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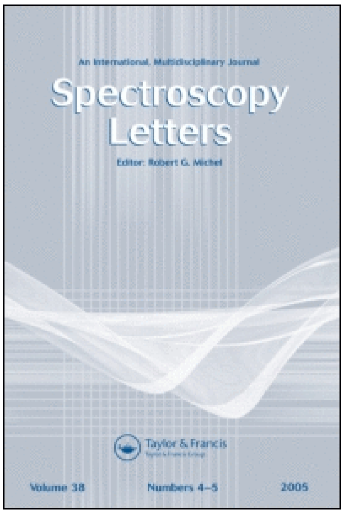

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Synthesis and Spectroscopic Studies of Some New Polyether Ligands of the Schiff Base Type

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Synthesis and Spectroscopic Studies of Some New Polyether Ligands of the Schiff Base Type

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ABSTRACT

New polyether ligands of Schiff base type (**3**–**13**) were synthesized from the reaction of diethylene glycol *bis*(2-aminophenyl)ether and triethylene glycol *bis*(2-aminophenyl)ether with salicylaldehyde, 5-methoxysalicylaldehyde, 5-bromosalicylaldehyde, 5-nitro salicylaldehyde, and 2-hydroxy-1-naphthaldehyde. The products were characterized by elemental analysis, IR, ^{1}H, ^{13}C NMR, and UV-VIS techniques. The UV-VIS spectra of those Schiff bases with an OH group in the ortho position to the imino group were studied in polar and nonpolar solvents in acidic and basic media. The compounds are in tautomeric equilibrium (enol-imine, $O{-}H\cdots N \rightleftharpoons$ keto-amine, $O\cdots H{-}N$ forms) in solvents, acidic chloroform, and benzene solutions and basic DMSO, chloroform, and benzene solutions.

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These tautomers were not observed in polar and non-polar solvents and in basic solutions of DMSO, chloroform, and benzene for the Schiff bases **5–10**. Tautomer proportions, which were obtained from ^{1}H NMR and UV-VIS data in DMSO, were compared for compounds **3**, **4**, **11**, and **12**.

Key Words: Schiff base; Tautomerism; Solvent effect; Polyether; Basic solutions.

INTRODUCTION

Schiff bases, with an OH group in the ortho position to the imino group, and their complexes derived from the reaction of salicylaldehyde and 2-hydroxy-1-naphthaldehyde with amines, have been extensively studied and a number of them are being used as models for biological systems.[1–9] Tautomerism in Schiff bases, with an OH group in ortho position to the imino group both in solution and in solid state, have been investigated using spectroscopy and x-ray crystallograpy techniques.[10–20] Schiff bases with an OH group in ortho position to the imino group are of interest mainly due to the existence of either O–H···N or O···H–N hydrogen bonds and due to tautomerism between the enol-imine and keto-amine form. In these compounds, short hydrogen bonds between the OH group in the ortho position to the imino group and the imine nitrogen is due to the stereochemistry. In some instances the hydrogen from the OH group is completely transferred to the imine nitrogen. In other words, enol-imine $\rightleftharpoons$ keto-amine equilibrium shifts predominantly to the keto-amine side.[10–13,15,16] In the UV-VIS spectra of Schiff bases with the OH group in ortho position to the imino group a new band at wavelengths greater than 400 nm is observed in polar and nonpolar solvents. The results indicate that the absorption band at 400 nm belongs to the keto-amine form of the Schiff base. This tautomer is always observed when the Schiff base is derived from 2-hydroxy naphthaldehyde and aromatic amine. In Schiff bases derived from salicylaldehyde and aromatic amine the keto-amine form is not observed in polar and nonpolar solvents, but it is observed in acidic media.[10,11,13,14,16,17,20] Although there are large numbers of crown ether, acyclicpolyether and *bis*(crown ether) Schiff base ligands,[21–26] no studies of the reactions of the acyclic aminopolyethers, with substituted 2-hydroxy-1-benzaldehyde to produce new polyether ligands of Schiff base type, have been published. Reported here are spectroscopic studies of Schiff bases **3–13** and the tautomerism of the Schiff bases **3**, **4**, and **9–12** formed by reaction of 1,5-di[oxyphenyl-2-amino]-3-oxapentane (**1**) and 1,8-di[oxyphenyl-2-amino]-3,6-dioxaoctane (**2**) (podand) with 5-methoxy-, 5-bromo-, 5-nitro-, 5-nitrosalicylaldehyde sodium salt, salicylaldehyde, and 2-hydroxy-1-naphthaldehyde, respectively.

