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Strengthening of the intramolecular hydrogen bond in 7-ethylsalicylidene aniline due to steric repulsion

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Abstract

In a newly synthesized orthohydroxy Schiff base, 7-ethylsalicylidene aniline (ESA), the hydrogen atom in C–C(H)=N group is replaced by an ethyl group. The crystal structures of ESA determined by X-ray crystallography and ab initio calculations at the level of B3LYP/6-31G** are performed. The results obtained indicate that the steric effects lead to the strengthening of intramolecular hydrogen bond (O–H···N) of ESA. We have compared the results of ESA with the results of another two previously studied Schiff bases, 2-(*N*-methyl-α-iminoethyl)-phenol (I) and 2-(*N*-benzyl-α-iminoethyl)-phenol (II). We have also constructed the potential energy surfaces on which the proton is supposed to move and analyzed the reaction path.

Keywords: Schiff base; Ab initio; Steric repulsion

1. Introduction

Results presented in this paper are a part of the earlier studies [1,2] on the influence of different factors for the proton transfer reaction. The problem is important to explain the mechanism of biological processes and technically useful reactions, where the proton transfer is the rate determining step [3]. Orthohydroxy Schiff bases are important compounds due to their thermochromic and photochromic properties related to intramolecular proton transfer reaction. The proton transfer properties makes them important materials for optical memory and optical switch devices [4]. It is shown earlier [5] that the formation of intramolecular hydrogen bond in orthohydroxy Schiff base is connected with the increase of keto resonance form in the molecule. Strong coupling between chelate and phenol rings leads to the increase in the strength of hydrogen bond and also decreases the energy of proton transfer state. In O–H···N intramolecular hydrogen bond about 20% keto resonance form was detected. On the other hand, in the proton transferred O···H–N form, the keto form was estimated to be about 50%. This type of hydrogen bond strengthening is characteristic of resonance assisted hydrogen bond [6]. Sekikawa et al. [4] observed double fluorescence also in the case of orthohydroxy Schiff bases. Grabowska et al. [7] have examined the luminescence studies with the aim to establish the structure of the basic molecular units responsible for double fluorescence. It is seen that 2-(*N*-methyliminophenyl)-phenol is such a unit.

In this work, we have examined the spectral properties and molecular structure of a new orthohydroxy

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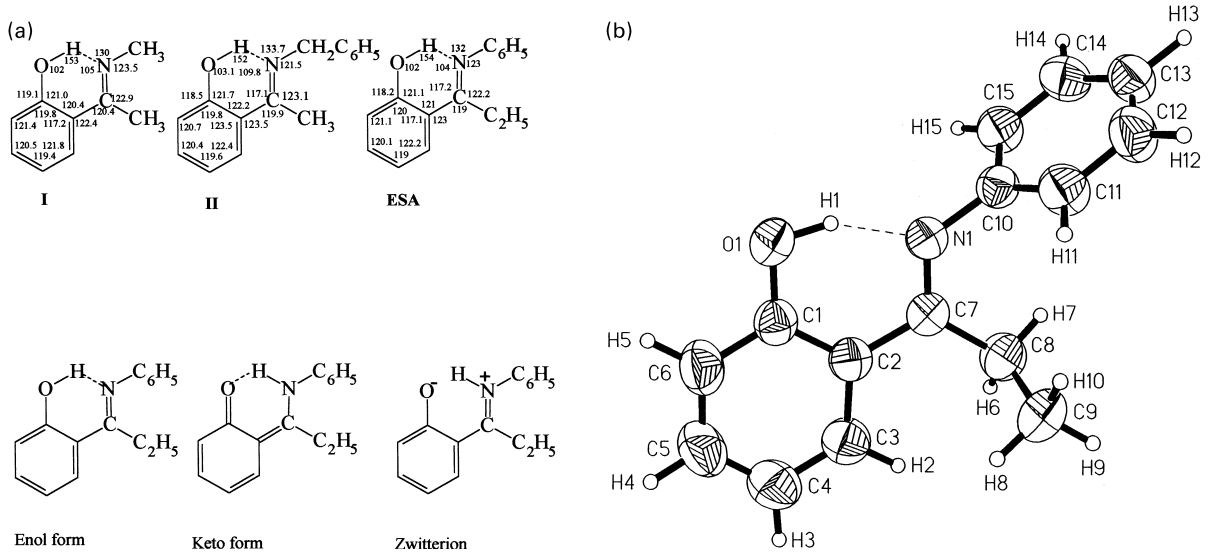

