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Intramolecular hydrogen bonding and tautomerism in Schiff bases: Part VI. Syntheses and structural investigation of salicylaldimine and naphthaldimine derivatives

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Abstract. Salicyclaldimines (**5–9**) and naphthaldimines (**10–13**) derived from condensation reactions of N_2O_2 donor type bifunctional aminopodands (**1–4**), [$(H_2NPhO)_2R$, where R = CH_2CH_2, $CH_2CH_2CH_2$ and CH_2PhCH_2], and hydrazine monohydrate with salicylaldehyde and 2-hydroxy-1-naphthaldehyde, respectively, have been prepared (scheme 1) and characterized by elemental analyses, UV-vis, FTIR, NMR and MS. NMR assignments were made using ^{1}H, ^{13}C NMR, DEPT and aided by 2D HETCOR and HMBC heteronuclear correlation techniques. The UV-vis spectra of the Schiff bases have been systematically studied in organic solvents of different polarity, acidic and basic media and found useful in understanding of tautomeric equilibria (phenol-imine, O–H...N and keto-amine, O...H–N forms) in this series. The molecular structure of **8** has been determined crystallographically, and observed that the compound is in the form of phenol-imine, defined by the strong intramolecular [O–H...N = 1·72(3), 1·81(2) Å] hydrogen bonds. Compound **8** crystallizes in the monoclinic space group $P2_1/a$ with a = 8·4675(7), b = 38·448(3), c = 9·3875(7) Å, β = 103·0780(10)°, V = 2976·9(4) Å^3, Z = 4 and D_x = 1·271 Mg m^{-3}, and contains acetonitrile molecule in the crystal lattice.

Keywords. 2-Hydroxy Schiff bases; hydrogen bonding and tautomerism; crystal structure; heteronuclear correlation techniques.

1. Introduction

2-Hydroxy Schiff bases formed by condensation reactions of salicylaldehyde and 2-hydroxy-1-naphthaldehyde with various amines have been extensively studied.[1–7] This originated from the fact that the 2-hydroxy Schiff bases and their metal complexes exhibit wide applications, especially in biological systems.[8–13] The presence of *ortho* hydroxyl group in Schiff bases has been regarded as one of the important elements favouring for the existence of intramolecular hydrogen bonds and also the tautomerism accounting for the formation of either phenol-imine (O–H...N) or keto-amine (O...H–N) tautomers. Intramolecular hydrogen bonds and tautomerism between phenol-imine and keto-amine forms in 2-hydroxy Schiff bases in solution and in the solid state have been investigated by using IR and UV-vis,[14–17] ^{1}H, ^{13}C and ^{15}N NMR spectroscopic[18,23] and X-ray crystallographic[24] techniques. The spectroscopic and crystallographic investigations into 2-hydroxy Schiff bases lies in the eminent importance of intramolecular hydrogen bonds for distinguishing their photochromic and thermochromic behaviours[25–32] as a consequence of intramolecular proton transfer between phenolic oxygen and imine nitrogen sites in the six-membered chelate ring formed. In solution, the existence of tautomeric equilibra in polar and non-polar solvents is observed.[33] It is claimed that phenol-imine form is dominant in salicylaldimine, while keto-amine form in naphthaldimine Schiff bases in solution.[34,35] In the solid state, it is generally specified by X-ray analysis that salicylaldimine and naphtaldimine Schiff bases also tend to form phenol-imine and keto-amine, respectively.[24,36,37] It was once claimed that the hydrogen bond type depends neither on the stereochemistry of the molecule, nor on the sort of the substituent

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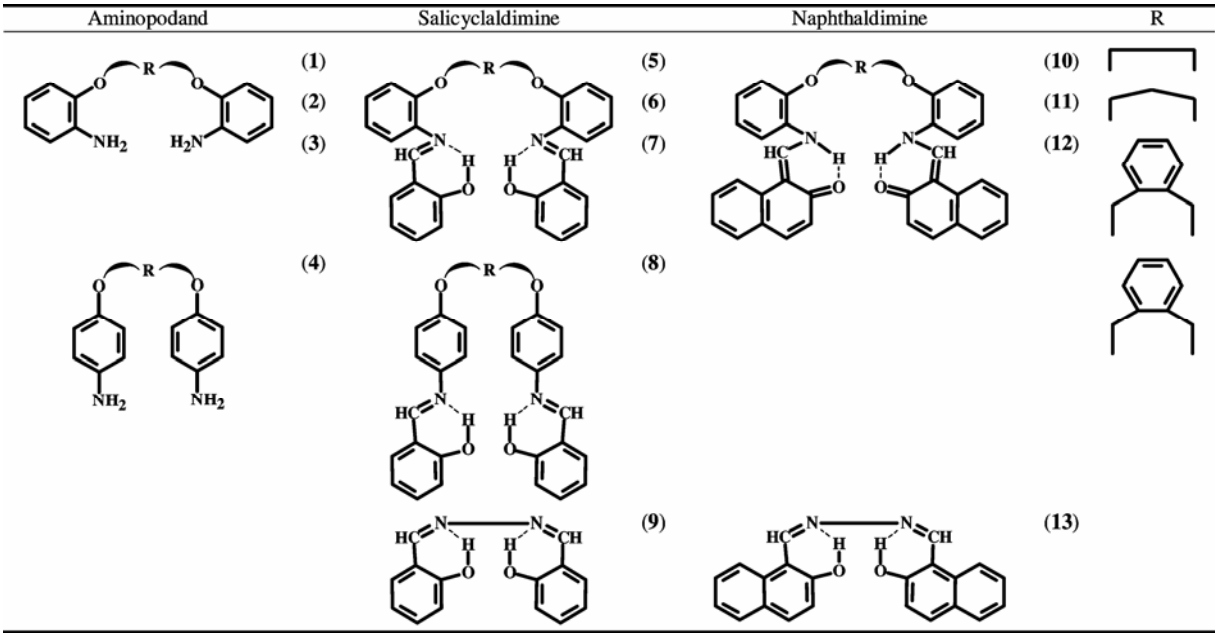


Scheme 1.

bonded to the imine nitrogen atom, but on the kind of aldehyde used,[36] with only an intramolecular O–H...N (phenol-imine form) type of hydrogen bond being observed in salicyclaldimines, and an O...H–N (keto-amine form) type in naphthaldimine.[24,36,37] Our crystallographic studies have shown an intramolecular [O–H...N (phenol-imine tautomer)] hydrogen bond for **13**, a naphthaldimine Schiff base,[38] which is contrary to the observations reported in the literature.[24,37] On the other hand, 4-{[(1*E*)-(2-hydroxynaphthyl)methylidene]amino}-1,5-dimethyl-2-phenyl-2,3-dihydro-1*H*-pyrazol-3-one[39] and *bis*(2-hydroxy-1-naphthaldehyde) oxaloyldihydrazone dihydrate[40] also indicate that the naphthaldimine can exist in the phenol-imine form. In addition, according to our crystallographic data 4-{[(1*E*)-(3,5-dinitro-2-hydroxyphenyl)-methylidene]amino}-1,5-dimethyl-2-phenyl-2,3-dihydro-1*H*-pyrazol-3-one, a salicylaldimine derivative, has neither phenol-imine nor keto-amine form,[41] which is also contrary to the observations reported in the literature.[24,36] The molecular structure observed in this compound corresponds to the situation where symmetric hydrogen bonds exist between the two forms, which might be artifact due to the disorder caused by proton transfer. Consequently, these results are clear evidences for the stereochemistry of the compounds and the N-substituents in 2-hydroxy Schiff bases. Therefore, there has been much interest in our laboratory on the subject of hydrogen bonds in salicylaldimine and naphthaldimine Schiff bases with different substituents.