EXPERIMENTAL

Reagents and Techniques

The ^1H and ^{13}C NMR spectra were recorded on a Bruker DPX FT-NMR spectrometer operating at 400 and 101.6 MHz. The ^1H and ^{13}C chemical shifts were measured using $SiMe_4$ as an internal standard. Infrared absorption spectra were obtained from a Perkin–Elmer BX II spectrometer in KBr discs and were reported in cm^{-1} units. The UV-VIS spectra were measured using a SHIMADZU 1208 series spectrometer. Carbon, nitrogen, and hydrogen analyses were performed on a LECO CHNS-932 analyzer. Melting points were measured on an Electro Thermal IA 9100 apparatus using a capillary tube. 2-Nitrophenol, diethyleneglycol, triethyleneglycol, salicylaldehyde, 2-hydroxy-1-naphthaldehyde, 5-methoxysalicylaldehyde, 5-bromosalicylaldehyde, 5-nitrosalicylaldehyde, hydrazinehydrate, Pd–C (10%), THF, $CHCl_3$, EtOH, benzene, DMSO, DMF, CF_3COOH, $(C_2H_5)_3N$, and $SOCl_2$ were purchased from Merck (Germany).

Synthetic Procedures

Synthesis of Aminopolyethers

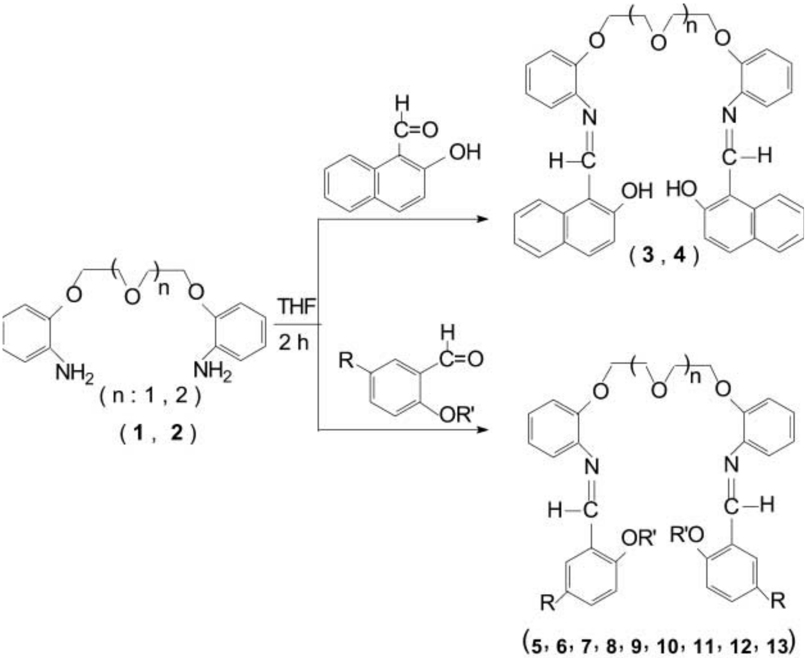
Diethylene glycol *bis*(2-aminophenyl)ether (**1**) and triethylene glycol *bis*(2-aminophenyl)ether (**2**) were prepared according to the published procedure.[27]

Synthesis of Schiff Bases

*Synthesis of 1,5-Di[N-2-oxyphenyl-2-oxo-1-naphthylidenemethylamino]-3-oxapentane (**3**)*

Diethylene glycol *bis*(2-aminophenyl)ether (**1**) (1.00 g, 0.0035 mol) was added to a dry THF (100 mL) solution of 2-hydroxy-1-naphthaldehyde (1.20 g, 0.0070 mol). The mixture was stirred and refluxed for 2 hr. Compound (**3**) was obtained from the evaporation of THF. It was crystallized from $CHCl_3$: n-hexane (3 : 1).

Other Schiff bases were obtained by the same method. The synthesis of Schiff bases is described in Sch. 1. Analytical and experimental details for all compounds are given in Table 1.



