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Synthesis and spectroscopic study of Schiff bases derived from *trans*-1,2-diaminocyclohexane. Deuterium isotope effect on ^{13}C chemical shift

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Abstract

The proton transfer in the intramolecular hydrogen bond in a series of Schiff bases derivatives of aromatic *ortho*-hydroxyaldehydes and *trans*-1,2-diaminocyclohexane has been studied by means of IR, UV–Vis, ^{1}H and ^{13}C NMR spectroscopies. The measurement of deuterium isotope effect on ^{13}C chemical shift suggests that the proton transfer equilibria in both salicylidene moieties are not independent. Substitution of H by D in one hydrogen bond shifts the proton transfer equilibrium in one direction in this moiety, while in the opposite direction in the other.

Keywords: Schiff bases; IR; UV–Vis; ^{1}H and ^{13}C NMR spectroscopy; Deuterium isotope effect on ^{13}C chemical shifts; Intramolecular proton transfer

1. Introduction

In the recent years, synthesis of chiral Schiff base ligands has received considerable attention due to the widespread application of their metal complexes in asymmetric syntheses [1–10]. Complexes of Schiff bases derived from 1,2-diaminocyclohexane, known as Jacobsen's catalysts, have been used in several asymmetric reactions like: epoxidation of alkenes, oxidation of sulfides, cyclopropanation of styrenes or Diels–Alder cycloaddition [1–7]. It has been shown that the catalytic properties of these complexes depend on the structure and electronic properties of the ligand [6,7].

In this work, the intramolecular hydrogen bond and proton transfer equilibrium in Schiff bases obtained by condensation of *trans*-1,2-diaminocyclohexane with salicylaldehydes (**1**–**5**) and 2-hydroxynaphthaldehyde (**6**, **7**) in $CHCl_3$ solution were studied by IR, UV–Vis and ^{1}H and ^{13}C NMR spectroscopies (Fig. 1). Several Jacobsen's complexes of similar Schiff bases have been synthesized [1–8,10], but the only ligand characterized by elemental analysis and UV–Vis, ^{1}H NMR [8], IR [2] and X-ray study [9] is compound **1**.

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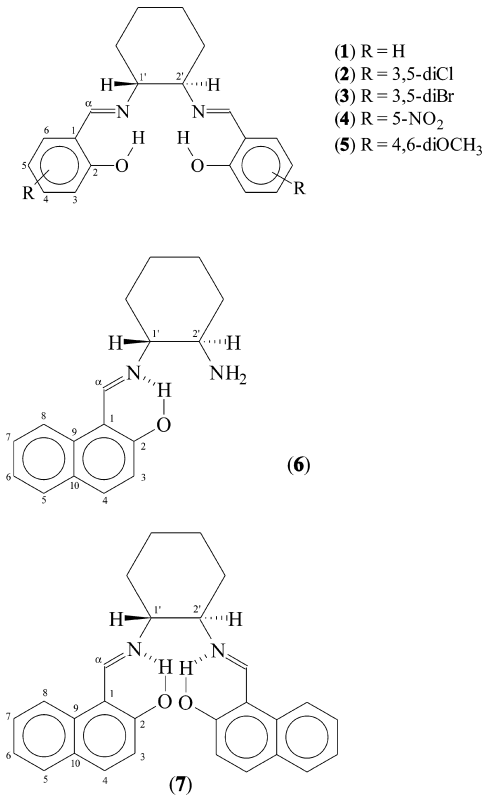

Fig. 1. Studied Schiff bases **1**–**7**.

2. Experimental

*2.1. trans-N,N′-Bis-(R-salicylidene)-1′2′-cyclohexanediamine (**1**–**5**)*

Portions of 0.002 mol of respective salicylaldehyde and 0.001 mol of *trans*-1,2-diaminocyclohexane in absolute ethanol were stirred at room temperature for 1–4 h. Solid products were filtrated and crystallised. The purity of the products was checked by elemental analysis.

1. *trans-N,N′*-Bis-(salicylidene)-1′,2′cyclohexanediamine; mp 116–118 °C (114 °C [8]); Anal. for $C_{22}H_{22}N_2O_2$ found C, 75.05; H, 6.94; N, 8.71; calcd C, 74.51; H, 6.94; N, 8.69.
2. *trans-N,N′*-Bis-(3,5-dichlorosalicylidene]-1′,2′-cyclohexanediamine; mp 104–105 °C; Anal. for $C_{20}H_{18}Cl_4N_2O_2$ found C, 51.81; H, 3.74; N, 6.13; calcd C, 52.20; H, 3.94; N, 6.09.
3. *trans-N,N′*-Bis-(3,5-dibromosalicylidene)-1′,2′-cyclohexanediamine; mp 234–236 °C; Anal. for $C_{20}H_{18}Br_4N_2O_2$ found C, 37.29; H, 2.67; N, 4.46; calcd C, 37.65; H, 2.84; N, 4.39.
4. *trans-N,N′*-Bis-(5-nitrosalicylidene)-1′,2′-cyclohexanediamine; mp 241–243 °C; Anal. for $C_{20}H_{20}N_4O_6$ found: C, 58.22; H, 4.79; N, 13.59; calcd C, 58.25; H, 4.89; N, 13.78.
5. *trans-N,N′*-Bis-(4,6-dimethoxysalicylide)-1′,2′cyclohexanediamine; mp 145–146 °C; Anal. for $C_{24}H_{30}N_2O_6$ found C, 64.50; H, 6.92; N, 6.35; calcd C, 65.14; H, 6,83; N, 6.33.