In this paper, we report (i) the synthesis of 2-hydroxy Schiff bases (**7**, **8** and **12**) where there are intrinsic aromaticity differences resulting from the condensation of salicylaldehyde and 2-hydroxy-1-naphthaldehyde with N_2O_2-donor type bifunctional aminopodands (**3** and **4**) (scheme 1) and (ii) tautomerism via hydrogen bonding. The tautomeric conformers in crystal and liquid phases are investigated by spectroscopic methods and X-ray diffraction techniques. In addition, total assignments of ^{1}H and ^{13}C NMR spectra for the structures are made with the help of C-H correlation spectroscopy (HETCOR), as well as heteronuclear multiple-bond correlation (HMBC).

2. Experimental

2.1 *General techniques*

Salicylaldehyde and 2-hydroxy-1-naphthaldehyde were purchased from Fluka and used without further purification. MeOH, EtOH, DMSO, CH_2Cl_2 and *n*-hexane were dried by standard methods prior to use. Melting points were measured on a Gallenkamp apparatus using a capillary tube. ^{1}H, ^{13}C NMR, DEPT, HETCOR and HMBC spectra were obtained on a Bruker 500 MHz ultrashield spectrometer equipped with a 5 mm PABBO BB-inverse gradient probe. Standard Bruker pulse programs[42] were used in the entire experiment. FTIR spectra were recorded on a Mattson 1000 FTIR spectrometer in KBr discs and

were reported in cm^{-1} units. Microanalyses were carried out by the microanalytical service of TÜBİTAK (Turkey), Mass Spectrometric analysis (APIMS) were performed on the AGILEND 1100 MSD spectrometer. UV-vis spectra were measured by using a UNICAM UV2-100 series spectrometer.

2.2 *Synthesis of Schiff bases*

N_2O_2 donor type bifunctional aminopodands 1,2-ethane dioxy *bis*(2-aminophenyl ether) (**1**), 1,3-propane dioxy *bis*(2-aminophenyl ether) (**2**), 1,2-xylylene dioxy *bis*(2-aminophenyl ether) (**3**) and 1,2-xylylene dioxy bis(4-aminophenyl ether) (**4**) have been synthesized from the reduction of the corresponding nitropodands with Pd/C and hydrazine hydrate (80%) in EtOH.[15,43] The salicyclaldimine (**5**–**9**) and naphthaldimine (**10**–**13**) Schiff bases have respectively been obtained from the reaction of corresponding aminopodands (**1**–**4**) and hydrazine monohydrate in MeOH (scheme 1). The preparation and crystallographic data of 1,3-*bis*[*N*-2-oxyphenyl-salicylidene]-propane (**6**) and 2-hydroxynapthaldehyde[(1*E*)-(2-hydroxynaphthyl)methylene]hydrazone (**13**) were reported by our group, previously,[38,44] but the MS, IR, NMR and UV data of these compounds will be discussed in this paper. The syntheses of 1,2-*bis*[*N*-2-oxyphenyl-salicylidene]-ethane (**5**),[45] 2-hydroxysalicylaldehyde[(1*E*)-(2-hydroxysalicyl) methylene]hydrazone (**9**),[46] 1,2-*bis*[*N*-2-oxyphenyl-2-oxo-1-naphthylidenemethylamino]-ethane (**10**)[47] and 1,3-*bis*[*N*-2-oxyphenyl-2-oxo-1-naphthylidene-methylamino]-propane (**11**)[48] have also been reported, previously. However, for compounds **5** and **10**, suitable spectral data are not available[45,47] and for compound **9** only the crystallographic results are present.[46] For the assignments of aromatic protons and carbons, we re-synthesized **5**, **6**, **9**–**11** and **13** and obtained the detailed NMR spectra of all the compounds for comparision purposes. Elemental analyses, FTIR, APIMS and all the NMR data are in agreement with the proposed structures of **7**, **8** and **12**. The MS spectra of the compounds (**5**–**13**) show protonated molecular ion $[MH]^+$ peaks. APIMS (I_r %): *m*/*z* 453 ($[MH]^+$, 100) for **5**, 467 ($[MH]^+$, 100) for **6**, 241 ($[MH]^+$, 8) for **9**, 553 ($[MH]^+$, 45) for **10**, 567 ($[MH]^+$, 63) for **11** and 341 ($[MH]^+$, 100) for **13**. IR (KBr, cm^{-1}): ν 3061 (C–H arom.), 1617 (C=N), 1585 (C=C), 1286;1253 (C–O arom.), 1149–1035 (C–O aliph.) for **5**, ν 3060 (C–H arom.), 1616 (C=N), 1589 (C=C), 1282; 1247 (C–O arom.), 1149–1040 (C–O aliph.) for **6**, 3043 (C–H arom.), 1627 (C=N), 1573 (C=C), 1260 (C–O arom.) for **9**, ν 3067 (C–H arom.), 1623 (C=N), 1589 (C=C), 1290; 1257 (C–O arom.), 1163–1034 (C–O aliph.), 1323 (C=O) for **10**, ν 3055 (C–H arom.), 1623 (C=N), 1591 (C=C), 1290;1253 (C–O arom.), 1157–1047 (C–O aliph.), 1321 (C=O) for **11** and ν 3063 (C–H arom.), 1622 (C=N), 1579 (C=C), 1281 (C–O arom.) for **13**.

2.2a *Synthesis of 1,4-bis[N-2-oxyphenyl-salicylidene]-1,2-xylylene* (**7**): A solution of **3** (0·80 g, 2·50 mmol) in dry MeOH (25 mL) was added dropwise to a solution of salicylaldehyde (0·61 g, 5·00 mmol) in dry MeOH (50 mL) over the period of 1 h. The mixture was refluxed for 4 h and then cooled to an ambient temperature. After filtration, compound **5** was obtained as a yellow solid. It was recrystallized from EtOH, m.p. 142°C, 1·04 g (79%) yield. Anal. calc. for $C_{34}H_{28}N_2O_4$: C 77·43, H 5·30, N 5·26; found: C 78·10, H 5·25, N 5·26. APIMS (I_r %): *m*/*z* 529 ($[MH]^+$, 100). IR (KBr, cm^{-1}): ν 3067 (C–H arom.), 1616 (C=N), 1586 (C=C), 1283; 1236 (C–O arom.), 1150–1030 (C–O aliph.).

2.2b *Synthesis of 1,4-bis[N-4-oxyphenyl-salicylidene]-1,2-xylylene* (**8**): Salicylaldehyde (0·23 g, 1·88 mmol) and **4** (0·30 g, 0·94 mmol) were used for the preparation of **8** as for **7**, 3 h, yellow solid, crystallization from CH_3CN, m.p. 149°C, 0·40 g (81%) yield. Anal. calc. for $C_{34}H_{28}N_2O_4$: C 77·43, H 5·30, N 5·26; found: C 77·48, H 5·30, N 5·30. APIMS (I_r %): *m*/*z* 529 ($[MH]^+$, 100). IR (KBr, cm^{-1}): ν 3061 (C–H arom.), 1616 (C=N), 1590 (C=C), 1286; 1244 (C–O arom.), 1153–1037 (C–O aliph.).