Compound	n	R	R′
1	1		
2	2		
3	1		
4	2		
5	1	H	H
6	2	H	H
7	1	OCH_3	H
8	2	OCH_3	H
9	1	Br	H
10	2	Br	H
11	1	NO_2	H
12	2	NO_2	H
13	1	NO_2	Na

Scheme 1.

Table 1. Experimental and analytical data.

Compound	Formula	MW	Color	Yield (%)	M.p. (°C)	Calculated (%)			Found (%)		
						C	H	N	C	H	N
(**3**)	$C_{38}H_{32}N_2O_5 \cdot H_2O$	614	Yellow	88	220	74.26	5.53	4.56	73.53	4.49	4.60
(**4**)[a]	$C_{40}H_{36}N_2O_6 \cdot H_2O$	658	Yellow	71	122	72.94	5.77	4.25	72.11	6.03	4.48
(**5**)	$C_{30}H_{28}N_2O_5$	496	Yellow	92	72	72.58	5.64	5.64	72.28	5.42	5.57
(**6**)[a]	$C_{32}H_{32}N_2O_6$	540	Yellow	80	96	71.11	5.92	5.18	70.81	5.51	5.25
(**7**)	$C_{32}H_{32}N_2O_7$	556	Yellow	67	115	69.06	5.75	5.03	68.76	5.40	5.05
(**8**)	$C_{34}H_{36}N_2O_8$	600	Yellow	70	73	68.00	6.00	4.66	67.7	6.02	4.33
(**9**)	$C_{30}H_{26}N_2O_5Br_2$	654	Yellow	58	129	55.04	3.97	4.28	54.80	3.65	4.20
(**10**)	$C_{32}H_{30}N_2O_6Br_2$	698	Yellow	55	103	55.03	4.32	4.01	54.85	4.11	3.98
(**11**)	$C_{30}H_{26}N_4O_9$	586	Red	61	212	61.43	4.43	9.55	61.55	4.45	9.50
(**12**)	$C_{32}H_{30}N_4O_{10}$	630	Red	62	163	60.95	4.76	8.88	61.03	4.75	8.80
(**13**)	$C_{30}H_{24}N_4O_9Na_2$	630	Yellow	50	190	57.14	3.80	8.88	56.85	3.89	8.58

[a] Experimental and analytical data were obtained from literature.[10]

RESULTS AND DISCUSSION

IR, ^{1}H NMR, ^{13}C NMR, and UV-VIS Spectroscopy

The IR spectra of the compounds are given in Table 2 Vibration bands with the wave numbers of 1612–1625 cm^{-1} ($\nu_{C=N}$), 3060–3080 cm^{-1} (ν_{C-H}, Ar-H), 2978–2868 cm^{-1} (ν_{C-H}, Csp^3-H), 1580–1600 cm^{-1} ($\nu_{C=C}$), and 1293–1046 cm^{-1} (ν_{C-O-C}, Csp^3–O–Csp^3) were observed. The observation of aromatic (ν_{C-O}) at 1316 and 1320 cm^{-1} for compounds **3** and **4**, respectively, are the evidence for the existence of the keto-amine form N–H···O intramolecular hydrogen bonding only in the solid state. The ν_{C-O} (Ar–O) and ν_{C-O-C} (–CH$_2$–O–CH$_2$–) vibration bands overlap with each other in compounds **5–13**. The stretching frequency observed at 2742–2748 cm^{-1} in **5–12** shows the presence of O–H···N intramolecular hydrogen bond.[10]