Fig. 1. (a) Molecular formula of 2-(N-methyl-α-iminoethyl)-phenol (I), 2-(N-benzyl-α-iminoethyl)-phenol (II) & ESA and possible configurations of ESA; (b) Molecular structure and atom lebelling system of 7-ethylsalicylideneaniline (ESA).

Schiff base, 7-ethylsalicylideneaniline (ESA,I). It is observed that by substitution of ethyl group in the C–C(H)=N unit introduces perturbations to intramolecular hydrogen bond and modified the potential for intramolecular proton transfer. The steric interaction of ethyl group decreases the O···N distance [8,9]. Due to inductive influence on the basic center, some strengthening of the hydrogen bond by the substituent is expected. The steric interaction of ethyl substituent, which by pushing the center of basicity in the direction of OH group should decrease the O···N distance. Steric shortening of the hydrogen bridge led to the stronger bond formation [8]. However, opposite effect can also be expected if the ethyl group makes the chelate rings less planar due to steric repulsion. The molecular structure of this new orthohydroxy Schiff base, 7-ethylsalicylidene aniline (ESA) are determined by X-ray crystallography and ab initio B3LYP/6-31G** calculations. The results are compared with two other orthohydroxy Schiff bases, 2-(*N*-methyl-α-iminoethyl)-phenol (I) and 2-(*N*-benzyl-α-iminoethyl)-phenol (II) [2]. The molecular structures of all the three compounds are shown in Fig. 1. In all the three Schiff bases the intramolecular O–H···N hydrogen bonds are relatively shorter as reported in literature so far.

Table 1
Crystal data and structure refinement for ESA

Compound	ESA
Empirical formula	$C_{15}H_{15}NO$
Formula weight	225.28
Temperature	293 K
Crystal system	Monoclinic
Space group	*C2/C*
Unit cell dimensions	$a = 23.763(5)$ Å
	$b = 7.850(2)$ Å
	$c = 17.022(3)$ Å
	$\beta = 103.78°(3)$
Volume	2433.5(9) Å^3
Density	1.230 mg m^{-3}
Absorption coefficient	0.603 mm^{-1}
Crystal size	$0.20 \times 0.25 \times 0.30$ mm^3
2θ range for data collection	9.7–160.6°
Reflection collected/unique	3400/2494 [R(int) = 0.0401]
Extinction coefficient	0.0037(2)

2. Experimental

Synthesis of the Schiff base from stoichiometric mixtures of particular salicylaldehyde and amine in methanol was performed by the standard procedure [10]. After recrystallization from methanol, the solid product was dried and studied by X-ray diffraction.

Table 2
Atomic coordinates and equivalent isotropic displacement parameters for ESA. U(eq) is defined as one third of the trace of the orthogonalized $\mathbf{U}_{ij}$ tensor