2.2c *Synthesis of 1,4-bis[N-2-oxyphenyl-2-oxo-1-naphthylidenemethylamino]-1,2-xylylene* (**12**): A solution of **3** (0·60 g, 1·88 mmol) in dry MeOH (25 mL) was added dropwise to a solution of 2-hydroxy-1-naphthaldehyde (0·65 g, 3·75 mmol) in dry MeOH (50 mL) over the period of 1 h. The mixture was refluxed for 4 h and then cooled to an ambient temperature. The precipitated yellow solid of **12** was filtered off and crystallized from EtOH, m.p. 218°C, 0·86 g (73%) yield. Anal. calc. for $C_{42}H_{32}N_2O_4$: C 80·24, H 5·13, N 4·46; found: C 79·82, H 5·15, N 4·50. APIMS (I_r %): *m*/*z* 629 ($[MH]^+$, 60). IR (KBr, cm^{-1}): ν 3058 (C–H arom.), 1620 (C=N), 1591 (C=C), 1290; 1248 (C–O arom.), 1161–1053 (C–O aliph.), 1323 (C=O).

Table 1. Crystal data and structure refinement for **8**.

CCDC No.	653274
Empirical formula	$C_{34}H_{28}N_2O_4.C_2H_3N$
Formula weight	569·64
Temperature (K)	273(2)
Wavelength (Å)	0·71073
Crystal System	Monoclinic
Space Group	$P2_1/a$
Unit cell dimensions	
a (Å)	8·4675(7)
b (Å)	38·448(3)
c (Å)	9·3875(7)
β (°)	103·0780(10)
Volume (Å^3)	2976·9(4)
Z	4
Density (calculated, mg/m^3)	1·271
Absorption coefficient (mm^{-1})	0·084
F (000)	1200
Crystal shape and color	Plate, colorless
Crystal size (mm^3)	0·35 × 0·25 × 0·10
Device type	Bruker 1000 CCD area-dedector diffractometer
Scan type	φ and ω scans
Intensity decay %	1
Counting time (min)	120
θ range for data collection (°)	2·12–28·27
Index ranges	$-11 \le h \le 11$ $-49 \le k \le 51$ $-12 \le l \le 12$
Reflections collected	31660
Independent reflections	7186 (R_{int} = 0·0238)
Observed reflections	4930 ($I > 2\sigma I$)
Data/restraints/parameters	7186/0/405
Goodness-of-fit on $F2$	1·048
Final R indices [$I > 2\sigma(I)$]	R_1 = 0·0539, wR_2 = 0·1294
R indices (all data)	R_1 = 0·0815, wR_2 = 0·1461
Largest diff. peak and hole (eA^{-3})	0·216 and –0·281
Extinction coefficient	None

$w = 1/[\sigma^2(F_o^2) + (0{\cdot}0576P)^2 + 0{\cdot}7621P]$, where $P = (F_o^2 + 2F_c^2)/3$

Table 2. Selected bond lengths (Å), bond angles (°) and torsion angles (°) for **8**.

O1−C1	1·345 (3)	O4−C30	1·350 (2)
O2−C11	1·3660(19)	O3−C22	1·365 (2)
O2−C14	1·4441 (19)	O3−C21	1·412 (2)
N1−C7	1·278 (2)	N2−C28	1·272 (2)
N1−C8	1·414 (2)	N2−C25	1·416 (2)
C1−C6	1·399 (3)	C29−C30	1·404 (2)
C6−C7	1·448 (3)	C28−C29	1·448 (3)
N3−C35	1·115 (4)	C35−C36	1·437 (4)
C11−O2−C14	118·24 (12)	C22−O3−C21	118·75 (14)
C7−N1−C8	122·06 (16)	C28−N2−C25	122·52 (15)
O1−C1−C6	121·07 (18)	O4−C30−C29	121·72 (17)
C1−C6−C7	121·95 (18)	C30−C29−C28	121·30 (17)
N1−C7−C6	121·62 (18)	N2−C28−C29	121·90 (17)
N3−C35−C36	179·8 (4)		
C8−N1−C7−C6	−175·45(15)	C25−N2−C28−C29	−179·12(16)
C1−C6−C7−N1	0·9(3)	C30−C29−C28−N2	−0·5(3)
C7−C6−C1−O1	−2·4(3)	C28−C29−C30−O4	−1·7(3)

2.3 *X-Ray crystallography*

The suitable crystals of compound **(8)** were obtained by recrystallization from CH_3CN. The X-ray diffraction data have been collected on a Bruker 1000 CCD area-dedector diffractometer with MoK_α radiation (λ = 0·71073 Å) at 273(2) K and no absorption correction was applied due to the low absorption coefficient. The structure was solved by direct methods SHELXS97.[49] Crystal data and structure refinement parameters are listed in table 1 and the crystallographic information file (CIF) is provided in the supplementary information. Selected bond lenghts (Å), bond angles (°) and torsion angles (°) are presented in table 2. H1A, H4A, H7 and H28 atoms were located from difference syntheses and refined isotropically. Since the difference syntheses did not clarify the positions of the remaining H atoms, they were positioned geometrically, with C–H = 0·93, 0·97 and 0·96 Å for aromatic, methylene and methyl H, respectively and constrained to ride on their parent atoms with $U_{iso}(H) = xU_{eq}$ (C), where x = 1·5 for methyl H and x = 1·2 for all other H atoms.

3. Results and discussion

3.1 *FTIR spectroscopy*

The relevant IR spectral bands that can provide diagnostic structural evidences for 2-hydroxy Schiff bases are given in Experimental Section. For salicyaldimines **(5–9)** and naphthaldimine **(13)**, relatively strong bands attributable to $\nu_{C=N}$ are detected at 1616–1627 cm^{-1} as in the Schiff bases possessing the formulation of ArCH=NAr with substituted aryl groups which is assigned to $\nu_{C=N}$ involved in intramolecular hydrogen bond with the *ortho* OH group.[17,36,50] The existence of intramolecular hydrogen bonds between the hydroxyl oxygens and the nitrogen atoms is further corroborated by X-ray structural data for **8**. The observation of very weak $\nu_{C=O}$ absorption bands at 1323, 1321 and 1323 cm^{-1} for naphthaldimines **(10–12)**, respectively, is the evidence for the existence of the keto-amine tautomer in the solid state. Contrary to the expectation, analogue **13** does not show a similar absorption band at ~1320 cm^{-1}. Because, it is in the form of phenol-imine. Moreover, X-ray crystallographic data of **13** also support that there are two strong intramolecular O–H...N hydrogen bonds showing phenol-imine tautomer.[38]