In the solution media of compounds, the existence of the intramolecular hydrogen bonding N–H···O has been confirmed by NMR spectroscopy in some Schiff bases.[17,28,29] The ^{1}H NMR data are given in Table 3 for compounds **3–13**. ^{1}H and ^{13}C NMR spectra of some Schiff bases prepared from 2-hydroxy-1-naphthaldehyde and substituted anilines were measured and assigned in a variety of solvents.[28,29] Based on the ^{13}C chemical shifts and $^3J_{(C\underline{H}N\underline{H})}$, the ratio of the keto-amine and enol-imine tautomers was derived using the ^{13}C chemical shifts and ^{1}H–^{1}H coupling constants; both methods give comparable results.[28] ^{1}H NMR spectra of some Schiff bases were measured in a range of solvents, and the presence of a $^3J_{(C\underline{H}N\underline{H})}$ coupling between the exchangeable and the olefinic proton, confirmed by decoupling, was interpreted as being due to the presence of the keto-amine tautomer. This coupling and $^1J_{(N\underline{H})}$ were measured in a range of solvents and, with a good reference value for this in a non-tautomeric situation of 96 Hz, it is then possible to deduce a value for $^3J_{(C\underline{H}N\underline{H})}$ for pure keto-amine tautomer of 11.6 Hz.[28] The results are comparable to the UV-VIS data and ^{1}H–^{1}H coupling constants. The calculated tautomer proportions for **3** and **4**, both based on the UV-VIS and ^{1}H NMR data are given Table 4, showing good agreement between the two methods. While the tautomerism for compounds **11** and **12** was observed only by UV-VIS in DMSO, it was observed by both UV-VIS and ^{1}H NMR in DMSO for compounds **3** and **4**. The ^{1}H NMR data for compounds **5–13** show that the tautomeric equilibrium favors the enol-imine in DMSO. The compounds **3** and **4** shift to the keto-amine form in the same solvent. The protons of the etheric group at Ar–OC$\underline{H_2}$– also gave a triplet, Ar–OCH$_2$C$\underline{H_2}$– triplet and –OC$\underline{H_2}$– triplets and singlets for **3**, **5**, **7**, **9**, **11**, and **13** and **4**, **6**, **8**, **10**, and **12**. According to the ^{13}C NMR spectra compounds (**5**, **9**, **11**, **13**), (**6**, **7**, **10**, **12**), and (**8**) have

Table 2. IR spectral data. The wave numbers, ν are reported in cm^{-1} units.

Compound	$\nu_{O\underline{H}}$	$\nu_{Ar-\underline{H}}$	$\nu_{Csp3-\underline{H}}$	$\nu_{C=N}$	$\nu_{C=C}$	$\nu_{Csp3-O-Csp3}$
(3)	3401 m	3062 m	2929 s, 2868 m	1625 s	1590 s	1292 s, 1259 s 1158 s, 1112 s
(4)	3412 br	3080 m	2927 s, 2876 m	1625 s	1600 s	1293 s, 1268 s 1165 s, 1140 s
(5)	3435 m 2748 w	3060 m	2966 s, 2934 s, 2876 m	1622 s	1580 s	1279 s, 1259 s 1144 s, 1112 s
(6)	3361 m 2748 w	3080 m	2978 m, 2927 s, 2876 s	1625 s	1600 s	1293 s, 1268 s 1140 s, 1114 s
(7)	3364 m 2742 w	3061 m	2960 s, 2876 m	1612 s	1584 s	1291 s, 1255 s 1150 s, 1041 s
(8)	3446 m 2742 w	3062 m	2931 m, 2874 s	1615 s	1589 s	1255 s, 1191 s 1078 s, 1046 s
(9)	3446 m 2745 w	3068 m	2931 s, 2875 m	1618 s	1590 s	1251 s, 1172 s 1116 s, 1037 s
(10)	3417 m 2745 w	3062 m	2822 s	1616 s	1590 s	1250 s, 1171 s 1118 s, 1074 s
(11)	3449 m 2748 w	3062 m	2925 s, 2874 m	1616 s	1592 s	1233 s, 1139 s 1094 s, 1048 s
(12)	3422 m 2748 w	3074 m	2876 s	1617 s	1595 s	1234 s, 1162 s 1092 s, 1054 s
(13)	—	3068 m	2935 s, 2874 s	1620 s	1593 s	1255 s, 1135 s 1095 s, 1053 s

Note: s, strong; m, medium; w, weak; br, broad.

Table 3. ^{1}H NMR spectral data in DMSO. Chemical shifts (δ) are reported in ppm.

