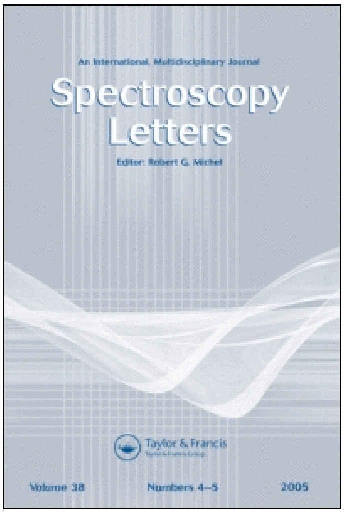


Spectroscopy Letters
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713597299

DFT Studies of the Structure and Vibrational Spectra of NH Tautomers of *trans-N,N'*-bis-Salicylidene-1',2'-cyclohexanediamines

Irena Majerz[a]; T. Dziembowska[b]
[a] Institute of Chemistry, University of Wrocław, Wrocław, Poland [b] Institute of Chemistry and Environmental Protection, Technical University of Szczecin, Szczecin, Poland

To cite this Article Majerz, Irena and Dziembowska, T.(2009) 'DFT Studies of the Structure and Vibrational Spectra of NH Tautomers of *trans-N,N'*-bis-Salicylidene-1',2'-cyclohexanediamines', Spectroscopy Letters, 42: 5, 246 — 257
To link to this Article: DOI: 10.1080/00387010902896879
URL: http://dx.doi.org/10.1080/00387010902896879

Spectroscopy Letters, 42:246–257, 2009

ISSN: 0038-7010 print/1532-2289 online
DOI: 10.1080/00387010902896879

Taylor & Francis
Taylor & Francis Group

DFT Studies of the Structure and Vibrational Spectra of NH Tautomers of *trans-N,N′*-bis–Salicylidene-1′,2′-cyclohexanediamines

Irena Majerz[1],
and T. Dziembowska[2]
[1]Institute of Chemistry,
University of Wrocław,
Wrocław, Poland
[2]Institute of Chemistry and
Environmental Protection,
Technical University of Szczecin,
Szczecin, Poland

ABSTRACT The structure and vibrational spectra of the tautomeric NH form of *trans-N,N′*-bis-(R-salicylidene)-cyclohexanediamines (R = H, 5-NO_2, 4,6-OCH_3, 3,5-Cl) and their analogues deuterated in the NH and CH imine groups were calculated using the DFT method at the 6-31G** level. The complicated nature of the normal modes was shown. The influence of the substituents on the hydrogen bond strength and nonequivalence of the two hydrogen bonds present in Schiff base molecules are discussed.

KEYWORDS Schiff bases, tautomerism, theoretical vibrational spectra

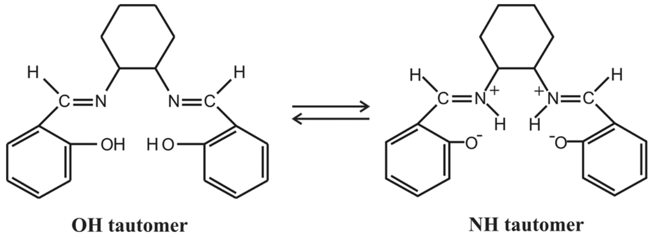
INTRODUCTION

Schiff base derivatives of aromatic 2-hydroxyaldehydes have received considerable attention due their physical and chemical properties that are interesting for their practical applications and the roles they play in biological systems.[1–3] The property that has attracted noticeable interest is their aptitude for forming stable complexes with the transition metals.[3] Several of these complexes exhibit catalytic properties. Particularly important appear to be complexes of Schiff base derivatives of chiral *trans*-1,2-diaminocyclohexane, which have been shown to be very effective as enantio-selective catalysts and which have found application in drug synthesis.[4,5]

Schiff base derivatives of *trans*-1,2-diaminocyclohexane and their complexes were the object of our previous interest.[6–11] As shown by NMR and UV-Vis experiments, some Schiff base derivatives of *trans*-diaminocyclohexane exist in solution as tautomeric mixtures of the OH and NH forms[6] (Scheme 1). IR spectra of these compounds were also measured,[6,7] however, the strong coupling of the vibrations and the complexity of the spectra made reliable assignments of the spectra impossible. The IR spectra were additionally complicated by the coexistence of the two tautomeric forms in solution. IR spectroscopy is known to be a very efficient tool for studying the complexes, particularly those with paramagnetic ions, where NMR methods have limited application.

Received 14 July 2008;
accepted 1 March 2009.

Address correspondence to
Irena Majerz, Institute of Chemistry,
University of Wrocław, Joliot-Curie
14, PL-50383, Wrocław, Poland.
E-mail: majerz@yahoo.com



SCHEME 1 **Tautometric equilibrium in trans–diaminocyclohexane Schiff base.**

In this situation, a theoretical analysis of the IR spectra of the OH and NH tautomers appeared to be advisable as the only method of investigating pure OH and NH tautomers. In the previous paper, vibrational analysis was performed on a series of the OH tautomeric form of *trans-N,N'*-bis-(R-salicylidene)-cyclohexanediamine (R = H, 5-NO_2, 4,6-OCH_3, 3,5-Cl) based on a comparison of B3LYP-calculated IR spectra of these compounds and their analogues deuterated in the OH and CH imine groups.[9] This method allowed the localization of the main bands attributed to the vibration of characteristic NH, C = N bonds and gave an explanation of the coupling of the vibrations in the chelate ring. In this study, we applied the same method for the vibrational analysis of the tautomeric NH form of *trans-N,N'*-bis-(R-salicylidene-cyclohexanediamine (R = H, 5-NO_2, 4,6-OCH_3, 3,5-Cl)) (Fig. 1). These theoretical studies are important because the Schiff bases under consideration do not exist as pure NH forms and consequently the experimental spectra have not been available.