	x	y	z	U(eq)
O(1)	0.07912(6)	0.22992(14)	0.23496(9)	0.0697(3)
N(1)	0.12117(6)	0.23702(14)	0.41359(8)	0.0520(3)
C(1)	0.08024(7)	0.40107(19)	0.23818(11)	0.0544(3)
C(2)	0.10119(7)	0.49058(17)	0.32509(10)	0.0519(3)
C(3)	0.10081(10)	0.6689(2)	0.32039(14)	0.0714(4)
C(4)	0.08183(11)	0.7531(3)	0.23550(16)	0.0855(6)
C(5)	0.06260(11)	0.6611(3)	0.15244(15)	0.0830(5)
C(6)	0.06106(9)	0.4880(2)	0.15314(13)	0.0716(4)
C(7)	0.12336(7)	0.40075(17)	0.41716(10)	0.0496(3)
C(8)	0.14943(10)	0.5010(2)	0.51027(13)	0.0664(4)
C(9)	0.22838(12)	0.5627(3)	0.57116(16)	0.0823(5)
C(10)	0.14034(7)	0.13470(17)	0.49624(10)	0.0502(3)
C(11)	0.21265(9)	0.1087(2)	0.58319(13)	0.0666(4)
C(12)	0.22888(10)	0.0033(2)	0.66019(13)	0.0734(5)
C(13)	0.17368(10)	−0.0770(2)	0.65113(13)	0.0677(4)
C(14)	0.10213(10)	−0.0537(2)	0.56427(13)	0.0670(4)
C(15)	0.08500(9)	0.0499(2)	0.48606(13)	0.0606(4)

The summary of the collected data is shown in Table 1. Atomic coordinate displacement parameter and hydrogen coordinates are shown in Tables 2–4. Selected bond lengths and angles are depicted in Tables 5 and 6. The atomic labeling in ESA are shown in Fig. 1B.

Table 4
Hydrogen coordinates and isotropic displacement parameters for ESA

	x	y	z	U(eq)
H(1)	0.0936(11)	0.197(3)	0.3008(17)	0.098(6)
H(2)	0.1144(10)	0.733(2)	0.3832(15)	0.083(5)
H(3)	0.0830(11)	0.878(3)	0.2407(15)	0.101(6)
H(4)	0.0498(11)	0.723(3)	0.0921(17)	0.098(6)
H(5)	0.0477(11)	0.423(3)	0.0929(15)	0.092(6)
H(6)	0.1141(9)	0.600(2)	0.4892(12)	0.069(4)
H(7)	0.1447(9)	0.427(2)	0.5521(13)	0.073(5)
H(8)	0.2320(11)	0.630(3)	0.5229(16)	0.103(6)
H(9)	0.2471(13)	0.625(3)	0.6335(18)	0.115(7)
H(10)	0.2633(12)	0.461(3)	0.5947(16)	0.102(7)
H(11)	0.2518(10)	0.169(2)	0.5907(13)	0.077(5)
H(12)	0.2809(10)	−0.015(2)	0.7201(14)	0.083(5)
H(13)	0.1880(10)	−0.158(3)	0.7121(15)	0.094(6)
H(14)	0.0596(9)	−0.113(2)	0.5535(12)	0.075(5)
H(15)	0.0367(10)	0.065(2)	0.4260(14)	0.072(5)

3. Results and discussion

The intramolecular hydrogen bonding in Schiff bases can be modified both by resonance and steric influence. Analysis of the bond lengths show that intramolecular hydrogen bonds exist as molecular hydrogen bond form in all the three compounds. Lesser amount of the *ortho* quinoic resonance structure is found in the molecular structure of ESA. On the

Table 3
Anisotropic displacement parameters ($A^2 \times 10^{-3}$) for ESA. The anisotropic displacement factor exponent takes the form: $-2\pi^2[h^2a^{*2}U11 + \cdots + 2hka^*b^*U12]$