*2.2. trans-1′-(2-Hydroxynaphthylidenamine)-2′-aminocyclohexan (**6**)*

A portion of 0.002 mol of 2-hydroxynaphthaldehyde in absolute ethanol was added to 0.002 mol of *trans*-1,2-diaminocyclohexane in absolute ethanol and the mixture was stirred at room temperature for 1 h. Mp decomp., Anal. for $C_{17}H_{20}N_2O$ found. C, 76.25; H, 7.38; N, 9.94; calcd. C, 76.09; H, 7.51; N, 10.44.

*2.3. trans-N,N′-Bis(2-hydroxynaphthylidene)-1′,2′-cyclohexanediamine (**7**)*

Portions of 0.002 mol of 2-hydroxynaphthaldehyde and 0.001 mol of 1,2-*trans*-cyclohexane-diamine in abs. ethanol were refluxed for 4 h. Products were crystallized from ethanol, mp198–200 °C. Anal. for $C_{28}H_{26}N_2O_2$ found C, 79.95; H, 6.80; N, 6.32; calcd C, 79.59; H, 6.20; N, 6.63.

IR spectra were recorded on Perkin–Elmer SPECTRUM ONE spectrometer in $CHCl_3$ solution ($c = 10^{-1}$ M)

UV–Vis spectra were recorded on Specord M-Carl Zeiss Jena spectrometer in $CHCl_3$ ($c = 10^{-4}$ M).

^1H and ^{13}C NMR spectra were measured on BRUKER DPX-400 spectrometer in $CDCl_3$ solution with TMS as internal standard. Measurements of the deuterium isotope effect on ^{13}C chemical shift were performed as one-tube experiment. Degree of deuteration was estimated by ^1H NMR spectroscopy.

Deuteration of the compounds was performed by heating the compounds in CH_3OD and evaporating the solvent under reduced pressure.

Table 1
IR spectroscopic data for Schiff bases **1**–**7** (cm^{-1})

Absorption bands (cm^{-1}) of Schiff bases **1**–**7** in $CHCl_3$							Modes
1	**2**	**3**	**4**	**5**	**6**	**7**	
					3374w		νNH_2
					3300br		
				2967sh	3000m	3011m	νCH
2939m	2942m	2942m	2942m	2942m	2939s	2944s	
2863m	2864m	2866m	2864m	2863w	2862m	2863m	$\nu OH/NH$
~2650	~2550	~2550	~2550w	br,w	br,w	br,w	
1632s	1632s	1630s	1637s	1628s,br	1629s	1628s	$\nu C{=}N$ ($\nu C{=}NH^+/\nu C{=}O$)
1582m	1600sh	1598sh	1623sh	1580sh	1600sh	1600sh	
	1572w	1556w	1582m		1547m	1547m	$\nu C{=}C$
			1531m*	1544m	1526w	1526w	$\nu C{=}N + \nu C{=}C + \nu C{=}O$
1498m			1487m	1513sh	1500w	1493w	
						1479w	$\nu C{=}C$, $^*\nu NO_2$
1462m	1457s	1450s	1450w	1450m	1450m	1451w	δCH, δCH_2, δOH
1420m					1405w	1403m	
1380sh	1374m	1370m	1343s*	1367m	1349m	1367sh	$\nu C{-}N$, $^*\nu NO_2$
	1292m	1289m		1348m		1350m	
1279s	1270sh	1276sh	1296m	1239m	1256w	1314m	νCO
						1246m	
1152m	1182s	1169s		1156s	1186m	1187m	δCH, $\nu C{-}N$
1143sh	1143w	1140sh	1144w		1143m	1143m	
1093m	1104w			1117m			
		1099w	1096m	1091w	1090w	1094m	
1044w	1040w	1043w		1048m	1051w	1035w	γCH
941w	942w	958, 939w	946w	938w			
894w	869s	866s	905w	866w	860sh	860sh	γOH, $\delta C{=}NC$
848m	854m		838m	820m	836m	828m	

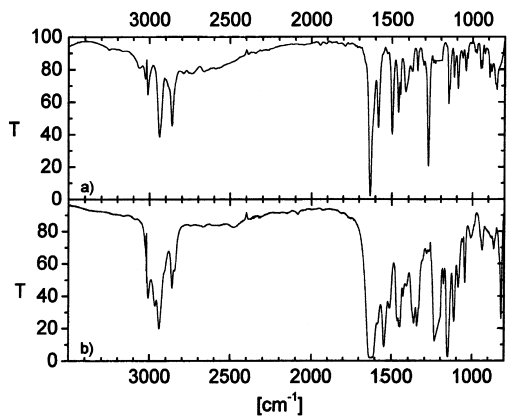

Fig. 2. IR spectra of: (a) *trans-N,N′*-bis-salicylidene-1′,2′-cyclohexanediamine (**1**), and (b) *trans-N,N′*-bis-(4,6-dimethoxysalicylidene)-1′,2′-cyclohexanediamine.