Despite of numerous studies of the IR spectra of the NH tautomers of the Schiff bases, the assignment of several vibrations is contradictory. Substitution of the hydrogen atom in the CH and NH groups by deuterium may facilitate the assignment of the bands and deliver information on the nature of the vibrations in the molecules by removing the coupling of some vibrations and identifications of the modes in which the NH and CH vibration participate.

MATERIALS AND METHODS

The *trans-N,N'*-bis-(R-salicylidene)-cyclohexanediamines (R = H, 5-NO_2, 4,6-OCH_3, 3,5-Cl) were obtained previously and their IR spectra in $CHCl_3$ solution were measured.[6] The optimization of the structures and calculations of the frequencies of the investigated compounds were performed using the Gaussian 1998 program with DFT B3LYP methods at the 6-31G(d,p) level.[12] The scale factor equal to 0.978 was used in scaling of the calculated harmonic wavenumbers in whole frequency range of the analyzed theoretical spectra. The simulated spectra were plotted using a Lorentzian band shape with a half-width of 5 cm^{-1}. Vibrational mode assignments were made by visual inspection of modes animated by using the gOpenMol program.

RESULTS

Geometric Parameters

The structures of the studied NH tautomers of *trans-N,N'*-bis-(R-salicylidene)-cyclohexanediamines (Fig. 1) were optimized using the B3LYP method at the 6-31G(d,p) level. The data for I were published previously.[10] The selected geometric parameters of compounds I–IV are collected in Table 1. The N···O distances of 2.53–2.55 Å indicate the presence of a medium-strength hydrogen bond. The differences in bond length between the two salicylidene moieties were observed for all the compounds but III. Differences in the effect of substituents on the geometric parameters were observed.

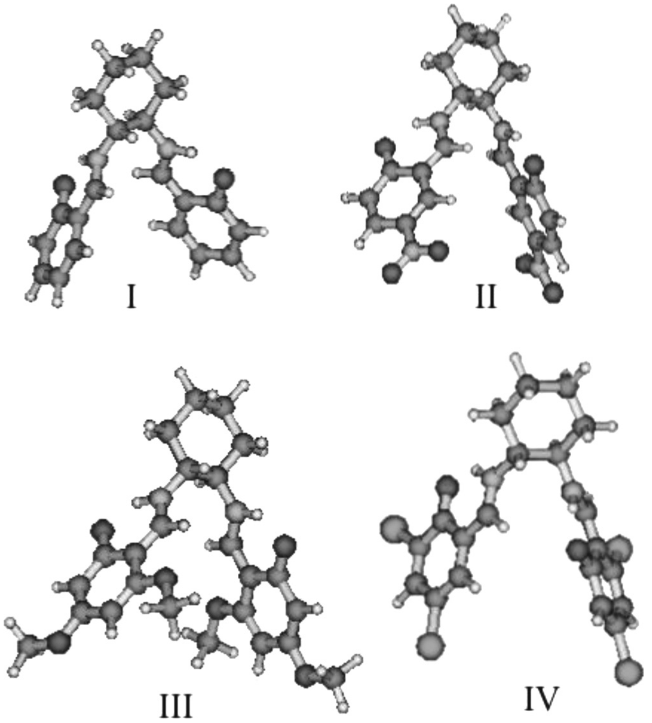


FIGURE 1 **The structures of the studied proton transfer tautomers of di-Schiff bases.**

TABLE 1 Selected Calculated Geometric Parameters for the NH Form of *N,N′*-bis-(R-Salicylidene)-Cyclohexanediamines

Substituent R	Bond distances (Å) N···O	O···H	NH	CO	OHN (°)
H	2.5502	1.6326	1.0538	1.270	142.4
(compound I)[10]	2.5373	1.6084	1.0580	1.274	143.4
5-NO$_2$	2.5426	1.6170	1.0566	1.2682	143.1
(compound II)	2.5601	1.6496	1.0520	1.2631	141.8
4,6-diOMe	2.5615	1.6585	1.0479	1.2679	141.3
(compound III)	2.5615	1.6586	1.0479	1.2679	141.3
3,5-di-Cl	2.5619	1.6642	1.0470	1.2599	140.7
(compound IV)	2.5293	1.6100	1.0540	1.2702	142.5