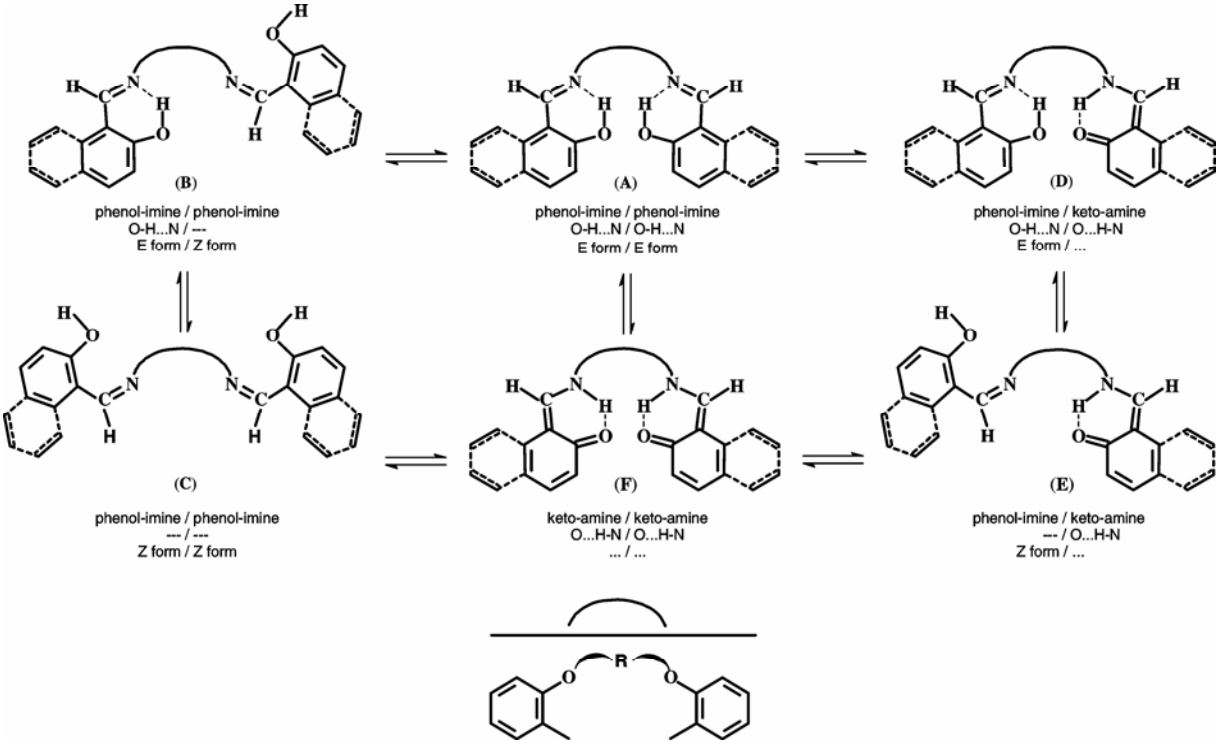
3.2 *NMR spectroscopy*

The ^1H and ^{13}C NMR data of the compounds are listed in tables S1, S2 and S3 in Supplementary materials. The expected tautomeric species of salicylaldimine **(5–9)** and naphthaldimine **(10–13)** Schiff bases in solution are depicted in schemes 2 and 3. In addition, in solution the tautomeric species of the 2-hydroxy Schiff bases determined by ^1H NMR spectroscopy are outlined in table 3. In $CDCl_3$, the ^1H NMR data for salicylaldimine derivatives **(5–8)** show the existence of only phenol-imine tautomer (scheme 2 (A)), while both keto-amine and phenol-imine forms have been observed for naphthaldimine derivatives **(10–12)** (scheme 2 (A) and (F), figure 1, table S2). It means that the ^1H NMR spectra of naphthaldimine derivatives **(10–12)** show that both phenol-imine and keto-amine forms are in equilibria. The relative ratios of keto-amine/phenol-imine tautomers are estimated from the spectra of **10**, **11** and **12** as 50/50, 83/17 and 95/5, respectively. In DMSO, phenol-imine tautomer is only observed for salicylaldimines **(5–8)**, while keto-amine tautomer for naphthaldimines **(10–12)**. For instance, the doublets observed at ~9·19 and ~15·80 ppm (table S2), respectively, for the protons of HC–NH and HC–NH of naphthaldimines **(10–12)** illustrate the keto-amine form as supported by the location of the hydrogen atom on nitrogen and leading to an N–H...O hydrogen bonding. Whereas, for salicylaldimines **(5–8)**, two signals each appeared as a singlet at ~8·76 and ~13·79 ppm (table S1) can be ascribed to HC=N and ArOH indicated that the tautomeric equilibrium in these compounds favours the phenol-imine form in both $CDCl_3$ and DMSO, showing N...H–O hydrogen bonding and *E*/*E* geometric isomer (scheme 2 (A)). According to ^1H NMR spectra of compound **9**, two geometric isomers (one of them is *E*/*E* (A), the other one is likely to be *E*/*E* (B) or *Z*/*E* (C), scheme 3) have been observed in $CDCl_3$ (figure 1). In compound **13**, a naphthaldimine derivative, only one of the geometric isomers of the phenol-imine form (possibly *E*/*E* (A) (scheme 3)) has been defined.

In the ^1H NMR spectra of salicyclaldimine **(6)** and naphthaldimine **(11)** Schiff bases in DMSO, the peaks at 7·59 (*d*, 2H); 7·40 (*t*, 2H); 6·95 (*t*, 2H); 6·96 (*d*, 2H); 7·15 (*d*, 2H); 7·02 (*t*, 2H); 7·24 (*t*, 2H); 7·46 (*d*, 2H) ppm for **6** and at 7·83 (*d*, 2H); 8·41 (*d*, 2H); 6·83 (*d*, 2H); 7·28 (*t*, 2H); 7·22 (*t*, 2H); 8·03 (*d*, 2H); 7·69 (*d*, 2H); 7·49 (*t*, 2H); 7·07 (*t*, 2H); 7·31 (*d*, 2H) ppm for **11** are assigned to be H2, H3, H4, H5, H8,

Table 3. Tautomeric species of the 2-hydroxy Schiff bases in solution.

Aldimine type	Compound		Tautomer found by NMR spectroscopy
Salicylaldimine	(**5**–**8**)	$CDCl_3$	Phenol-imine (one tautomer; A)
		DMSO	Phenol-imine (one tautomer; A)
	(**9**)	$CDCl_3$	Phenol-imine (two tautomers; A and B or C)
		DMSO	Phenol-imine (one tautomer; A)
Naphthaldimine	(**10**–**12**)	$CDCl_3$	Keto-amine (F); phenol-imine (A)
		DMSO	Keto-amine (F)
	(**13**)	$CDCl_3$	Phenol-imine (one tautomer; A)
		DMSO	Phenol-imine (one tautomer; A)
		$CDCl_3$/DMSO	Phenol-imine (one tautomer; A)