3. Results and discussion

Condensation of the *trans*-1,2-diaminocyclohexane with salicylaldehyde and its substituted analogs (3,5-diCl, 3,5-diBr, 5-NO_2 and 4,6-di-OCH_3) in ethanol at room temperature gave bis-substituted Schiff bases (**1**–**5**), irrespective of whether the substrates were used at 1:2 or 1:1 molar ratio. The equimolar mixture of 2-hydroxy-naphthaldehyde and *trans*-1,2-diaminocyclohexane in abs. ethanol stirred at room temperature gave the mono-substituted Schiff base (**6**). However, this compound is unstable at high temperatures. Crystallization of **6** in ethanol gave a mixture of mono- and bis-substituted (**7**) compounds. Purification of the mixture on the silica-gel column yielded compound **7**. These results show that the obtained mono-substituted derivatives of 1,2-diaminocyclohexane are energetically unstable relative to their bis-substituted equivalents, what confirms that

Table 2
The UV–Vis data for **1**–**7** in $CHCl_3$

Compound	λ (nm)	$\varepsilon \times 10^4$ ($mol^{-1}\,cm^{-1}$)	λ (nm)	$\varepsilon \times 10^4$ ($mol^{-1}\,cm^{-1}$)
1	319.4	1.06	–	–
2	338.5	0.77	437.1	0.09
3	339.8	0.71	436.7	0.12
4	319.5	2.69	405.3	0.18
5	–[a]	–[a]	382.4	0.69
6	365	0.46	404.5	0.98
			421.6	1.00
7	362.4	0.96	405.6	1.28
			425.1	1.25

[a] Masked by $\pi-\pi^*$ bands.

the reactions of condensation is under thermodynamical control [7]. The problems related to syntheses of mono-substituted derivatives of 1,2-diaminocyclohexane and salicylic aldehydes are known [7,10]. It is worth noting that synthesis of pure mono-substituted Schiff bases is important for obtaining unsymmetrical ligands [7,10].

3.1. IR spectroscopy

The main absorption bands are given in Table 1, and the exemplary spectra are shown in Fig. 2. The large weak absorption in the region 2000–3000 cm^{-1} indicates the presence of the relatively strong resonance assisted hydrogen (RAHB), with a large amplitude of the OH stretching vibration or the proton transfer equilibrium.

Full assignment of the IR spectra of Schiff bases is very difficult due to the extensive vibrational coupling in the molecules [11–17]. The bands observed in the 'fingerprint' region are a result of strongly mixed vibrations. In spite of numerous literature data, the assignment of several bands is still controversial [13,14,16]. Table 1 gives the main modes participating in the absorption bands in the respective regions of the spectra. Some information concerning the presence of proton transfer equilibrium can be obtained from analysis of the region 1700–1500 cm^{-1}. In the IR spectrum of compound **1** (Fig. 2a), the narrow bands at 1632 and 1582 cm^{-1} were observed in the region typical of the bands corresponding to the νC=N vibration coupled with the νC=C vibrations [12], which suggested that compound **1** existed in the OH-form. The sensitivity of the IR spectra of Schiff bases was too low to provide the evidence of the presence of the second tautomer in solution of compounds **2**–**4**. In the spectrum of **5** (Fig. 2b), a broadening of the band at about 1620 cm^{-1} and the appearance of the band at 1545 cm^{-1} [13,14] strongly suggested the existence of proton transfer equilibrium. The spectra of compounds **6** and **7** were similar; the spectrum of the former revealed the νNH_2 bands of the free amine group. The absorption in region 1628–1540 cm^{-1} was similar to that of other N-alkyl and N-aryl derivatives in which both tautomers coexisted [17].

3.2. UV–Vis spectroscopy

UV–Vis is known to be a very sensitive method for studying tautomeric equilibrium in Schiff bases. The two long-wave bands observed in the electronic spectra of these compounds have been assigned to the OH- and NH-forms [18–20]. The data for Schiff bases **1**–**7** are given in Table 2. The bands in region 320–365 nm observed in spectra of all studied compounds were assigned to the OH-form. For all compounds except **1**, the bands assigned to the NH-forms were observed in the region 380–437 nm. For compounds **6** and **7** two bands of NH-form were present in the spectra, similarly to the other Schiff bases derivatives of 2-hydroxynaphthaldehyde [18]. In the spectra of some compounds the OH-form bands overlapped with the $\pi-\pi^*$ bands. Since the molar extinction coefficients for pure NH-forms were unknown, we were unable to perform a quantitative analysis and could only compare the molar integral intensity of the NH-form bands. The lack of the NH-form absorption band in the spectrum of **1** showed that this compound existed entirely as the OH-tautomer. The small integral intensity of the NH-form band observed for compounds **2**–**4**, indicated that the proton transfer occurs and the equilibrium is strongly shifted towards the OH-form. A comparison of the respective molar integral intensity ε (for one chromofor group) with those found for similar *N*-salicylidene-alkylamines [19,20] showed that in these di-Schiff bases the position of equilibrium was shifted to the left. It is particularly marked for the Schiff bases with the NO_2 substituent in the salicylic ring [19]. Relatively greater intensity of the long-wave absorption band was observed for compound **5**,