	U11	U22	U33	U23	U13
O(1)	0.0905(8)	0.0586(7)	0.0562(6)	−0.0073(5)	0.0454(6)
N(1)	0.0555(7)	0.0513(6)	0.0509(6)	−0.0006(5)	0.0350(8)
C(1)	0.0473(8)	0.0600(9)	0.0492(7)	0.0004(6)	0.0280(9)
C(2)	0.0465(8)	0.0519(8)	0.0519(8)	0.0014(6)	0.0292(10)
C(3)	0.0802(12)	0.0530(9)	0.0678(10)	0.0036(8)	0.0415(11)
C(4)	0.0938(14)	0.0605(11)	0.0785(12)	0.0168(10)	0.0446(11)
C(5)	0.0837(12)	0.0843(13)	0.0639(10)	0.0223(10)	0.0396(11)
C(6)	0.0697(10)	0.0818(12)	0.0517(9)	0.0074(8)	0.0336(7)
C(7)	0.0458(7)	0.0527(8)	0.0524(7)	−0.0026(6)	0.0325(9)
C(8)	0.0864(12)	0.0597(9)	0.0668(10)	−0.0064(8)	0.0555(10)
C(9)	0.0923(14)	0.0740(12)	0.0636(11)	−0.0169(10)	0.0423(13)
C(10)	0.0540(8)	0.0491(7)	0.0511(7)	−0.0022(6)	0.0354(9)
C(11)	0.0550(9)	0.0726(10)	0.0671(9)	0.0073(8)	0.0369(6)
C(12)	0.0600(10)	0.0804(12)	0.0613(9)	0.0128(9)	0.0306(5)
C(13)	0.0826(12)	0.0614(9)	0.0646(10)	0.0068(8)	0.0498(11)
C(14)	0.0724(11)	0.0622(9)	0.0788(11)	0.0046(8)	0.0542(13)
C15	0.0535(9)	0.0646(9)	0.0616(9)	0.0017(7)	0.0359(10)

Table 5
Selected bond lengths (Å) and angles (°) for ESA. (Symmetry transformations used to generate equivalent atoms)

O(1)–C(1)	1.3442(18)
O(1)–H(1)	0.97(2)
N(1)–C(7)	1.2861(18)
N(1)–C(10)	1.4172(17)
C(1)–C(6)	1.386(2)
C(1)–C(2)	1.4085(19)
C(2)–C(3)	1.402(2)
C(2)–C(7)	1.4733(18)
C(3)–C(4)	1.375(2)
C(3)–H(2)	1.029(19)
C(4)–C(5)	1.378(3)
C(4)–H(3)	0.99(2)
C(5)–C(6)	1.360(3)
C(5)–H(4)	0.99(2)
C(6)–H(5)	1.00(2)
C(7)–C(8)	1.501(2)
C(8)–C(9)	1.526(3)
C(8)–H(6)	1.025(17)
C(8)–H(7)	0.978(17)
C(9)–H(8)	1.03(2)
C(9)–H(9)	0.98(2)
C(9)–H(10)	1.03(2)
C(10)–C(15)	1.382(2)
C(10)–C(11)	1.385(2)
C(11)–C(12)	1.379(2)
C(11)–H(11)	0.976(19)
C(12)–C(13)	1.372(2)
C(12)–H(12)	0.985(19)
C(13)–C(14)	1.371(3)
C(13)–H(13)	1.07(2)
C(14)–C(15)	1.379(2)
C(14)–H(14)	1.017(17)
C(15)–H(15)	0.932(17)
C(1)–O(1)–H(1)	103.6(12)
C(7)–N(1)–C(10)	122.82(11)
O(1)–C(1)–C(6)	117.71(14)
O(1)–C(1)–C(2)	121.72(13)
C(6)–C(1)–C(2)	120.57(15)
C(3)–C(2)–C(1)	116.96(14)
C(3)–C(2)–C(7)	121.56(13)
C(1)–C(2)–C(7)	121.48(13)
C(4)–C(3)–C(2)	121.70(17)
C(4)–C(3)–H(2)	121.8(10)
C(2)–C(3)–H(2)	116.5(10)
C(3)–C(4)–C(5)	119.69(18)
C(3)–C(4)–H(3)	114.4(12)
C(5)–C(4)–H(3)	125.9(12)
C(6)–C(5)–C(4)	120.50(18)
C(6)–C(5)–H(4)	120.3(12)
C(4)–C(5)–H(4)	119.2(12)
C(5)–C(6)–C(1)	120.57(17)
C(5)–C(6)–H(5)	119.8(11)

Table 5 (*continued*)