Vibrational Spectra

The *trans-N,N′*-bis–(R-salicylidene)-1′,2′-cyclohexanediamines (II–IV) exist in CHCl$_3$ solution in tautomeric equilibrium, whereas only the OH tautomer has been found for the derivative salicylic aldehyde (I).[6] The experimental IR spectra of *N*-bis-(R-salicylidene)-1,2-cyclohexanediamines were measured previously [6]; however, due to their complexity, only a tentative assignment has been done. Following the method applied earlier for OH tautomers,[9] we calculated the spectra of the NH tautomers of the Schiff bases under study and their CH- and NH-deuterated analogues. As previously, we focused our attention on the assignment and elucidation of the coupling of the vibrations of the C = N, NH, CO, and imine CH groups. These bands are important in the application of IR spectroscopy in the investigation of proton transfer and complex formation. For the simplest compound of the series, *trans-N,N′*-bis–salicylidene-1′,2′-cyclohexanediamine (I), a detailed vibrational analysis was previously performed, and the assignment of all frequencies in the 3100–400 cm^{-1} region was given in Table 2 in Ref. 9. In this paper, we also performed the calculation for its CH- and NH-deuterated analogues. Comparison of the spectra of the *N*- bis-(R-salicylidene)-1, 2-cyclohexanediamines with their NH- and CH-deuterated analogues are shown in Figs. 2–5.

Trans-N,N′-bis-(R-Salicylidene)-cyclohexanediamine (I)

The νNH frequencies occur at 2794 and 2730 cm^{-1} for the two moieties, indicating two hydrogen bonds of different strength. The νNH frequency changes

TABLE 2 Calculated Frequencies (cm^{-1}) and Intensities (km/mol) for *trans-N,N′*-bis-(5-Nitrosalicylidene)-1′, 2′-Cyclohexanediamine

Mode	ν (cm^{-1})	A (km/mol)	Assignment
26	354	1	τC = N
27	358	3	τC = N, γCH$_{im}$
28	378	13	τC = N, γNH, γCO
29	413	17	αC = NC
30	431	6	αC = NC
31	438	4	γCH$_{im}$, γCH$_{ar}$, γNH
32	445	5	αCC = N, γCH$_{ar}$, γCH$_{im}$
33	448	7	γCH$_{ar}$, γCH$_{im}$, δCH$_2$
34	468	4	αC = NC, γCO, γCH$_{ar}$, γNH
35	478	2	αC = NC, δCH$_{im}$, δCO, γNO$_2$
36	485	11	δCH$_{im}$, δCO, γNO$_2$
37	505	2	τ$_{ar}$ ring
38	508	2	τ$_{ar}$ ring
39	526	12	νNC, δ$_{al}$ ring
40	534	0	δ$_{al}$ ring, δ$_{ar}$ ring, δCH$_{im}$
41	539	3	δ$_{al}$ ring, δ$_{ar}$ ring, δCH$_{im}$
42	550	5	δ$_{al}$ ring, γNH
43	613	4	δ$_{ar}$ ring, νC = O
44	613	15	δ$_{ar}$ ring, νC = O
45	671	9	δ$_{ar}$ ring, γNH, αC = NC
46	673	12	δ$_{ar}$ ring, γNH, αC = NC
47	706	12	δ$_{ar}$ ring, γCH$_{im}$
48	707	11	δ$_{ar}$ ring, γCH$_{im}$
49	734	18	γ$_{ar}$CH, τ$_{ar}$ ring, γCH$_{im}$
50	734	4	γCH$_{ar}$, τ$_{ar}$ ring
51	745	25	δ$_{ar}$ ring, δCH$_{im}$
52	750	8	γCH$_{im}$, δ$_{ar}$ ring
53	769	0	δ$_{al}$ ring
54	809	9	δNO$_2$, δNH, ν$_{im}$CC
55	810	14	δNO$_2$,γNH, νCO
56	824	13	γ CH$_{ar}$, δ$_{al}$ ring
57	824	16	γ CH$_{ar}$, δ$_{al}$ ring
58	826	17	γCH$_{ar}$
59	842	3	δ$_{al}$ ring
60	878	15	δ$_{al}$ ring, γNH, γCH$_{im}$
61	885	7	δ$_{ar}$ ring, δ$_{al}$ ring, γCH$_{ar}$
62	887	22	γCH$_{im}$, δ$_{al}$ ring
63	907	2	δCH$_2$, γNH, γCH$_{im}$,γCH$_{ar}$
64	913	3	γNH, γCH$_{im}$γCH$_{ar}$
65	920	9	δ$_{al}$ ring, γCH$_{ar}$, δCH$_{im}$
66	923	8	δCH$_2$, γNH, γCH$_{ar}$, γCH$_{im}$
67	925	11	CH$_2$, γNH, γCH$_{ar}$, γCH$_{im}$
68	932	15	γCH$_{ar}$, γNH, γ$_{im}$CH, δCH$_2$
69	968	1	γCH$_{ar}$
70	969	0	γCH$_{ar}$
71	985	46	γNH, γCH$_{ar}$
72	990	101	γNH, γCH$_{ar}$
73	1013	1	δCH$_2$
74	1016	35	δCH$_2$, γNH, γCH$_{im}$
75	1033	35	δCH$_2$, γNH, γCH$_{im}$
76	1052	4	δCH$_2$, γNH

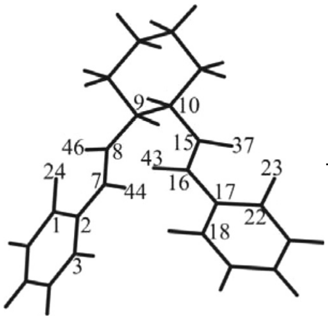
(*Continued*)