Table 3
^{1}H and ^{13}C chemical shifts assignments in compounds **1**–**5** in $CDCl_3$ (ppm)

Compound	T (K)	δ	Position								Others
			1	2	3	4	5	6	α	1′	
1 Sal	295	C	118.61	160.91	116.74	132.13	118.57	131.45	164.67	72.62	33.08;24.16
		H	–	13.33	6.88	7.23	6.79	7.14	8.25	3.31	1.95;1.89;1.72;1.48
	270	C	118.46	160.73	116.63	132.10	118.56	131.12	164.54	72.56	33.00;24.06
		H	–	13.46	6.89	7.26	6.81	7.17	8.27	3.33	1.94;1.89;1.72;1.47
	250	C	118.33	160.58	116.56	132.08	118.57	131.40	164.44	72.51	32.94;23.98
		H	–	13.58	6.91	7.28	6.84	7.19	8.29	3.34	1.89;1.72;1.46
	230	C	188.22	160.44	116.50	132.07	118.58	131.40	164.33	72.49	32.89;23.91
		H	–	13.70	6.92	7.29	6.86	7.22	8.31	3.36	1.89;1.79;1.46
2 diCl	295	C	119.21	156.29	122.61	132.32	122.92	129.22	163.38	72.19	32.86;23.89
		H	–	14.20	–	7.35	–	7.08	8.18	3.36	1.91;1.71;1.47
	270	C	119.01	156.20	122.43	132.22	122.77	129.20	163.30	72.08	32.76;23.70
		H	–	14.35	–	7.36	–	7.10	8.20	3.37	1.92;1.70;1.48
	250	C	118.83	156.18	122.30	132.15	122.64	129.20	163.25	71.97	32.67;23.70
		H	–	14.50	–	7.37	–	7.12	8.21	3.38	1.93;1.70;1.47
	230	C	118.61	156.21	122.19	132.10	122.48	129.20	163.21	71.85	32.58;23.62
		H	–	14.67	–	7.38	–	7.14	8.23	3.39	1.94;1.70;1.48
3 diBr	295	C	119.67	157.73	112.12	137.78	109.80	132.94	163.23	72.08	32,.88;23.90
		H	–	14.35	–	7.65	–	7.26	8.15	3.36	1.91;1.70;1.47
	270	C	119.46	157.67	112.05	137.65	109.70	132.90	163.15	71.95	32.78;23.79
		H	–	14.51	–	7.66	–	7.27	8.16	3.36	1.92;1.69;1.46
	250	C	119.27	157.65	112.00	137.55	109.61	132.87	163.08	71.82	32.68;23.69
		H	–	14.66	–	7.66	–	7.29	8.17	3.37	1.92;1.96;1.46
	230	C	119.06	157.72	112.01	137.47	109.51	132.87	163.06	71.69	32.59;23.61
		H	–	14.82	–	7.67	–	7.30	8.18	3.38	1.93;1.68;1,.47
4 NO_2	295	C	117.09	167.30	118.35	127.89	139.52	128.14	163.66	71.98	32.72; 23.93
		H	–	14.29	6.96	8.14	–	8.17	8.35	3.46	1.96;1.75;1.55
	270	C	116.89	167.39	118.37	127.95	139.22	128.16	163.61	71.84	32.63;23.83
		H	–	14.42	6.97	8.17	–	8.18	8.36	3.48	1.99;1.77;1.52
	250	C	116.71	167.56	118.43	128.06	138.96	128.22	163.61	71.68	32.54;23.74
		H	–	14.54	6.98	8.18	–	8.20	8.37	3.50	1.99;1.78;1.53
	230	C	116.48	167.84	118.56	128.30	138.65	128.22	163.63	71.48	32.45;23.66
		H	–	14.66	7.00	8.20	–	8.22	8.39	3.53	2.00;1.79;1.54
5 diOMe	295	C	102.18	172.25	95.10	166.07	88.19	160.88	159.19	68.87	55.30;55.29;32.73;24.17
		H	–	14.28	5.88	–	5.60	–	8.31	3.22	3.76;3.64;2.04;1.85;1.42
	270	C	101.89	173.14	94.41	166.21	87.88	160.74	158.95	68.35	55.35;55.28;32.61;24.09
		H	–	14.26	5.87	–	5.57	–	8.28	3.23	3.76;3.64;2.06;1.86;1.43
	250	C	101.68	173.95	94.41	166.35	87.19	160.65	158.74	67.92	55.40;55.27;32.58;24.04
		H	–	14.24	5.88	–	5.57	–	8.27	3.27	3.78;3.65;2.09;1.88;1.44
	230	C	101.49	174.86	94.45	166.49	87.38	160.57	158.52	67.47	55.49;55.26;32.53;24.01
		H	–	14.14	5.85	–	5.54	–	8.23	3.28	3.76;3.63;2.09;1.88;1.41

with two electron donor substituents in the positions *ortho* and *para* to the imine group. The UV–Vis spectra of Schiff bases with 2-hydroxynaphthylidene moieties (**6** and **7**) [Table 2] indicated the existence of the proton transfer equilibrium. The molar integral intensity of NH-form band for compound **6** with unsubstituted NH_2 group is greater than the corresponding value for **7** (calculated for one naphthylidene moiety), which means that in di-Schiff bases, the position of the proton transfer equilibrium is shifted