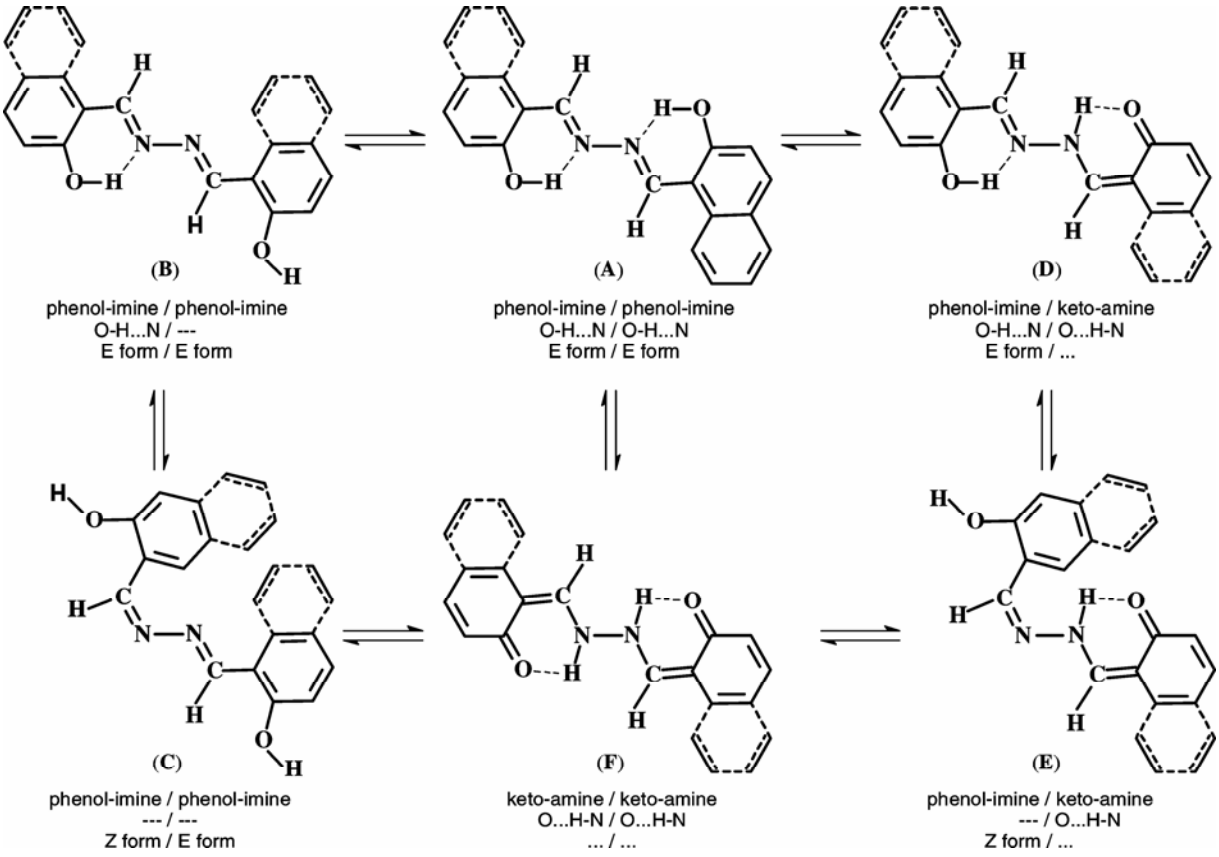


Scheme 2.

H9, H10 and H11 for **6** and H2, H3, H8, H9, H10, H11, H13, H14, H15, H16 for **11** (table S1). All of the possible carbon peaks are observed in the ^{13}C NMR spectra, as expected. Assignments of the aromatic protons and carbons have been made ambiguously by two-dimensional heteronuclear-correlated experiments (HETCOR) using the values corresponding to $^{1}J_{(C,H)}$, heteronuclear multiple bond correlation (^{1}H–^{13}C HMBC) using the values corresponding to $^{2}J_{(C,H)}$ or $^{3}J_{(C,H)}$ between the carbons and protons and DEPT spectra. As examples, figure 2, S2 in Supplementary materials and 4 of **6** and figures S1 in Supplementary materials, 3 and 5 of **11** are given. In these figures, all of the aromatic proton and carbon signals are labeled. The other salicycladimine and naphthaldimine derivatives show similar characteristics as those discussed in compounds **6** and **11** in both DMSO and $CDCl_3$ (tables S1, S2 and S3). All of the aliphatic protons and carbons are easily distinguishable. In compounds **7**, **8** and **12** which contain *o*-xylylene precursor, the C1′, C2′ and C3′ carbons and H2′ and H3′ protons are also easily distinguished and assigned by using HETCOR, HMBC and DEPT methods (tables S1 and S2). ^{1}H–^{13}C HMBC multiple bond correlations, a modified version of HETCOR, were applied on **6**

Table 4. 2D ^{1}H–^{13}C HETCOR and HMBC correlations for **6** and **11**.

		HETCOR	HMBC [J(C, H)]			
	Atom	^{1}J	^{2}J	^{3}J	^{4}J	$^{Spatial}J$
6	H2	C2	C1, C3	–	–	–
	H3	C3	C2	C1	–	–
	H4	C4	C5	–	–	–
	H5	C5	C4	–	–	–
	H8	C8	C7, C9	–	–	–
	H9	C9	C8	C7	–	–
	H10	C10	C11	C12	–	–
	H11	C11	C10, C12	–	–	–
	HC=N	HC=N	C6	C1, C7	–	–
	OH	–	C1	C6	C5	–
11	H2	C2	C1	C4	–	
	H3	C3	–	–	–	C7, C8
	H8	C8	C7	C10	–	–
	H9	C9	C10	–	–	–
	H10	C10	C11	C12	–	–
	H11	C11	C10, C12	–	–	–
	H13	C13	C4, C14	–	–	–
	H14	C14	C13	C4	–	–
	H15	C15	C16	C5	–	–
	H16	C16	C5, C15	–	–	–
	HC–N	HC–N	C1, C5	C7	–	C15



Scheme 3.