TABLE 2 Continued

Mode	ν (cm^{-1})	A (km/mol)	Assignment
77	1065	53	γNH, γCH$_{im}\gamma_{ar}$CH
78	1071	110	δCH$_{ar}$, γNH
79	1073	35	δCH$_{ar}$
80	1106	21	δCH$_{ar}$
81	1108	15	δCH$_{ar}$
82	1111	18	δCH$_{ar}$, δCH$_2$
83	1121	67	δCH$_{ar}$, δ NH, δCH$_{im}$
84	1169	13	δCH$_{ar}$, δ NH, δCH$_{im}$
85	1171	22	δCH$_{ar}$, δNH
86	1184	0	δCH$_2$
87	1209	84	δNH, δCH$_2$, δCH$_{im}$, δCH$_{ar}$
88	1216	95	δNH, δCH$_2$, δCH$_{im}$, δCH$_{ar}$
89	1229	12	δCH$_2$, δCH$_{ar}$
90	1232	3	δCH$_2$
91	1261	15	δCH$_{ar}$, δNH, δCH$_{im}$, δCH$_2$
92	1267	17	δCH$_{ar}$, δNH, δCH$_{im}$, δCH$_2$
93	1276	20	δCH$_{ar}$, δNH, δCH$_{im}$, δCH$_2$
94	1298	16	δCH$_2$, δNH
95	1301	26	δCH$_2$, δNH
96	1319	17	δCH$_2$, δNH, δCH$_{im}$
97	1322	60	δCH$_2$, δNH, δCH$_{im}$
98	1326	429	ν_sNO$_2$, δNH, δCH$_{im}$, δCH$_2$
99	1329	110	ν_sNO$_2$, δNH, δCH$_{im}$, δCH$_2$
100	1333	892	ν_sNO$_2$, δNH, δCH$_{im}$, δCH$_2$
101	1336	49	δCH$_{im}$, δCH$_{ar}$
102	1340	6	δCH$_2$
103	1342	6	νCO, δNH, δCH$_{im}$, δCH$_{ar}$
104	1344	18	νCO, δNH, δCH$_{im}$, δCH$_{ar}$
105	1350	21	δCH$_2$, δCH$_{im}$
106	1358	10	δCH$_2$, δCH$_{im}$
107	1381	42	δCH$_{im}$, δCH$_{ar}$, δNH
108	1388	84	δCH$_{im}$, δCH$_{ar}$, δNH
109	1431	13	δCH$_{ar}$, δCH$_{im}$
110	1433	18	δCH$_{ar}$, δCH$_{im}$
111	1442	1	δCH$_2$
112	1443	2	δCH$_2$
113	1447	11	δCH$_2$
114	1459	2	δCH$_2$
115	1506	55	νCC$_{ar}$, δNH, δCH$_{im}$
116	1508	55	νCC$_{ar}$, δNH, δCH$_{im}$
117	1544	17	δNH, νCC$_{ar}$, νCO
118	1550	9	δNH, νCC$_{ar}$, νCO
119	1572	180	ν_{as}NO$_2$,δNH
120	1574	444	ν_{as}NO$_2$,δNH
121	1619	395	νCO, δNH, δCH$_{im}$
122	1622	155	νCC$_{ar}$, δNH, νC$=$N, νCO
123	1627	478	νC$=$N, δCH$_{im}$, δNH
124	1640	1155	νC$=$N, δCH$_{im}$, δNH
125	2756	166	νNH
126	2830	188	νNH
127	2912	2	νCH$_2$
128	2913	15	νCH$_2$
129	2916	10	νCH$_2$
130	2921	6	νCH$_2$
131	2923	22	νCH$_2$
132	2934	41	νCH$_2$
133	2972	45	νCH$_2$
134	2974	31	νCH$_2$
135	2977	14	νCH$_2$
136	2980	34	νCH$_2$
137	3035	1	νCH$_{im}$
138	3041	0	νCH$_{im}$
139	3091	2	νCH$_{ar}$
140	3093	1	νCH$_{ar}$
141	3094	2	νCH$_{ar}$
142	3094	1	νCH$_{ar}$
143	3112	2	νCH$_{ar}$
144	3114	2	νCH$_{ar}$

(*Continued*)

νCC$_{ar}$ aromatic ring stretching.
νCC$_{al}$ aliphatic ring stretching.
νCC$_{im}$ stretching of the C2-C7 (A) and C16C17 (B) bonds.
νC$=$N stretching C7N8 (A) and C16N15 bonds.
νNC stretching C9N8 and and C10N15 bonds.
νCO stretching C1O24 and C22O23 bonds.
νCH$_{ar}$ stretching of the aromatic CH bonds.
νCH$_2$ stretching of the aliphatic CH bonds.
ν_{im}CH stretching of the C7H44 (A) and C16H4 3 (B) bonds.
νNH stretching of the N8H46 (A) and N15N37 (B) bonds.
δCH$_{ar}$ in-plane bending of aromatic CH bonds (A,B).
γCH$_{ar}$ out-of-plane bending of aromatic CH bonds (A,B).
δ_{al}CH$_2$ deformation of The CH$_2$ bonds of the cyclohexane ring.
δCH$_{im}$ deformation in-plane of C7H44 (A) and C16H43 (B) bonds.
γCH$_{im}$ deformation out-of-plane of C7H44 (A) and C16H43 bonds.
δ_{ar} ring deformation in-plane of the angles in the aromatic ring.
τ_{ar} ring deformation out-of-plane of the aromatic ring.
δ_{al} ring deformation in-plane of the angles in the cyclohexane ring.
αCC$=$N in-plane bending of the C2C7N8 and C17C16N15.
αC$=$NC in-plane bending of C9N8C7 and C10N15C16 bonds.
τC$=$N torsional angles C9N8C7C2 and C10N15C16C17.