Table 4
^{1}H and ^{13}C chemical shifts assignments in compounds **6** and **7** in $CDCl_3$ (ppm)

Compound	T (K)	δ	Position												Others
			1	2	3	4	5	6	7	8	9	10	α	1′	
6 1:1	295	C	106.62	175.16	124.45	136.92	129.20	122.73	127.91	118.04	133.71	126.34	157.54	71.07	54.74;34.05;32.79; 24.82;24.61
		H	–	14.57	6.95	7.69	7.62	7.24	7.43	7.89	–	–	8.88	3.00	2.83;2.18–1.25;1.38
	270	C	106.25	176.23	124.79	137.25	129.18	122.66	127.93	117.85	133.62	126.04	157.33	70.58	54.54;33.83;32.63 24.74;24.45
		H	–	14.51	6.94	7.70	7.62	7.24	7.45	7.89	–	–	8.86	3.03	2.84;2.04–1.27;1.38
	250	C	105.94	177.25	125.13	137.57	129.17	122.62	127.97	117.71	133.57	125.80	157.16	70.15	54.36;33.64;32.50 24.68;24.32
		H	–	14.43	6.94	7.72	7.63	7.24	7.46	7.88	–	–	8.84	3.06	2.85;2.05–1.14;1.38
	230	C	105.60	178.33	125.51	137.91	129.17	122.56	128.01	117.55	133.53	125.54	156.97	69.72	54.17;33.45;32.34 24.62;24.16
		H	–	14.29	6.93	7.74	7.64	7.25	7.47	7.87	–	–	8.82	3.09	2.88;2.07–1.28;1.41
7 1:2	295	C	107.13	172.30	122.84	136.45	128.83	122.79	127.78	118.37	133.17	126.50	159.17	69.04	32.67;24.25
		H	–	14.66	6.85	7.52	7.45	7.13	7.30	7.72	–	–	8.75	3.41	2.10;1.93;1.75;1.49
	270	C	106.81	173.16	123.10	136.72	128.81	122.73	127.80	118.20	133.07	126.24	158.92	68.55	32.49;24.15
		H	–	14.66	6.85	7.54	7.46	7.14	7.31	7.72	–	–	8.73	3.43	2.20;1.93;1.75;1.49
	250	C	106.55	173.99	123.36	136.99	128.80	122.69	127.84	118.06	133.00	126.03	158.70	68.13	32.30;24.08
		H	–	14.64	6.85	7.55	7.47	7.15	7.33	7.72	–	–	8.71	3.44	2.21;1.94;1.75;1.47
	230	C	106.28	174.93	123.68	137.28	128.80	122.65	127.88	117.93	132.96	125.80	158.45	67.65	32.21;24.03
		H	–	14.58	6.85	7.56	7.48	7.16	7.35	7.72	–	–	8.69	3.45	2.22;1.94;1.74;1.48

Table 5
Deuterium isotope effects ΔC_{DH} and ΔC_{DD} (in parentheses) on ^{13}C NMR in compounds **1**–**5** in $CDCl_3$ (ppb) (see text)

Compound	R	T (K)	Position								Others	^3J(NH,H) (Hz)
			C-1	C-2	C-3	C-4	C-5	C-6	C-α	C-1′		
1		295	n.o.	n.o.	n.o.	n.o.	n.o.	n.o.	n.o.	n.o.		
		270	–	426	122	n.o.	n.o.	n.o.	135	−109		
		250	−48	438	133	56	−100	−40	144	−125		
		230	−57	452	137	56	−108	−46	148	−125		
2	3,5-diCl	295	−125	527	93	n.o.	−152	n.o.	152	−142		
		270	−158	549	131	62	−182	−68	193	−176		
		250	−157	577 (517)	138	73	−192 (−164)	−77	203 (241)	−183		
		230	−170	606 (530)	146 (127)	78	−208 (−162)	−80	212 (264)	−196		
3	3,5-diBr	295	−130	534	164	n.o.	−188	n.o.	172	−162		
		270	−148	570 (522)	177	66	−183	−69	193 (241)	−180		
		250	−153	579 (512)	190 (164)	69	−210 (−173)	−75	205 (255)	−185		
		230	−162	604 (517)	196 (159)	71	−221 (−166)	−79	221 (270)	−197		
4	5-NO_2	295	∼ −140	571	∼88	n.o.	n.o.	n.o.	148	−122		
		270	∼ −135	n.m.	137	n.o.	−135	n.o.	202	−177		
		250	−145	590 (513)	152	n.o.	−143	n.o.	215	−183		
		230	−163	594 (474)	153	n.o.	−144	n.o.	227	−173		
5 45%D	4,6-diOMe	295	n.o.	78	n.o.	n.o.	n.o.	n.o.	310	n.o.		–
		270	n.o.	0	−45	−65	n.o.	−32	341	94		5.84
		250	n.o.	−98 (−35)	−66	−91	n.o.	−39	373 (329)	116		7.16
		230	n.o.	−208 (−89)	−88	−120 (−97)	n.o.	−47	400 (346)	193		8.00
75%D		270	n.o.	0	−43	−63	n.o.	−29	341	92		
		250	n.o.	−106 (−38)	−67	−96	n.o.	−38	377 (329)	∼145		
		230	n.o.	−207 (−90)	−91	−115 (−87)	n.o.	−48	406 (349)	192		