Compound	δ O$\underline{\mathrm{H}}$	δ N=C$\underline{\mathrm{H}}$	δ Ar–$\underline{\mathrm{H}}$	δ ArOC$\underline{\mathrm{H}_2}$	δ ArOCH$_2$C$\underline{\mathrm{H}_2}$	δ OC$\underline{\mathrm{H}_2}$	δ OC$\underline{\mathrm{H}_3}$
(3)	15.77 d, 2 H ($^{3}J_{HH} = 8.6$ Hz)	9.50 d, 2 H ($^{3}J_{HH} = 8.6$ Hz)	6.80–8.38 m, 20 H	4.32 t, 4 H ($^{3}J_{HH} = 4.7$ Hz)		4.05 t, 4 H ($^{3}J_{HH} = 4.7$ Hz)	
(4)	15.57 d, 2 H ($^{3}J_{HH} = 7.6$ Hz)	9.2 d, 2 H ($^{3}J_{HH} = 7.6$ Hz)	6.75–7.97 m, 20 H	4.23 t, 4 H ($^{3}J_{HH} = 4.9$ Hz)	4.19 t, 4 H ($^{3}J_{HH} = 4.9$ Hz)	3.83 s, 4 H	
(5)	13.66 s, 2 H	8.86 s, 2 H	6.81–7.48 m, 16 H	4.10 t, 4 H ($^{3}J_{HH} = 4.7$ Hz)		3.79 t, 4 H ($^{3}J_{HH} = 4.7$ Hz)	
(6)	13.75 s, 2 H	8.73 s, 2 H	6.89–7.39 m, 16 H	4.18 t, 4 H ($^{3}J_{HH} = 4.8$ Hz)	3.89 t, 4 H ($^{3}J_{HH} = 4.8$ Hz)	3.72 s, 4 H	
(7)	13.93 s, 2 H	8.86 s, 2 H	6.73–7.34 m, 14 H	4.12 t, 4 H ($^{3}J_{HH} = 4.7$ Hz)		3.80 t, 4 H ($^{3}J_{HH} = 4.7$ Hz)	3.69 s, 6 H
(8)	13.88 s, 2 H	8.85 s, 2 H	6.73–7.32 m, 14 H	4.03 t, 4 H ($^{3}J_{HH} = 4.4$ Hz)	3.66 t, 4 H ($^{3}J_{HH} = 4.4$ Hz)	3.52 s, 4 H	3.27 s, 6 H
(9)	13.80 broad, 2 H	8.87 s, 2 H	6.80–7.71 m, 14 H	4.14 t, 4 H ($^{3}J_{HH} = 4.7$ Hz)		3.82 t, 4 H ($^{3}J_{HH} = 4.7$ Hz)	
(10)	13.42 s, 2 H	8.88 s, 2 H	6.82–7.72 m, 14 H	4.07 t, 4 H ($^{3}J_{HH} = 4.3$ Hz)	3.70 t, 4 H ($^{3}J_{HH} = 4.3$ Hz)	3.56 s, 4 H	
(11)	15.59 s, 2 H	9.22 s, 2 H	6.85–8.13 m, 14 H	4.27 t, 4 H ($^{3}J_{HH} = 4.4$ Hz)		3.95 t, 4 H ($^{3}J_{HH} = 4.4$ Hz)	
(12)	15.93 s, 2 H	9.23 s, 2 H	6.89–8.10 m, 14 H	4.17 t, 4 H ($^{3}J_{HH} = 4.9$ Hz)	3.81 t, 4 H ($^{3}J_{HH} = 4.9$ Hz)	3.33 s, 4H	
(13)	—	9.98 s, 2 H	6.36–8.90 m, 14 H	3.96 t, 4 H ($^{3}J_{HH} = 3.3$ Hz)		3.72 t, 4 H ($^{3}J_{HH} = 3.3$ Hz)	

Note: s, singlet; t, triplet; m, multiplet.

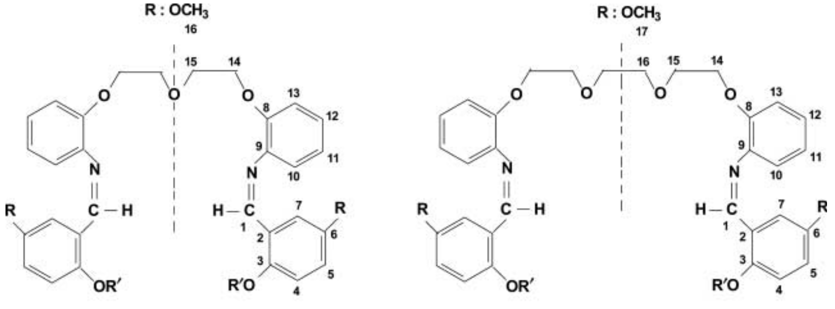
Table 4. Tautomer proportion in DMSO solution.