C(1)–C(6)–H(5)	119.6(11)
N(1)–C(7)–C(2)	116.88(12)
N(1)–C(7)–C(8)	123.41(13)
C(2)–C(7)–C(8)	119.68(13)
C(7)–C(8)–C(9)	112.14(14)
C(7)–C(8)–H(6)	109.8(9)
C(9)–C(8)–H(6)	111.7(9)
C(7)–C(8)–H(7)	107.2(10)
C(9)–C(8)–H(7)	111.0(10)
H(6)–C(8)–H(7)	104.5(13)
C(8)–C(9)–H(8)	108.6(12)
C(8)–C(9)–H(9)	113.5(14)
H(8)–C(9)–H(9)	113.4(18)
C(8)–C(9)–H(10)	110.5(12)
H(8)–C(9)–H(10)	104.5(17)
H(9)–C(9)–H(10)	105.9(17)
C(15)–C(10)–C(11)	119.37(14)
C(15)–C(10)–N(1)	118.39(13)
C(11)–C(10)–N(1)	122.10(12)
C(12)–C(11)–C(10)	120.11(15)
C(12)–C(11)–H(11)	120.3(11)
C(10)–C(11)–H(11)	119.5(10)
C(13)–C(12)–C(11)	120.36(17)
C(13)–C(12)–H(12)	121.4(10)
C(11)–C(12)–H(12)	118.2(10)
C(14)–C(13)–C(12)	119.59(15)
C(14)–C(13)–H(13)	121.9(10)
C(12)–C(13)–H(13)	118.5(10)
C(13)–C(14)–C(15)	120.79(15)
C(13)–C(14)–H(14)	122.3(9)
C(15)–C(14)–H(14)	116.9(9)
C(14)–C(15)–C(10)	119.73(15)
C(14)–C(15)–H(15)	121.6(10)
C(10)–C(15)–H(15)	118.7(10)

Table 6
Selected torsion angles (°) for ESA. (Symmetry transformations used to generate equivalent atoms)

O(1)–C(1)–C(2)–C(3)	179.63(14)
C(6)–C(1)–C(2)–C(3)	0.6(2)
O(1)–C(1)–C(2)–C(7)	0.35(19)
C(6)–C(1)–C(2)–C(7)	−178.63(13)
C(1)–C(2)–C(3)–C(4)	− 0.8(2)
C(7)–C(2)–C(3)–C(4)	178.44(15)
C(2)–C(3)–C(4)–C(5)	0.0(3)
C(3)–C(4)–C(5)–C(6)	1.1(3)
C(4)–C(5)–C(6)–C(1)	− 1.3(3)
O(1)–C(1)–C(6)–C(5)	− 178.60 (16)
C(2)–C(1)–C(6)–C(5)	0.4(2)
C(10)–N(1)–C(7)–C(2)	− 179.41(11)
C(10)–N(1)–C(7)–C(8)	2.8(2)
C(3)–C(2)–C(7)–N(1)	179.33(14)
C(1)–C(2)–C(7)–N(1)	− 1.43(18)
C(3)–C(2)–C(7)–C(8)	− 2.8(2)
C(1)–C(2)–C(7)–C(8)	176.48(12)
N(1)–C(7)–C(8)–C(9)	100.15(18)
C(2)–C(7)–C(8)–C(9)	− 77.62(19)
C(7)–N(1)–C(10)–C(15)	108.61(16)
C(7)–N(1)–C(10)–C(11)	− 75.70(18)
C(15)–C(10)–C(11)–C(12)	− 2.1(2)
N(1)–C(10)–C(11)–C(12)	− 177.74(15)
C(10)–C(11)–C(12)–C(13)	0.3(3)
C(11)–C(12)–C(13)–C(14)	0.9(3)
C(12)–C(13)–C(14)–C(15)	− 0.2(3)
C(13)–C(14)–C(15)–C(10)	− 1.6(3)
C(11)–C(10)–C(15)–C(14)	2.7(2)
N(1)–C(10)–C(15)–C(14)	178.54(13)