n.o.—no observed; n.m.—not measured; $\Delta C_{DH} = \delta C_{HH} - \delta C_{D(H)}$; $\Delta C_{DD} = \Delta C_{HH} - \Delta C_{DD}$.

Table 6
Deuterium isotope effects ΔC_{DH} and ΔC_{DD} (in parentheses) on ^{13}C chemical shifts for compounds **6** and **7** in $CDCl_3$ (ppb) (see text)

Compound	T (K)	Position												^3J(NH,H) (Hz)
		1	2	3	4	5	6	7	8	9	10	α	1′	
6 1:1	295	n.o.	~ −299	−188	−126	n.o.	n.o.	n.o.	n.o.	n.o.	n.o.	473	226	6.01
	270	87	−412	−222	−156	n.o.	n.o.	n.o.	n.o.	−109	n.o.	496	279	8.69
	250	106	−483	−250	−176	n.o.	n.o.	n.o.	n.o.	−117	n.o.	513	307	9.47
	230	121	−535	n.o.	−183	n.o.	n.o.	n.o.	n.o.	−118	n.o.	515	326	10.23
7 1:2	295	n.o.	n.o.	n.o.	n.o.	n.o.	n.o.	n.o.	n.o.	n.o.	n.o.	399	n.o.	–
	270	n.o.	−159	−118	−95	n.o.	n.o.	n.o.	n.o.	−79	n.o.	447	146	6.54
	250	62	−270 (−201)	−185 (−155)	−122	n.o.	n.o.	n.o.	n.o.	−92	n.o.	484 (447)	182	7.28
	230	73	−389 (−283)	−198 (−149)	−151	n.o.	n.o.	n.o.	n.o.	−109	n.o.	520 (471)	239 (167)	7.94

n.o.—no observed; $\Delta C_{DH} = \delta C_{HH} - \delta C_{D(H)}$; $\Delta C_{DD} = \delta C_{HH} - \delta C_{DD}$.

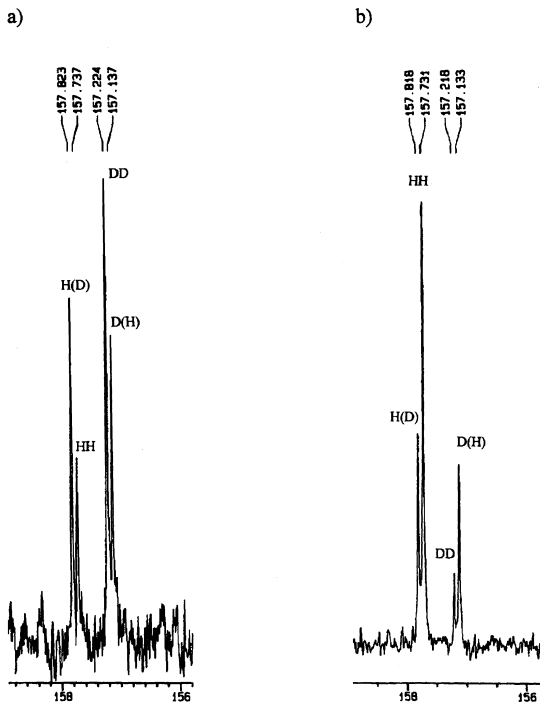

Fig. 3. Splitting of the C-2 signals in ^{13}C NMR spectrum of partially deutrated *trans-N,N′*-bis-(3,5-dibromosalicylidene)-1′,2′-cyclohexanediamine at different degree of deuteration: (a) 75%; (b) 30%.