	Keto-amine tautomer (%)	
Compound	UV-VIS	^{1}H NMR
3	72	74
4	64	66
11[a]	39	—
12[a]	44	—

[a]Not observed.

15, 16, and 17 signals, respectively showing that the structures in solution are symmetrical. Scheme 2 shows the numbering of the Schiff base carbons. The corresponding signal is not observed in DMSO for compounds **3** and **4**. The ^{13}C NMR spectra data of the compounds are given in Table 5.

The UV-VIS spectra of the compounds were studied in polar and non-polar solvents in both acidic and basic media. The calculated keto-amine form is given in Table 6. The Schiff bases show absorption in the range greater than 400 nm in polar and non-polar solvents.[14] It should be pointed out that the new band belongs to the keto-amine form of the Schiff bases with OH group in ortho position to the imino group in polar and non-polar solvents in both



R	R′	Compound
H	H	5
OCH_3	H	7
Br	H	9
NO_2	H	11
NO_2	Na	13

R	R′	Compound
H	H	6
OCH_3	H	8
Br	H	10
NO_2	H	12

Scheme 2.

Table 5. ^{13}C NMR spectral data in DMSO.[a]

Compound	δC1	δC2	δC3	δC4	δC5	δC6	δC7	δC8	δC9
(5)	163.26	114.32	161.47	120.07	133.62	128.75	133.07	152.61	137.19
(6)	162.76	113.81	161.96	119.90	133.32	128.25	132.52	152.56	137.52
(7)	163.49	114.55	152.68	120.05	120.30	120.21	122.03	152.48	137.05
(8)	163.55	114.40	152.68	120.01	120.34	148.92	121.99	152.36	134.98
(9)	161.93	110.21	160.91	120.21	136.05	120.05	134.87	152.89	122.03
(10)	190.53	110.25	161.95	129.46	152.87	121.94	139.34	160.88	136.66
(11)	173.12	113.13	162.30	114.11	130.13	132.15	124.30	137.03	119.10
(12)	171.63	114.40	161.08	119.66	131.72	138.30	130.71	152.30	132.89
(13)	191.57	113.69	181.16	117.05	126.60	139.02	127.55	146.27	130.12
	δC10	δC11	δC12	δC13	δC14	δC15	δC16	δC17	
(5)	117.38	121.84	120.15	119.40	69.98	68.92			
(6)	117.71	121.70	120.44	119.14	71.45	70.05	68.91		
(7)	116.24	128.93	124.75	118.90	70.13	67.09	56.67		
(8)	116.12	128.96	124.73	118.94	70.88	69.81	68.91	56.60	
(9)	129.40	128.63	136.20	114.52	70.14	69.10			
(10)	114.35	136.07	134.91	120.22	70.92	69.82	68.92		
(11)	121.23	116.13	122.24	113.96	69.10	67.01			
(12)	117.82	130.12	122.04	120.57	70.98	69.77	69.10		
(13)	114.89	123.45	117.11	114.99	68.89	70.09			

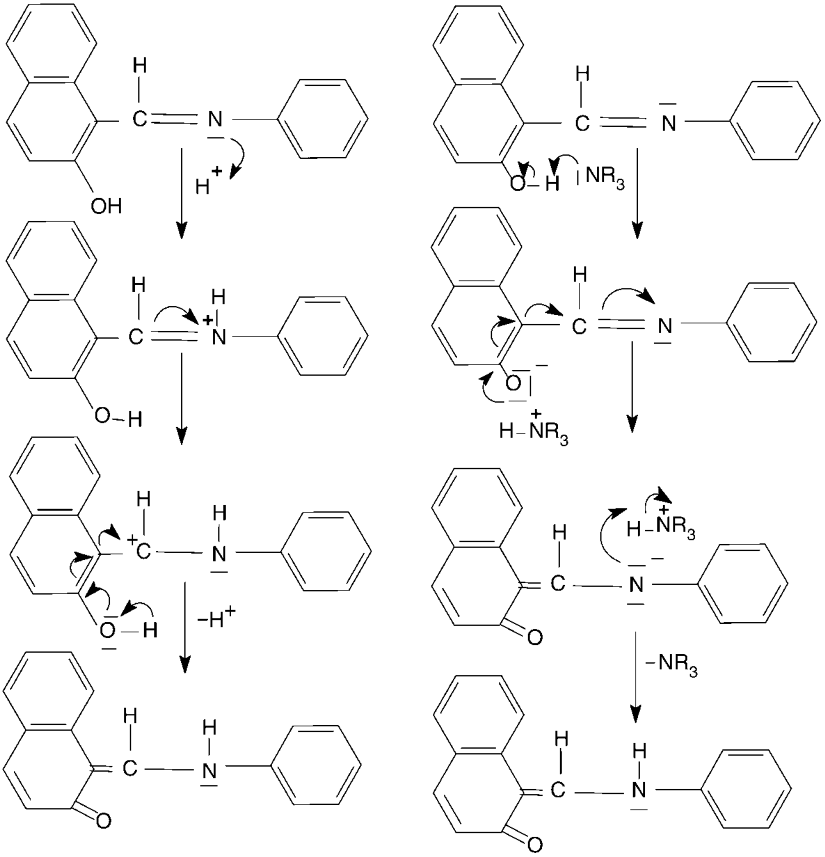
[a] Chemical shifts (δ) are reported in ppm.