with the strength of the hydrogen bond expressed by the N···O distance according to the well-known relation[13] although the theoretical νNH frequency is higher than the experimental one. The scaling factor of 0.978 common for all frequencies in the IR spectrum correctly reproduces the fingerprint region but

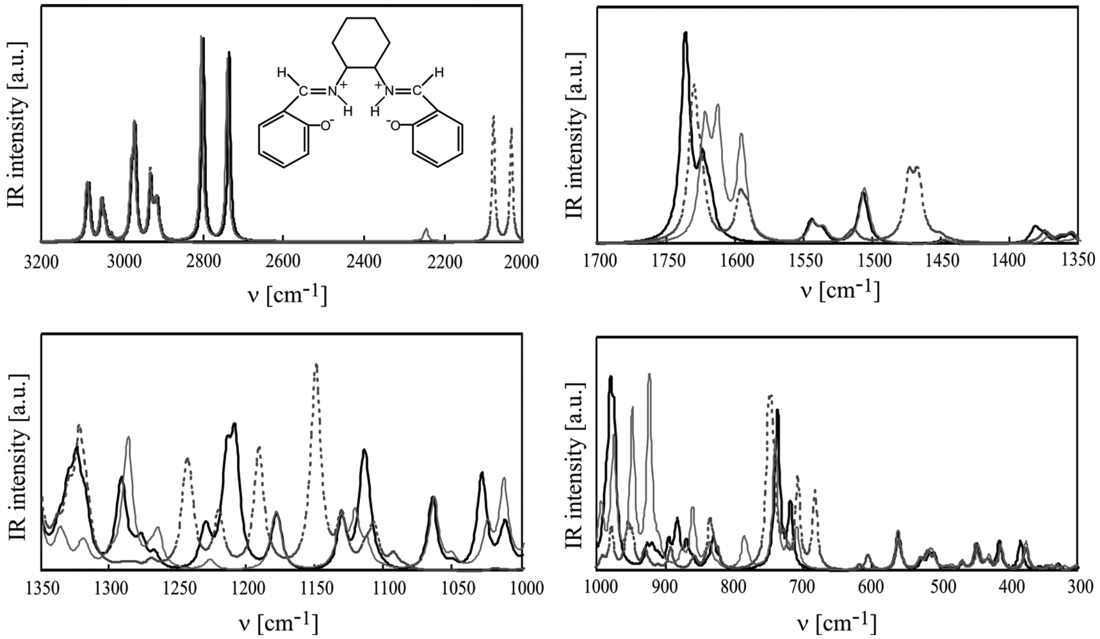


FIGURE 2 Calculated IR spectra of NH tautomer of *trans-N,N′*-bis-(salicylidene)-1′,2′-cyclohexanediamine R = H (I) (solid line) and its analogues where H in the OH group is replaced by D (dotted line) and H in the CH imine group is replaced by D (thin line).

the frequencies above 3000 cm^{-1} are too high. After deuteration, these bands shift by a factor of 1.35 to 2072 and 2027 cm^{-1}, which indicates pure NH vibrations. The stretching frequency of the CH imine group (νCH_{im}) gives rise to hardly visible bands at 3030 and 3023 cm^{-1}, which after deuteration give one broad band at 2230 cm^{-1}. The very intensive band at 1635 cm^{-1} and a medium-intensive band at 1623 cm^{-1} sensitive to the deuteration of the CH_{im} and NH group are assigned to mixed $\nu C=N$, δNH, δCH_{im}, and νCO vibrations. The vibrations at 1619 and 1617 cm^{-1} assigned to the δNH, δCH_{im}, and $\nu C=C$ modes are observed as a shoulder. The δNH vibration is strongly coupled with the $\nu C=N$