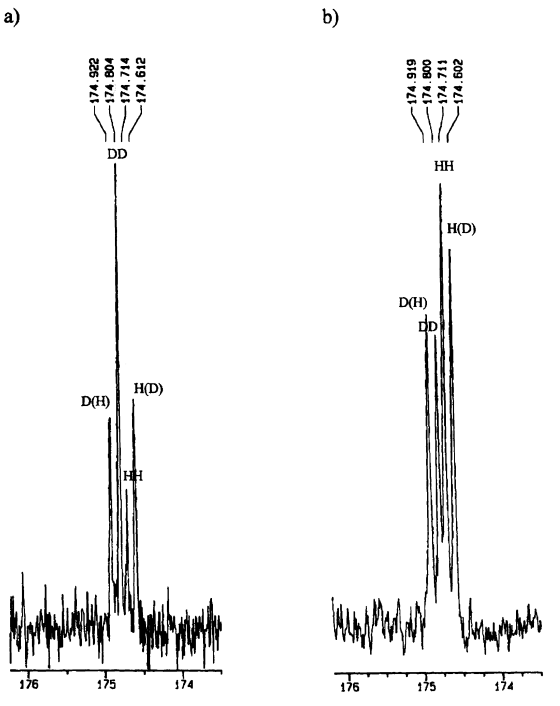

Fig. 4. Splitting of the C-2 signals in ^{13}C NMR spectrum of partially deutrated *trans-N,N′*-bis-(4,6-dimethoxysalicylidene)-1′,2′-cyclohexanediamine at different degree of deuteration: (a) 75%; (b) 45%.

towards the OH-form relative to that in the mono-Schiff bases.

3.3. ^{1}H and ^{13}C NMR spectroscopy. Deuterium isotope effect on ^{13}C NMR chemical shifts

In order to obtain more information concerning the proton transfer equilibrium in the Schiff bases studied we investigated the ^{1}H and ^{13}C NMR spectra and measured the deuterium isotope effect on ^{13}C chemical shifts. The NMR spectra showed the equivalence of both imine moieties in compounds **1**–**5**, **7** (Tables 3 and 4). The values of the chemical shifts of the proton of proton donor group δH indicate the presence of a hydrogen bond of medium strength. With decreasing temperature, the signal δH in the spectra of compounds **1**–**4** is shifted to higher frequency, while those in the spectra of **5**–**7** to the opposite direction. In the spectrum of mono-substituted **6**, the signals assigned to the proton of the NH_2 group were observed. For compounds **5**–**7** the splitting of the imine proton signals, increasing with decreasing temperature was observed (Tables 5 and 6), evidencing the existence of the tautomeric NH-form in equilibrium. The magnitude of $^{3}J_{NH,H}$ values permitted an estimation of the molar ratio of this form, when the respective values for the pure NH-form were known. For the NH-form of Schiff bases the $^{3}J_{NH,H}$ value is known to depend on the structure of the compound; for *N*-(salicylidene)-alkylamines, the values of 12.6 Hz [20] and for 2-hydroxynaphthylidene-methylamine—12 Hz [22] were found. We estimated the mole fraction of the NH-form for **5** to be 0.5 at 270 K and 0.6 at 230 K. The estimated mole fraction of the NH-form for these compounds increased from 0.7 to 0.85 for **6** and from 0.55 to 0.65 for **7** with decreasing temperature.

The deuterium isotope effects on ^{13}C NMR chemical shifts for the Schiff bases studied, measured at different temperatures, are given in Tables 5 and 6. This method is known to be a very useful tool in studying proton transfer equilibrium in resonance-assisted hydrogen bond [21–25]. The obtained results are in agreement with those of UV–Vis studies and

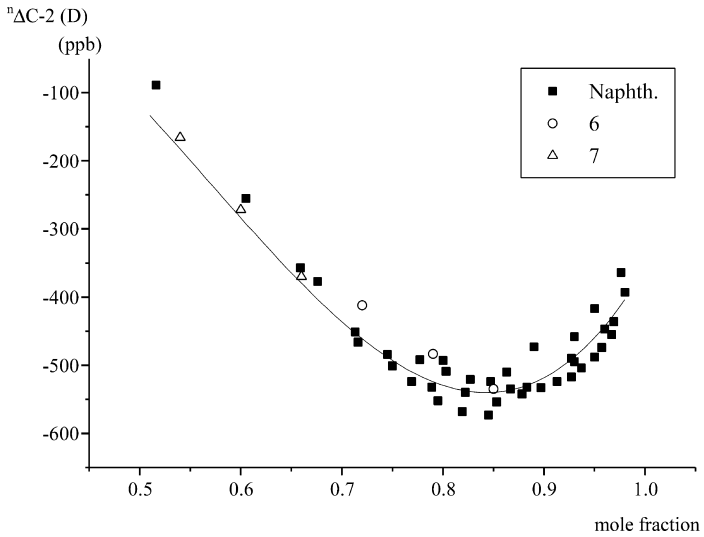

Fig. 5. The plot $^{n}\Delta$-2C(D) vs. mole fractions of NH-form for *N*-(2-hydroxynaphthylidene)-methylamine [21] and compounds **6** (○) and **7** (△).

provided additional interesting information on the proton transfer equilibrium in the Schiff bases studied. For compound **1** the magnitude of $^{n}\Delta$C-2(D) was similar to those observed previously for Schiff bases with the proton localized in one minimum [21].