Table 6. Effect of solvent, acid, and base on the UV spectra of compounds (3–13).

		Keto-amine tautomer (%)		
Compound	Solvent	Solvent media	Acidic media[a]	Basic media[b]
(3)	DMSO	72	—	94
	$CHCl_3$	70	77	86
	Benzene	37	69	44
(4)	DMSO	64	—	85
	$CHCl_3$	62	69	76
	Benzene	57	90	63
(5)	DMSO	—	—	—
	$CHCl_3$	—	58	—
	Benzene	—	4	—
(6)	DMSO	—	—	—
	$CHCl_3$	—	56	—
	Benzene	—	5	—
(7)	DMSO	—	—	—
	$CHCl_3$	—	14	—
	Benzene	—	6	—
(8)	DMSO	—	—	—
	$CHCl_3$	—	12	—
	Benzene	—	6	—
(9)	DMSO	—	—	—
	$CHCl_3$	—	10	—
	Benzene	—	11	—
(10)	DMSO	—	—	—
	$CHCl_3$	—	9	—
	Benzene	—	6	—
(11)	DMSO	39	—	54
	$CHCl_3$	17	22	45
	Benzene	12	20	24
(12)	DMSO	44	—	61
	$CHCl_3$	20	29	56
	Benzene	13	22	28
(13)	DMSO	41	—	47
	$CHCl_3$	14	31	42
	Benzene	6	11	14

[a] CF_3COOH; pH = 3.

[b] $[(C_2H_5)_3N]$; pH = 9.



Effect of acid on the keto-amine form of the Schiff Base

Effect of base on the keto-amine form of the Schiff Base

Scheme 3.

acidic and basic media.[10,11,13] The band was observed at wavelengths greater than 400 nm in polar (DMSO and chloroform) and non-polar (benzene) solvents and in acidic (CF_3COOH) solutions of chloroform and benzene and basic [$(C_2H_5)_3N$] solutions of DMSO, chloroform, and benzene for compounds (**3**, **4**, **11**, **12**, and **13**) but it is not observed in acidic DMSO solution. The compounds (**5–10**) showed no absorption above 400 nm in polar (DMSO and chloroform) and non-polar (benzene) solvents, and basic DMSO, chloroform, and benzene solutions. The band was observed with value greater than 400 nm in acidic solutions of chloroform and benzene for (**5–10**). The enol-imine tautomer is dominant only in the acidic DMSO solution for compounds **3** and **4**, while it is dominant in both acidic and basic DMSO and benzene solutions for compounds **5–10** and in both acidic and basic chloroform solution for compounds **7–10**. In contrast, keto-amine tautomer was increased by 10%, 11%, 29%, 45%, 121% and 86%, 58%, 66%, 69%, 83%, respectively, in the acidic chloroform and benzene solutions and 23%, 23%, 164%, 180%, 200%; 19%, 11%, 100%, 115%, 133%; and 31%, 33%, 38%, 39%, 15%, respectively, in the basic chloroform, benzene, and DMSO solutions with respect to the pure solvent media for **3**, **4**, **11**, **12**, and **13**. The absence of keto-amine form in the acidic DMSO solution may be explained by the hydrogen bonding to CF_3COOH.[10]

On the basis of the results obtained, the interaction between acid–base and the Schiff base molecules conceivably proceeds as given in Sch. 3.

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