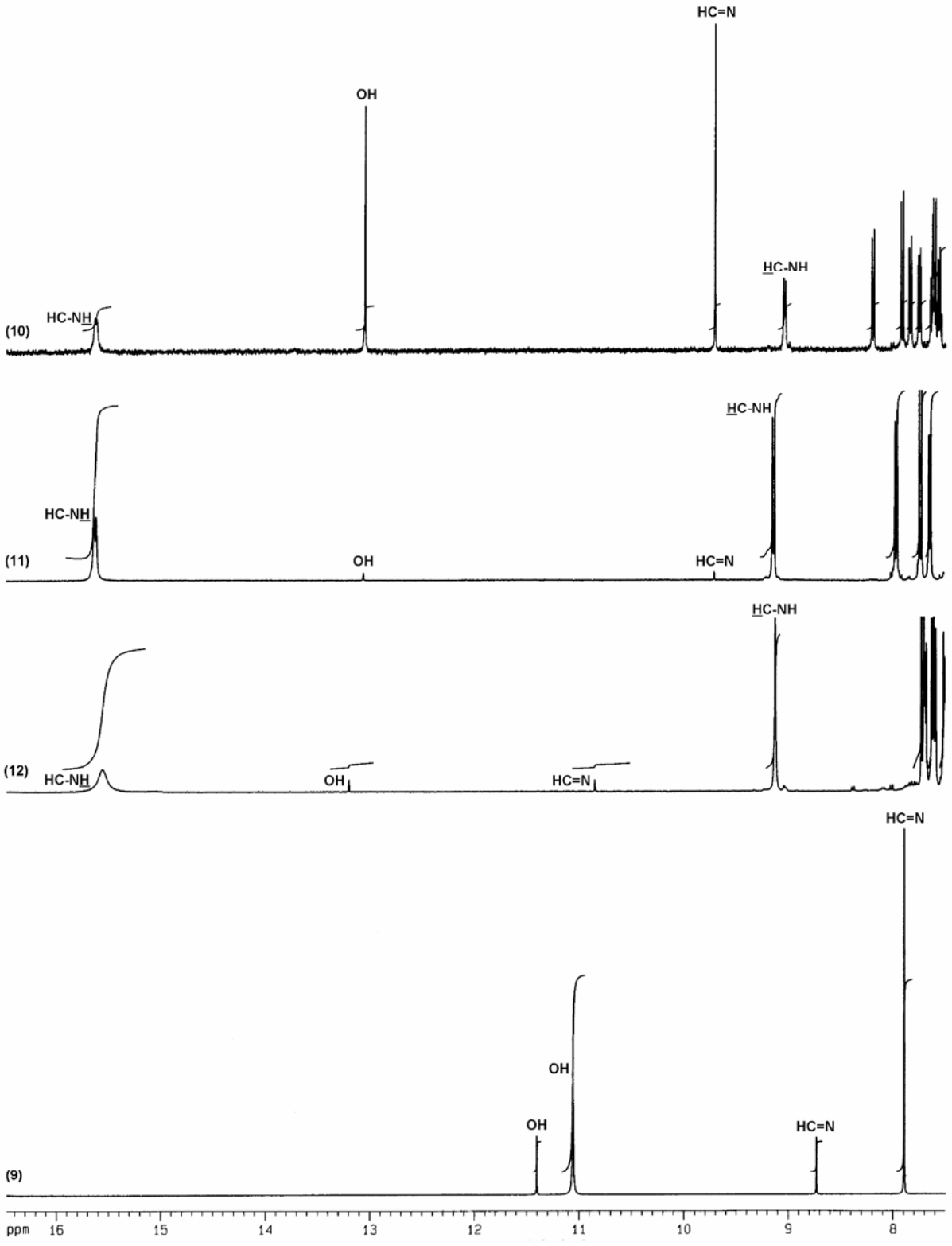


Figure 1. ^{1}H NMR spectra of naphthaldimine (**10**–**12**) and salicylaldimine (**9**) derivatives in $CDCl_3$.

and **11** in order to determine the long range ^{1}H–^{13}C connectivities (figures S2 and 3, table 4). The HCN protons of **6** and **11** were located near to C7 rather than hydroxyl proton (O–H...N) or amine proton (O...H–N) owing to the relationship observed; HCN protons are correlated with C1, C6 and C7 atoms for

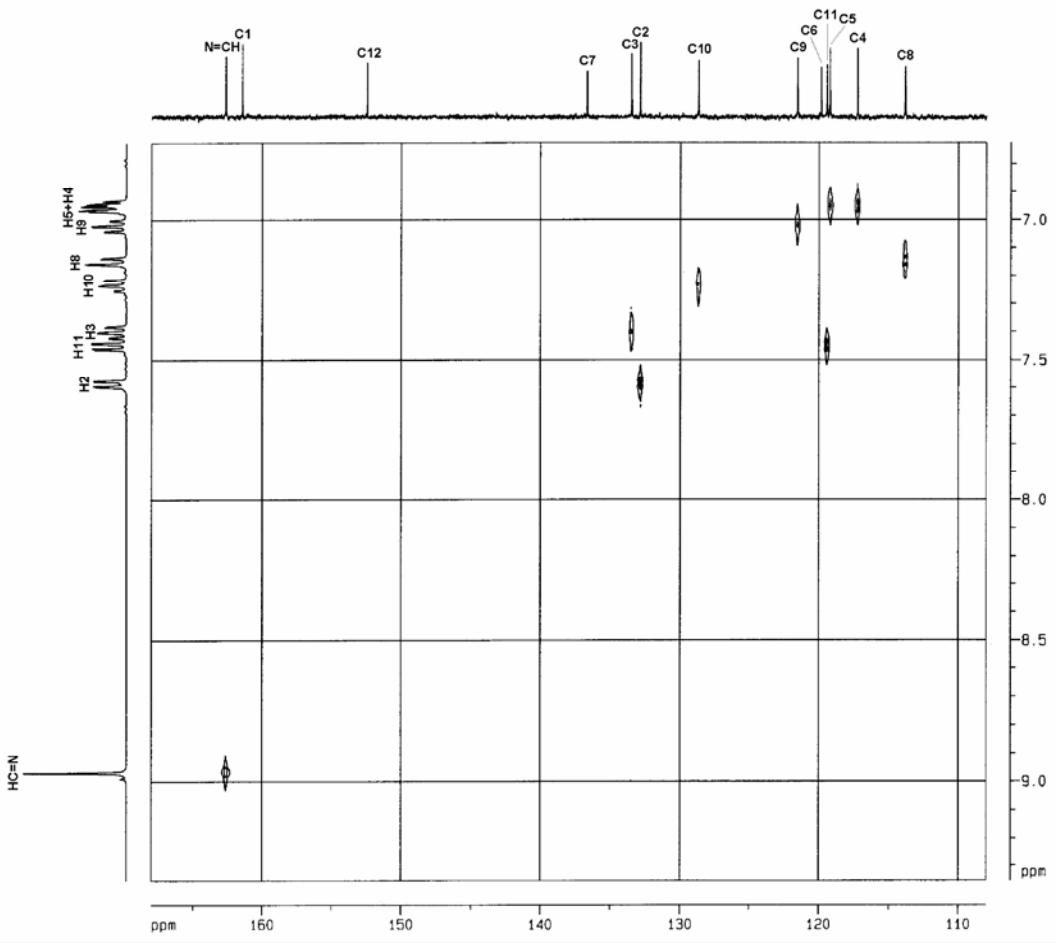


Figure 2. HETCOR spectrum of **6**.

6 and C1, C5, C7 and C15 atoms for **11**. Consequently, according to the NMR results (HETCOR and HMBC), the possible conformations of **6** and **11** in DMSO solution are illustrated in figure 6.

3.3 *UV-visible spectroscopy*

In the UV-visible spectra of salicylaldimine and naphthaldimine derivatives, four main bands are to be expected; namely the first (210–234 nm) and second (240–282 nm) bands are atributed to the $\pi \rightarrow \pi^*$ transitions of aromatic rings. The third band at 300–340 nm is assigned to the $\pi \rightarrow \pi^*$ transitions of C=N group. The forth band at >400 nm involves $n \rightarrow \pi^*$ transitions of C=O group. The UV-vis spectra of the compounds (**5**–**13**) were studied in polar and non-polar solvents both in acidic (CF_3COOH) and basic (NEt_3) media. The keto-amine isomer ratios of the compounds in various solvents, acidic and basic media are listed in table S4 in Supplementary materials. The UV spectra of (**6** and **11**) and (**9** and **13**) in different solvents are illustrated in figures S3 and S4 in Supplementary materials, respectively as examples, indicating the phenol-imine/keto-amine tautomeric forms. In addition, figure S5 in Supplementary materials shows the acidic and basic effects of **8** in CH_2Cl_2 solution, which is also an example for salicylaldimines. Generally, the keto-amine tautomer was always observed when the Schiff bases were derived from 2-hydroxynaphthaldehyde.[37,51] For Schiff bases derived from salicylaldehyde, the keto-amine form was not observed in polar and non-polar solvents. No absorption bands were observed above 400 nm in DMSO, EtOH, CH_2Cl_2 and *n*-hexane for compounds (**5**–**9**). However, for the compounds (**10**–**13**) new additional bands were detected at >400 nm, in the same solvents. The keto-amine/phenol-imine tautomeric equilibria (calculated in table S4) are present for the compounds. In naphthaldimine compounds (**10**–**12**), the keto-amine form was dominant in solvent, acidic and basic media. But, for compound **13**, in solid-state[38] and in $CDCl_3$