basis of the structural parameters of the phenol ring neither a strong electronic coupling nor a strong strengthening of hydrogen bond in the molecule can be predicted owing to the resonance effects [4,11]. The phenyl ring situation seems to be similar in all the three molecules (ESA, I and II). In ESA bonds which are double in resonance structure are shortened (C3–C4 and C5–C6) in comparison to those which are single ones (C1–C2, C6–C1, C5–C4, C2–C3). The C1–C2 bonds are elongated which are characteristic of the collective effect of substituents and extended by the formation of chelate ring (Table 5). These effects are less pronounced in compounds without alkyl or phenyl substituents [7]. Coupling of bonds with different kinds of substituents is not so much effective as it leads to mild differentiation of bond lengths. It is shown earlier [5] that a coupling increases the population of keto form and leads to bond differentiation in opposite to general resonance effects, which gives complete equalization of all bonds in benzene ring.

Inspite of all these facts, an analysis of the geometry of the chelate ring indicates the possibility of strong intramolecular hydrogen bond, with predominating molecular form (Table 7). The chelate rings are planar and coupled with phenol ring, the torsional angles characterizing deviations from last plane are less than 2° (Table 6). The C8 atom is practically located in the phenol ring plane where the torsional angle is $<3°$. Both compound II and ESA contain the *N*-benzyl group while compound I consists of *N*-methyl group. The steric repulsion leads to a strong increase of $C(H_3)$–C=N and C=N–C angles both in II and ESA. A pronounced decrease of $H\cdots N–CH_3$ and N=C–C angle is also observed. Moreover, shortening of distances between CH_3 group and the neighbouring C and H atoms are observed in the structure of ESA. The calculated values of strain energy are 4.821 and 4.634 kJ/mol for II and ESA, respectively. This shows that there is no substantial difference of steric repulsion in both the compounds. The strain energy for I is 3.982 kJ/mol. Total steric interaction between substituents can be estimated by the energy of non-bonded interactions of methyl or ethyl group with C3 and C9 atoms as well as H atoms attached to C3 and C9 atoms (Fig. 1B).

The analysis of the structure of compounds indicates that the intramolecular steric repulsion is the main factor and is responsible for the shortening of the hydrogen bridge. This repulsion can be characterized by shortening of non-bonded distances with respect to sum of the vander Waals radii [12]. According to non-geminal interactions the C18–C13 and C18–C19 distances are determined to be 2.975 and 2.895 Å, respectively. These are shortened by 0.425 and 0.505 Å, respectively with respect to the sum of vander Waals radii (3.4 Å). The distances between C18 atom and H-atoms attached to it, C13 and C19 atoms and H-atoms attached to it are also shortened. This shortening generates a strong strain within the molecules, which is partially released by change of valence angles. The position of angles is shown in Fig. 1A. Hence, the valence angles in ESA, I and II are compared with C–C(H)=N unit. The data of I and II are taken from Ref. [9]. The steric repulsion leads to an increase of $C(CH_3)$–C=N and C=N–C angles in I and II compounds compared to ESA. Moreover,

Table 7
Hydrogen bond parameters and selected bond lengths (Å) and angles (°) in pseudoaromatic chelate rings

	Form of HB	OH	ON	HN	α(OHN)	β(COH)	γ(C_7HN)	δ(C_9NH)	
Measured X-ray									
I	O···H–N	1.20(4)	2.459(3)	1.32(3)	152(1)	102(1)	106(1)	130(1)	
I	O–H···N	1.15(4)	2.460(3)	1.38(2)	153(1)	103(2)	106(1)	131(1)	
II	O–H···N	1.10(2)	2.497(3)	1.47(3)	152(3)	103.1(12)	104.8(9)	133.7(9)	
ESA	O–H···N	1.06(3)	2.490(3)	1.46(3)	154(1)	103(1)	105(1)	133(1)	
*Ab initio B3LYP6-31G***									
	Form of HB	OH	ON	HN	α(OHN)	β(COH)	γ(C_7NH)	δ(C_9NH)	ΔE^a
I	O···H–N	1.503	2.484	1.074	148.7	101.5	110.3	121.8	2.77
	O–H···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···N	1.009	2.548	1.627	149.4	105.7	103.8	133.3	0.00
ESA	O···H–N	1.499	2.490	1.066	149.1	101.6	110.6	121.6	2.28
	O–H···N	1.008	2.520	1.590	150.1	105.2	104.2	131.1	0.00

decrease of H···N–CH_3 and N=C–C angles are also observed in ESA. In spite of this deformation of valence angles, significant shortening of distances between CH_3 group and the neighbouring C and H atoms are observed in all the three compounds.

