	0.196 (3)	0.093 (2)	0.085
H (3)	0.5620 (2)	0.3077 (3)	-0.09997(10)	0.064
H (4)	0.7551 (2)	0.4500 (3)	-0.06858 (12)	0.068
H (5)	0.9367 (2)	0.5841 (3)	0.0333 (2)	0.077
H (6)	1.0233 (3)	0.6545 (3)	0.1592 (2)	0.090
H (7)	0.9170 (2)	0.5715 (3)	0.25403 (14)	0.086
H (8)	0.7215 (2)	0.4249 (3)	0.22161 (12)	0.071
H (12A)	0.4113 (7)	0.0561 (14)	-0.1111 (3)	0.087
H (12B)	0.3375 (14)	0.2250 (3)	-0.1290 (2)	0.087
H (12C)	0.2655 (8)	0.078 (2)	-0.0991 (2)	0.087
H (13A)	0.2321 (2)	-0.0543 (3)	0.00997 (12)	0.070
H (13B)	0.1513 (2)	0.1095 (3)	-0.01131 (12)	0.070
H (15)	0.0075 (2)	0.1829 (3)	0.0674 (2)	0.081
H (16)	-0.0675 (3)	0.1595 (4)	0.1785 (2)	0.096
H (17)	0.0516 (3)	0.0077 (3)	0.2809 (2)	0.093
H (18)	0.2510 (3)	-0.1156 (3)	0.27224 (14)	0.091
H (19)	0.3244 (2)	-0.0942 (3)	0.16076 (14)	0.082

Table 5 contains the results of *ab initio* B3LYP/6-31G** calculations for both molecular and zwitterionic forms of intramolecular hydrogen bonded species. The results indicate the formation of two conformers due to the rotation of the N-CH₃ group. It is observed that one conformer is more stable by 0.438 kcal/mol for the primary form and 0.665 kcal/mol for the zwitterionic form. This may be explained as due to the increase in steric repulsion by methyl group. However, crystal packing conditions in the solid state are in favour of the primary form. The differences in calculated energies of the primary and proton transfer states are shown at the end of the last column of Table 5. The increase in steric effects and shortening

Table 5—Hydrogen bond parameters and selected bond lengths (Å) and angles (degree) in pseudoaromatic chelate ring of BEIN

Form of HB	OH	ON	HN	$\alpha(\text{OHN})$	$\beta(\text{COH})$	$\gamma(\text{C7NH})$	$\delta(\text{C9NH})$	
Measured X-ray								
O...H-N	1.22	2.449	1.32	155	103	105	133	
	1.18	2.462	1.39	154	104	105	134	
O-H...N	1.11	2.501	1.48	153	103.3	105	133.9	
Calculated <i>ab initio</i> B3LYP6-31G**								
Form of HB	OH	ON	HN	$\alpha(\text{OHN})$	$\beta(\text{COH})$	$\gamma(\text{C7NH})$	$\delta(\text{C9NH})$	ΔE^a
O...H-N	1.531	2.494	1.101	148	101.6	110	122.3	2.81
O-H...N	1.10	2.551	1.631	148	105.9	131	134	0.00

of the hydrogen bridges strongly modifies the potential for the proton transfer so as to make it happen easily. This can have significant consequences for thermochromic properties of the system. Crystal packing forces probably increase the intramolecular steric repulsion. Observed spectroscopic effects can be explained from the point of view of the steric interaction and the change of basicity by replacing the substituent. The pK values of base part of methylamine is 10.8 while that of benzylamine is 9.4 (ref. 16). The effective resonance coupling in proton transferred structure leads to a decrease of the energy of proton transfer state making this state accessible. The calculated ΔH°_{PT} for BEIN is 4.61 kcal/mol in the gas phase. Similar calculations on related Mannich bases in the gas phase show that the ΔH°_{PT} values are more than 15 kcal/mol¹⁷. This comparison suggests promotion of the proton transfer reaction in *ortho*-hydroxy Schiff bases, a feature that can be the basis of the thermochromic properties in Schiff bases.

In Schiff bases there exists the possibility of direct electronic coupling between acidic and basic centres of the hydrogen bridge (Fig. 1). It is shown that the flow of electrons through the coupled bonds compensates the increase of the atomic charges caused by the proton transfer process. This leads to a strengthening of the intramolecular bond^{13,14}. It was pointed out earlier that the resonance enhancing of the hydrogen bond strength is the most effective in symmetrical OHO and NHN bonds¹⁴. The importance of this effect in intramolecular N-H...O hydrogen bond is also significant. It is shown that the geometry changes correlate well with the amount of ionic resonance forms which describe the interactions between phenolic moiety and pseudoaromatic chelate ring. The O...H and H...N distances commonly vary within 1.25–1.35 Å. The shortest hydrogen bridge in Schiff bases is estimated to be 2.51 ± 0.01 Å. It seems quite likely that

sum ($d_{OH} + d_{NH}$) can be larger than d_{ON} , because of the bending of all such hydrogen bridges (Table 5). In intermolecular OHO systems strict linearity exists for the shortest hydrogen bridges¹⁸.

To conclude, molecular structure of a newly synthesized Schiff base, BEIN has been determined by crystallographic method and *ab initio* calculations. An unusual strengthening of the intramolecular O-H...N hydrogen bridge is detected due to steric shortening of the hydrogen bridge (O...N distance equal to 2.56 Å). Replacement of the phenol ring by naphthol moiety does not change the steric effects significantly. However, replacement of N-CH₃ group by N-C₆H₅ moiety decreases the hydrogen bond strength due to the change in the pK_a of the basic part of the hydrogen bridge. This study indicates that the steric effect leads to substantial strengthening of intramolecular hydrogen bonds. On the basis of our results some characteristic features of intramolecular hydrogen bond in both molecular and zwitterionic forms of BEIN can be noticed. The form after the proton transfer can be described as a hybrid of nearly equal amounts of keto and zwitterionic resonance structures.

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