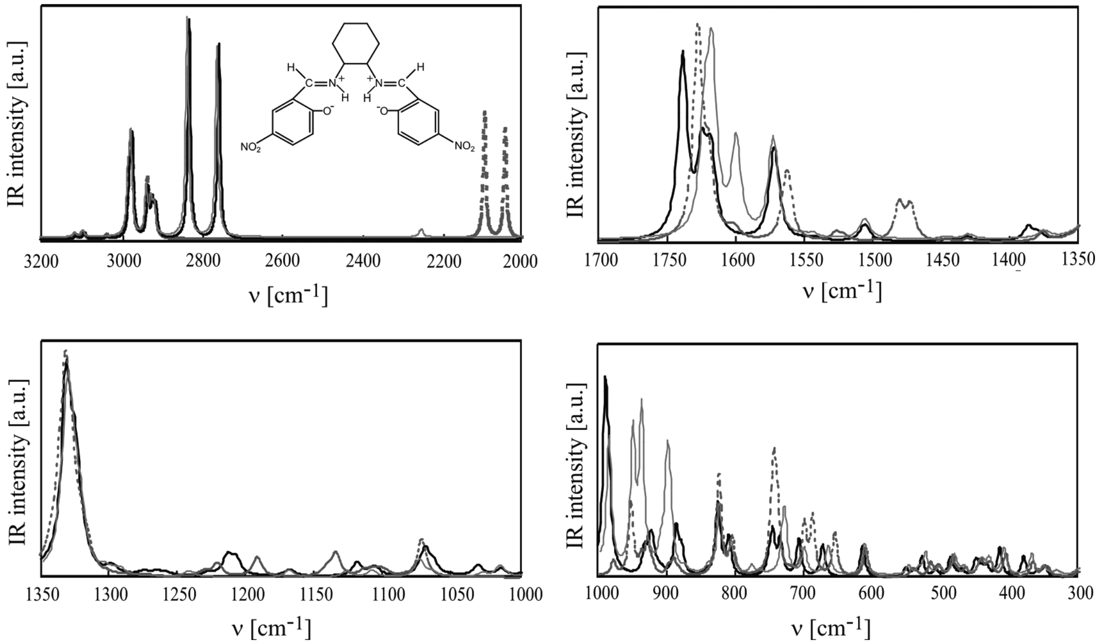


FIGURE 3 Calculated IR spectra of NH tautomer of *trans-N,N′*-bis–(5-nitrosalicylidene)-1′,2′-cyclohexanediamine R = 5-NO$_2$(II) (solid line) and its analogues where H in the OH group is replaced by D (dotted line) and H in the CH imine group is replaced by D (thin line).

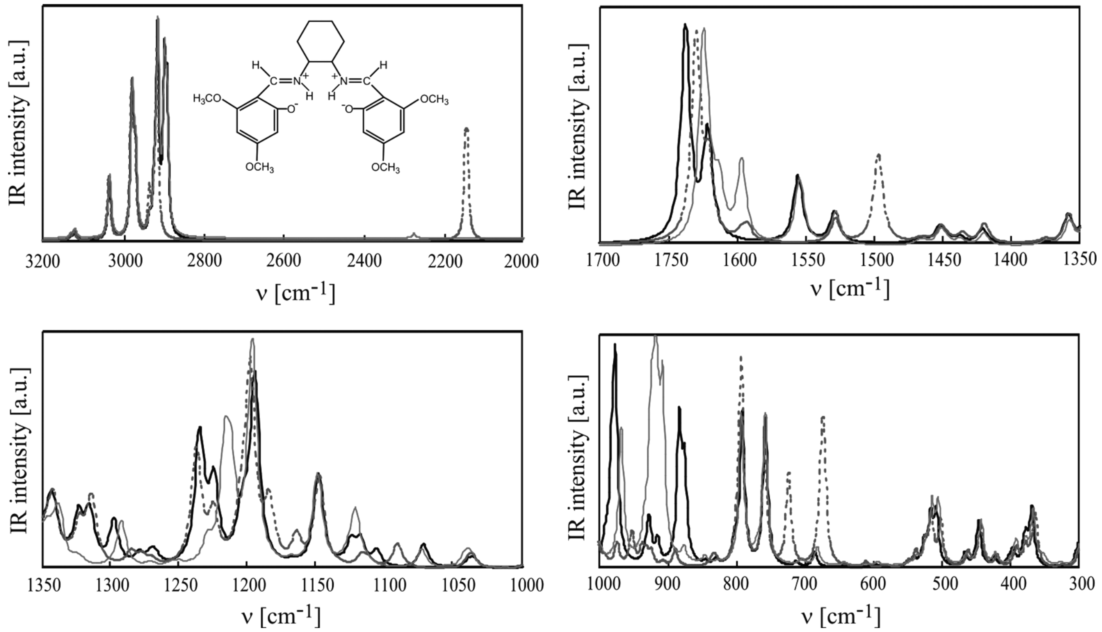


FIGURE 4 Calculated IR spectra of NH tautomer of *trans-N,N′*-bis-(4,6-dimethoxysalicylidene)-1′,2′-cyclohexanediamine R = 4,6-OCH_3 (III) (solid line) and its analogues where H in the OH group is replaced by D (dotted line) and H in the CH imine group is replaced by D (thin line).

vibration and with the $\nu C=C_{ar}$ stretching and δCH_{ar} deformation aromatic ring bands. Two weak absorption bands at 1544 and 1536 cm^{-1} are ascribed to the $\nu C=C$ stretching coupled with $\nu C=O$ and with the δNH vibrations. Comparison of the 1350–1000 cm^{-1} region of the IR spectra of I with its ND and CD imine analogues shows coupling of the NH and δCH imine vibration with the δCH cyclohexyl and δCH aromatic vibrations. The inequality of both the imine moieties additionally complicates the spectrum. The γNH vibration absorbs at 981 and 975 cm^{-1}, coupled with the γCH_{im}. The γNH and γCH_{im} vibrations also