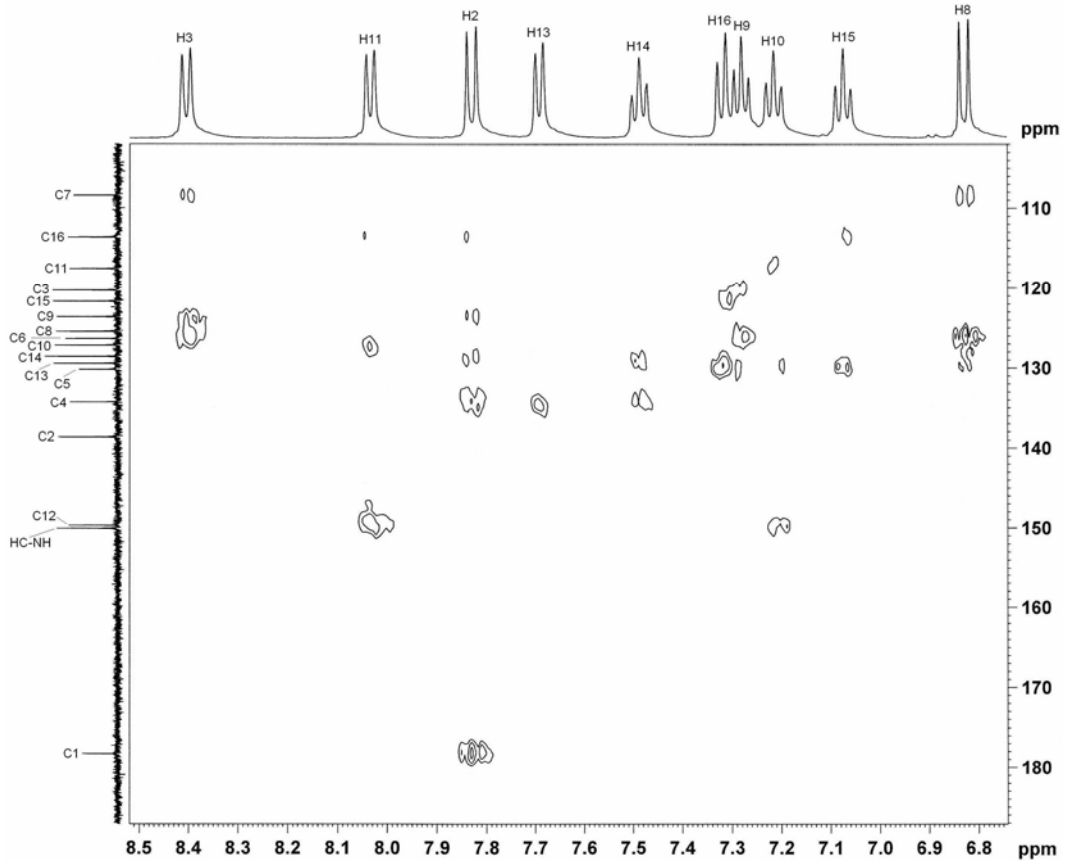


Figure 3. HMBC correlations for **11**.

solution (table S3), there is only phenol-imine tautomer, whereas in DMSO, EtOH, CH_2Cl_2 and *n*-hexane, keto-amine tautomer is dominant. In addition, in Schiff bases derived from the salicylaldehyde (**5**–**9**), only the phenol-imine form was observed in pure solvents and basic media, while the keto-amine tautomer was dominant only in acidic solution of CH_2Cl_2 and *n*-hexane, except **9**. These results in acidic solution indicate that salicylaldimines (**5**–**8**) give salts with CF_3COOH, but **9** does not seem to afford any salt with CF_3COOH. For the compounds (**5**–**9**), the absence of keto-amine form in acidic solutions of DMSO and EtOH may probably be explained by the hydrogen bonding to CF_3COOH. In basic solution, the keto-amine (O...H–N) and phenol-imine (O–H...N) ratios were approximately the same as in the respective pure solvent media of all the compounds. In acidic solution, for the naphthaldimine derivatives of the compounds (**10**–**12**) the keto-amine tautomer ratio (%) was increased to 61–70 with respect to pure solvents. The bathochromic shifts both above and below 400 nm in all of the solvents studied (DMSO, EtOH, CH_2Cl_2 and *n*-hexane) do not depend on the solvent polarities for all the compounds.

3.4 *X-Ray analysis of* **8**

Single crystal X-ray structure of compound **8** is reported to further corroborate the structural assignments. The molecular structure with atom-numbering scheme is shown in figure 7. The bond lengths and angles with some selected torsion angles are given in table 2. Compound **8** is in the phenol-imine form in solution, at least in $CDCl_3$ according to the NMR result (table S1), in DMSO, EtOH, CH_2Cl_2 and *n*-hexane (table S4). The two strong intramolecular O–H...N hydrogen bondings [O1–H1A 0·96(3), H1A...N1 1·72(3), O1...N1 2·596(2) Å, O1–H1A...N1 150(2)° and O4–H4A 0·88(3), H4A...N2 1·81(2), O4...N2 2·599(2) Å, O4–H4A...N2 148(2)°] also show that compound **8** is in phenol-imine form (figure 7, table S5 in supplementary materials) in the solid state. On the basis of crystal studies of intramolecular hydrogen bonds, a short hydrogen bond

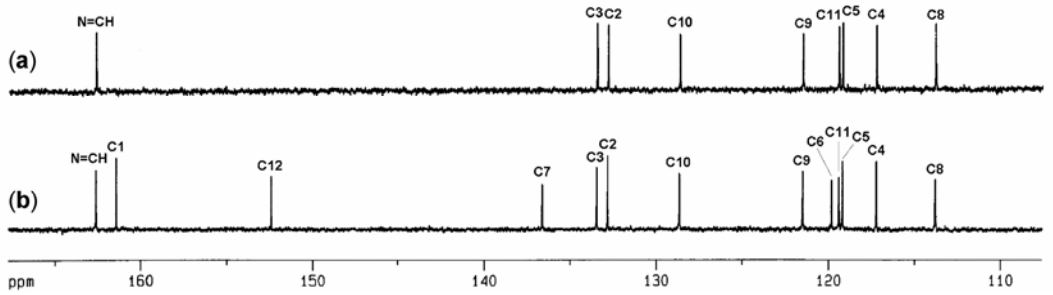


Figure 4. (**a**) DEPT and (**b**) ^{13}C NMR spectrum of **6**.