In the spectra of partially deuterated *N*,*N*′-bis-(*R*-salicylidene)-1′,2′-cyclohexanediamine **2**–**5** and *N*,*N*′-bis-(2-hydroxynaphthylidene)-1′,2′-cyclohexane-diamine **7**, in which the proton transfer equilibrium existed, the exceptional splitting of some ^{13}C signals to four resonance lines, was observed at low temperatures (Tables 5 and 6, Figs. 3 and 4). This feature has not been observed for the di-Schiff bases studied previously [25]. On the basis of a comparison of the spectra of the compounds deuterated to a different degree, we have assigned these signals to the non-deuterated δC_{HH}, the doubly deuterated δC_{DD}, and to the mono-deuterated $\delta C_{D(H)}$ and $\delta C_{H(D)}$ species (Figs. 3 and 4). As far as the proton transfer equilibrium is concerned, the most informative was the deuterium isotope effect observed on the C-2 atom. For this carbon we assigned the signals δC_{DD}, δC_{HH} to the carbon atoms linked to the OD and OH groups, respectively; while $\delta C_{H(D)}$ to the C atom linked to the OH group and $\delta C_{D(H)}$ to the OD group in mono-deuterated compounds (Figs. 3 and 4). In order to explain the observed splitting of the signals two hypotheses should be considered. The first one presumes the non-equivalence of both hydrogen bonds, the second one—an interrelationship between the proton transfer equilibria in both hydrogen bonds. Assuming the inequivalence of the two chelate rings in the molecules, the signals in the H and ^{13}C NMR spectra might be assigned to the averaged values of the chemical shift of the respective atoms. When only one proton in the OH···N hydrogen bond in di-Schiff bases was substituted by deuterium it would be probably the one with a weaker hydrogen bond. The signal δC_{HH} would correspond to the averaged values in the parent base, the signal $\delta C_{H(D)}$ would be assigned to the chemical shift of the C-2 atom in the second chelate ring with non-substituted H atom. Similarly, the δC_{DD} would correspond to the averaged chemical shift in of the C-2 atoms for species with both H atoms substituted by D, and the $\delta C_{D(H)}$ the chemical shift of the C-2 atom in mono-deuterated compound. However, this hypothesis is less probable than the second one, as we have observed the splitting of the signals only in these compounds in which the proton transfer equilibrium occurs. In mono-deuterated compounds, the change in the position of the proton transfer equilibrium and in a charge density on one chelate ring may influence the proton transfer equilibrium in the second hydrogen bond. For compounds **2**–**4** existing mainly in the OH form, the deuterium isotope effect $\Delta C_{D(H)}$ resulting from a substitution of one H atom by D, measured as a difference $\delta C_{HH} - \delta C_{D(H)}$ is positive, indicating the

predominance of the OH form. The substitution of H by D in one hydrogen bridge OH···N shifts the proton transfer equilibrium towards the OH-form. At the same time, the signal $\delta C_{H(D)}$ assigned to the C-2 carbon atom linked to OH in the other chelate ring is shifted to the higher frequencies. This indicates the shifts of the equilibrium in opposite direction, towards the NH-form. The isotope shift $\Delta C_{DH} = \delta C_{HH} - \delta_{CD(H)}$ increased with the lowering temperature as well as with increasing acidity of the OH group in range **2** < **3** < **4**. However, for *N*-(5-NO_2 salicylidene)-alkylamines Schiff bases, the influence of increasing acidity of the OH group has been much more important [26]. In compound **5**, the mole fraction of the NH-form is greater than 0.5 at low temperatures and the negative values of the ΔC_{DH} are observed below 270 K. Inspection of Fig. 4 shows that contrary to the previous compounds, the signal $\delta C_{H(D)}$ is observed at lower frequencies than the δC_{HH}. This shows that the deuteration-induced shift of the equilibrium towards the right in one hydrogen bridge causes a shift of the equilibrium in the other one in the opposite direction. The substitution of both protons by deuterons leads to the isotope effect $\Delta C_{DD} = \delta C_{HH} - \delta_{CDD}$ which corresponds mainly to the intrinsic isotope effect, however, the contribution of the equilibrium isotope effect cannot be excluded. In fact this value is not much temperature-sensitive (Table 5).

For Schiff base **6** with one 2-hydroxynaphthylidene moieties we have not observed the splitting of the signal. It is worth noting that the values $^{n}\Delta$C-2(D) measured for compounds **6** and **7** fit very well to the plot $^{n}\Delta$C-2(D) vs. mole fractions obtained before for *N*-(2-hydroxynaphthylidene-metylamine [22] (Fig. 5).

4. Conclusion

In di-Schiff bases derivatives of *trans*-1,2-diaminocyclohexane the imine moieties are spectroscopically equivalent. In all compounds except **1**, the intramolecular proton transfer equilibrium exists. The position of the tautomeric equilibrium in the series of di-Schiff bases under study is shifted towards the OH-form in comparison to that in the mono-Schiff bases. Moreover, it is more influenced by an increase of the basicity of N atom than an increase in the acidity of the phenolic group.

The observed splitting of the some ^{13}C signals to four lines in partly deuterated compounds suggests that substitution of H by D in one hydrogen bond affects the proton transfer equilibrium in the other one. The shift the equilibrium in one direction in the OD···N bridge induces a similar shift in the opposite direction in the other hydrogen bond. The obtained results suggest that the proton transfer processes in both hydrogen bridge in di-Schiff bases derived from trans-1,2-diaminocyclohexane and aromatic *ortho*-hydroxyaldehydes are not independent.

Acknowledgments

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