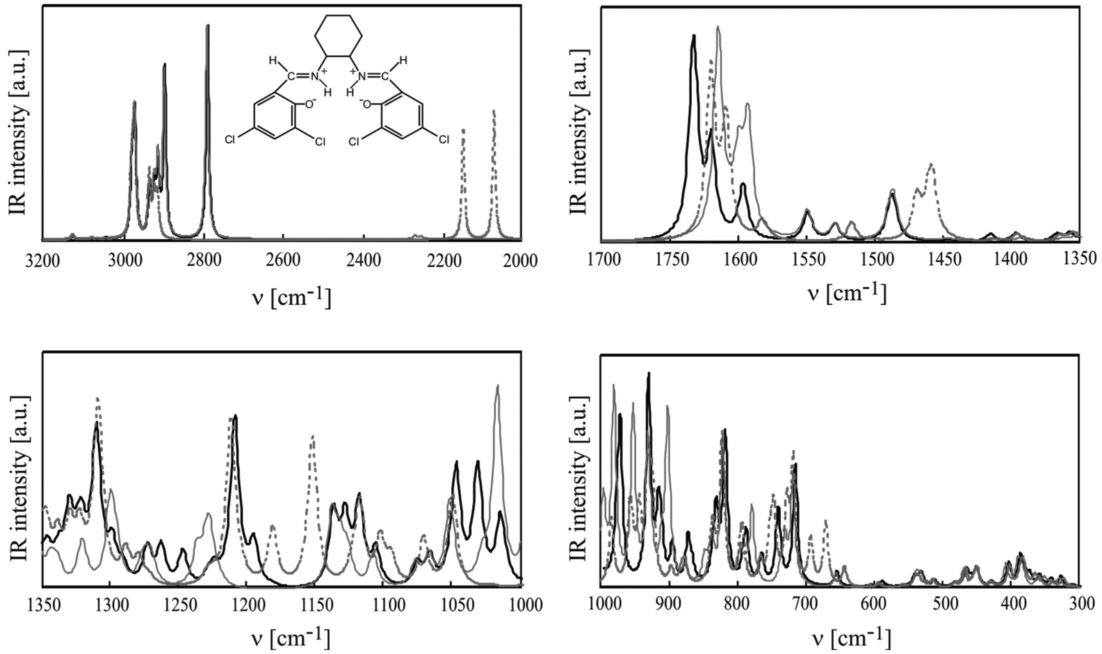


FIGURE 5 Calculated IR spectra of NH tautomer of *trans-N,N′*-bis–(3,5-dichlorosalicylidene)-1′,2′-cyclohexanediamine R = 3,5-Cl (IV) (solid line) and its analogues where H in the OH group is replaced by D (dotted line) and H in the CH imine group is replaced by D (thin line).

contribute to numerous very weak bands in the 1000–300 cm^{-1} region. A detailed assignment of the bands is in[10] Table 2.

Trans-N,N′-bis-(5-Nitrosalicylidene)-cyclohexanediamine (II)

The νNH vibration absorbs at 2830 and 2756 cm^{-1}, indicating the presence of the two different hydrogen bonds that are weaker than those in I (Fig. 3, Table 2). These bands shift after NH deuteration to 2094 and 2043 cm^{-1}. The change by a factor of 1.35 is almost exactly what would be expected for the pure NH mode. The νCH$_{im}$ vibration gives rise to very weak bands at 3041 and 3035 cm^{-1}. The very strong imine band at 1640 and the weaker one at 1627 cm^{-1} are assigned to the νC=N vibration coupled with the δNH and δCH$_{im}$ vibrations. The δNH and δCH$_{im}$ mixed with the νC=O and νC=C gives rise to a band at 1620 cm^{-1}. The δNH vibration also contributes to the band at 1574 cm^{-1} attributed to the ν_{as}NO$_2$ vibration. The mixed νCO, νC=C, and δNH vibrations give rise to a very weak absorption at 1550 cm^{-1}. The δNH vibration coupled with the aromatic stretching vibration absorbs at 1508 cm^{-1}, while those coupled with the δCH$_{im}$ and δCH$_{ar}$ vibrations absorb at 1388 and 1381 cm^{-1}. The 1350 to 1000 cm^{-1} region is dominated by a strong asymmetric band with a maximum at about 1330 cm^{-1}. The BLYP calculations give nine normal modes in the 1345–1320 cm^{-1} region. The mode of frequencies at 1344 cm^{-1} and 1340 cm^{-1} involves the νCO, δNH, δCH$_{im}$, and δCH$_{ar}$ vibrations. The symmetric νNO$_2$ vibrations predominate in the mode at 1333 cm^{-1} of the great intensity, which also involves δCH$_{ar}$ and δCH$_2$. Comparison of the spectra of II and its deuterated analogues indicates that the δNH and δCH$_{im}$ vibrations contribute to all the bands in the 1300–1100 cm^{-1} region. The γNH vibration coupled to the γCH$_{im}$ vibration gives rise to medium-intensity bands at 990 and 985 cm^{-1}. These vibrations also contribute to the modes at 932 and 925 cm^{-1}.