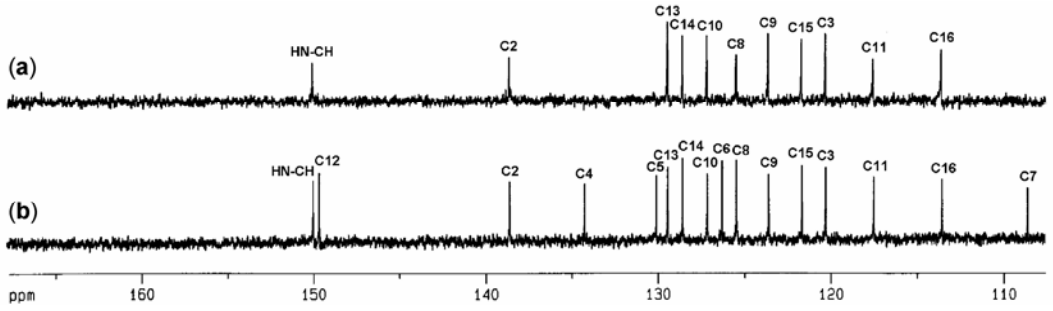


Figure 5. (**a**) DEPT and (**b**) ^{13}C NMR spectrum of **11**.

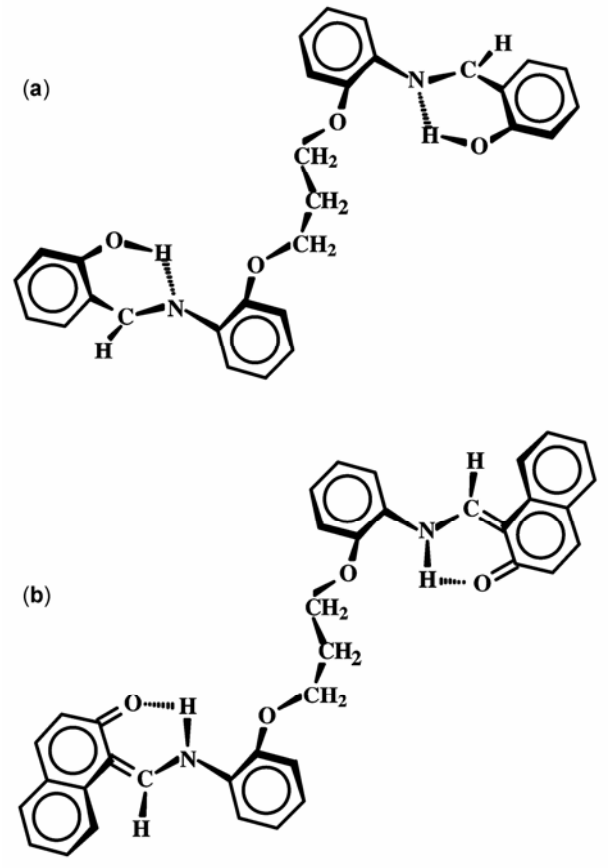


Figure 6. The possible conformers of (**a**) compound **6** and (**b**) compound **11** at ambient temperature in DMSO.

associated with a charge flow through the system of conjugated double bonds is denoted 'resonance-assisted hydrogen bonding'[44,52] and a delocalization parameter, $Q = (d_1 - d_4) + (d_3 - d_2)$, is defined (distances d_1 to d_4 are as defined in table S5). In general, the Q values have positive and negative signs in phenol-imine and keto-amine tautomers, respectively, except for XIV and XV (table S5). Compounds XIV and XV have OH groups located on the salicylidene moieties, and in the asymmetric units where there are two independent molecules. The molecules are linked by strong intra- and intermolecular O–H...O hydrogen bonds into a three dimensional network.[64,65] Hence, the O–H...O hydrogen bonds may change the charge flow through the system of conjugated double bonds and Q values of XIV and XV. In compound **8**, Q values are calculated as 0·116(3) and 0·122(2) Å indicating also that the compound is in the phenol-imine form. These values are comparable with the corresponding values in the analogous compounds (table S5). There is no clear relationship between the corresponding Q and N...O values.

In **8**, the C2=C3 [1·376(4) Å] and C31=C32 [1·364(3) Å] bonds are shorter than the expected value [~1·40 Å]. The C1=O1 [1·345(3) Å] and C30=O4 [1·350(2) Å] bonds are longer, while N1=C7 [1·278(2) Å] and N2=C28 [1·272(2) Å]

bonds are shorter than those of naphthaldimine derivatives, which can be explained by the quinoidal structure.[73] These values also support that the compound is in phenol-imine form in the solid state. The Φ_{CN} torsion angles C8–N1–C7–C6 [–175·45(15)°] and C25–N2–C28–C29 [–179·12(16)°] show that the configurations about the N1=C7 and N2=C28 bonds are *anti* (1*E*), which are in accordance with the phenol-imine (*E* form)/phenol-imine (*E* form) [scheme 1, (A)].

4. Conclusions

On the basis of the imine backbone, a straightforward method was used to prepare the 2-hydroxy salicylaldimines and naphthaldimines, which are likely to be intramolecular hydrogen bonding agents, e.g. O–H...N (phenol-imine tautomer) and O...H–N (keto-amine tautomer). In this study, the salicylaldimine and naphthaldimine derivatives have been systematically characterized in detail by using IR, MS, UV-vis, 1D (DEPT, ^{1}H and ^{13}C) and 2D (HETCOR and HMBC) NMR techniques. 2D-techniques are very useful for assignments of the all aromatic protons and carbons. The structure of the representative compound **8**, which is a salicyaldimine derivative, has been unequivocally confirmed from single crystal X-ray diffraction analysis to establish the intramolecular hydrogen bonds and phenol-imine tautomer. The tautomeric equilibria of the compounds have also been investigated in polar and non-polar solvents by using NMR and UV-vis spectral data. In addition, for 2-hydroxy Schiff bases in table S5, delocalization parameters 'Q' have been calculated in order to discuss the tautomerism in the solid state. As known, tautomerism is a very complex phenomenon and more detailed investigations on these types of compounds are needed.

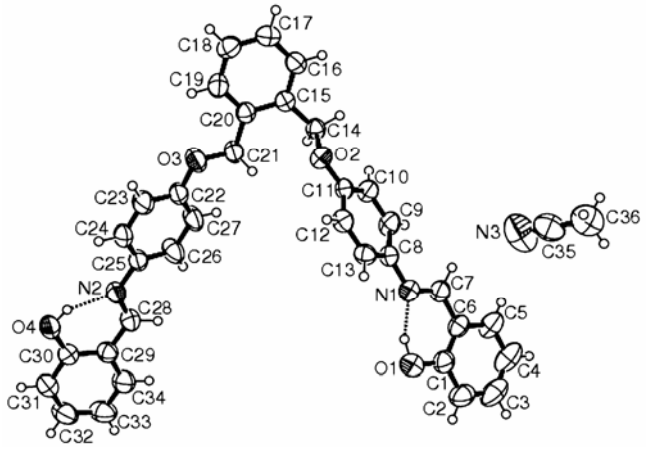


Figure 7. Molecular structure of **8**. Thermal ellipsoids are drawn at the 40% probability level. Hydrogen bonds are shown as dashed lines.

Supplementary materials

The X-ray crystallographic data in the CIF format for the structure reported in this paper have been deposited with the Cambridge Crystallographic Data Center, and the supplementary crystallographic data can be obtained free of charge on request at www.ccdc.cam.ac.uk/conts/retrieving.html (or from The Director, Cambridge Crystallographic Data Center, CCDC, 12 Union Road, Cambridge CB2 1EZ, UK; fax: +44(0)1223-336033; e-mail: deposit@ccdc.cam.ac.uk), quoting the CCDC number 653274. NMR characterization (tables S1, S2 and S3 and figures S1 and S2), UV-vis data (table S4 and figures S3, S4 and S5) and table S5 are available free of charge on the Internet.

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