Position of proton in II and ESA is more on the side of oxygen and length of hydrogen bonds are higher compared to I. This is due to the decrease of basicity by replacing the methyl group by benzyl group. The hydrogen bonds in ESA and II (with N···O distance less than 2.5 Å) are shorter than I. The H···N distances are less than 1.5 Å in all the three compounds. The observed differences in spectroscopic properties can be explained from the point of view of the steric interaction and the change of basicity upon replacement of methyl group by benzyl group. The pk_a of methylamine is 10.7 while that of benzylamine is 9.4 [13].

No significant strengthening of the hydrogen bonding is observed in ESA in comparison to II resulting from the CH_3 group replaced by ethyl group. This may be due to the electronic and not steric effects, which determine the strengthening of hydrogen bond.

Table 7 shows the results of ab initio B3LYP calculations for all the three molecular and zwitterionic forms of intramolecular hydrogen bonding. In the case of I very short hydrogen bond was found ($d_{N\cdots O} = 2.45913(3)$ Å). The proton is localized near the central position, $d_{O\cdots H} = 1.20$ Å, $d_{H\cdots N} = 1.32(3)$ Å. The OHN angles are 153 and 154° in I and ESA, respectively. In the primary form more asymmetric proton localization was found to be $d_{O\cdots H} = 1.15(4)$ Å, $d_{H\cdots N} = 1.38(2)$ Å in I and that in the case of ESA are $d_{O\cdots H} = 1.06(3)$ and $d_{H\cdots N} = 1.46(3)$ Å. The length of the hydrogen bond is also quite different, 2.460(3) and 2.490(3) Å, respectively (Table 7). The hydrogen bonds in I, II and ESA with N···O distances are less than 2.5 Å which are quite short in O–H···N type hydrogen bonds. The α(OHN) angles are more or less similar in all the three compounds. According to the sequence of the C–C bond lengths, the structures of the compounds reveal properties of *o*-quinoic system quite distinctly. The last column of Table 7 shows the differences in calculated energy of molecular and zwitterionic states. The significant steric effects and short O···N distance would explain the difference in energy between molecular and proton transfer state. Shortening of the hydrogen bridges modifies the potential for the proton transfer making the transfer forms easily accessible in ESA. Moreover, crystal packing forces probably increase the intramolecular steric repulsion. The planarity of the chelate ring formed by intramolecular hydrogen bonds mainly depends on crystal packing conditions. Replacement of the methyl group by benzyl moiety reduces the strength of the hydrogen bond. Hydrogen bonds are much shorter and stronger than non-substituted compounds.

4. Conclusion

The ab initio calculation shows strengthening of the

intramolecular O–H···N hydrogen bridge due to steric shortening of the hydrogen bridge. The O···N distance is less than 2.5 Å. Replacing N–CH_3 group by *N*-benzyl moiety does not change significantly the steric effects, but decreases the hydrogen bond strength due to change of pk_a of the basic part of the bridge. In this study, molecular structure and spectroscopic properties of the hydrogen bond are determined. It is shown that in alkyl substituted compound both the steric and electronic interaction of alkyl group lead to hydrogen bond strengthening. On the other hand phenyl group attracts the electrons and decreases the basicity of imine N-atom. The hydrogen bonds are weaker in compounds with phenyl substituents compared to alkyl group. Replacing the *N*-alkyl group by *N*-benzyl group decreases the strength of the hydrogen bond.

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