Trans-N,N′-bis-(4,6-Dimethoxysalicylidene)-cyclohexanediamine (III)

The νNH vibration absorbs at 2892 and 2885 cm^{-1}, indicating two NH···O hydrogen bonds of almost equal strength (Fig. 4, Table 3). The higher frequencies,

TABLE 3 **Calculated Frequencies (cm^{-1}) and Intensities (km/mol) for *trans-N,N′*-bis-(4,6-Dimethoxy-Salicylidene)-1′,2′-Cyclohexanediamine**

Mode	ν (cm^{-1})	A (km/mol)	Assignment
34	365	24	τC=N, γCO(CH$_3$)
35	374	12	τC=N
36	379	3	αC=NC, αCC=N, γCH$_{im}$, γNH
37	381	0	αC=NC, αCC=N, γCH$_{im}$, γNH
38	393	7	αCC=N, γCH$_{im}$, γCO(CH$_3$)
39	399	2	δ_{al} ring, αCC=N
40	420	5	δ_{al} ring, αCC=N
41	442	2	δ_{al} ring, αCC=N
42	443	18	τC=N, δ_{al} ring
			τC=N, δ_{al} ring, δCO(CH$_3$), δ_{al} ring, δ_{ar} ring
43	449	1	δ_{al} ring
44	463	6	τC=N
45	505	22	δ_{ar} ring, δCO(CH$_3$), δCO
46	510	1	δCO(CH$_3$), δCO
47	513	19	δCO(CH$_3$), δCO
48	523	9	δ_{ar} ring
49	538	4	δ_{ar} ring, γCH$_{im}$, δCO(CH$_3$)
50	548	2	γCH$_{im}$, δ_{ar} ring
51	585	0	αC=NC, δ_{ar} ring
52	593	1	αC=NC, δ_{ar} ring
53	609	0	τ_{ar} ring
54	610	0	τ_{ar} ring
55	640	1	τ_{ar} ring
56	640	1	τ_{ar} ring
57	682	3	δCH$_{ar}$
58	684	4	δCH$_{ar}$
59	710	1	τ_{ar} ring, γCO
60	711	1	τ_{ar} ring, γCO
61	755	53	γCH$_{ar}$
62	756	7	δCH$_{ar}$, γCH$_{ar}$
63	757	4	δCH$_2$, αC=NC
64	789	34	τ_{ar} ring, γCH$_{ar}$, γCO
65	789	32	τ_{ar} ring, γCH$_{ar}$, γCO
66	797	3	δCH$_2$
67	801	7	δCH$_2$
68	828	3	δCH$_2$
69	843	1	δCH$_2$
70	874	39	γNH, γCH$_{im}$
71	881	59	γNH, γCH$_{im}$
72	884	0	γNH, γCH$_{im}$
73	913	10	δCH$_2$, γNH, δCH$_{ar}$
74	925	8	δCH$_2$, γNH, δCH$_{ar}$
75	926	10	δCH$_2$, γNH, δCH$_{ar}$
76	931	3	δCH$_2$, γNH, δCH$_{ar}$
77	975	80	γNH, δCH$_{ar}$, δCH$_3$, γCH$_{im}$
78	980	32	γ NH, δCH$_{ar}$, δCH$_2$, γCH$_{im}$
79	988	4	γCH$_2$, δCH$_3$
80	990	5	γCH$_2$, δCH$_3$
81	1009	0	δCH$_2$

(*Continued*)

TABLE 3 Continued

Mode	ν (cm^{-1})	A (km/mol)	Assignment
82	1016	0	δCH_2
83	1022	0	δCH_2
84	1033	20	δCH_2, δCH_3, δCH_{ar}
85	1037	18	δCH_2, δCH_3, δCH_{ar}
86	1054	2	δCH_{ar}
87	1070	63	δNH, δCH_{ar}, δCH_2, $\nu N{-}C$, $\nu CO(CH_3)$
88	1104	11	δNH, δCH_{im}, δCH_{ar}, δCH_{ar}
89	1104	30	δNH, δCH_{im}, δCH_{ar}, δCH_{ar}
90	1116	62	δCH_3, δCH_2, δNH
91	1123	60	δCH_3, δNH
92	1132	1	δCH_3, $\delta COCH_3$
93	1132	1	δCH_3, $\delta COCH_3$
94	1133	1	δCH_3, $\delta COCH_3$
95	1133	1	δCH_3, $\delta COCH_3$
96	1146	140	νCO, (CH_3)
97	1148	112	νCO, (CH_3)
98	1165	5	δCH_2, δ CH_{ar},
99	1167	4	δCH_2, δ CH_{ar},
100	1183	0	δCH_2, δ CH_{ar},
101	1193	202	νCO
102	1194	292	νCO
103	1201	84	δCH_{ar}, δCH_{im},
104	1205	57	δCH_{ar}, δCH_{im},
105	1223	117	δCH_2, δCH_{im}, δCH_{ar}, δNH
106	1224	88	δCH_2, δCH_{im}, δCH_{ar}, δNH
107	1232	98	δCH_2, δ CH_{im}
108	1234	253	νNC δCH_2, δCH_{ar}
109	1267	26	δCH_2, δCH_{im}
110	1270	20	δNH δCH_{im}, δCH_2,
111	1278	29	δNH δCH_{im}, δCH_2,
112	1296	80	δNH δCH_{im}, δCH_2,
113	1297	34	δNH δCH_{im}, δCH_2,
114	1313	75	δCH_{im}, δCH_2
115	1316	68	δCH_{im}, δCH_2
116	1322	114	δCH_{im}, δNH
117	1330	14	δCH_{im}, δNH
118	1338	37	δCH_{im},δCH_2 δCH_{ar}
119	1341	105	δCH_{im}, δCH_2 δCH_{ar}
120	1344	57	δCH_{im}, δCH_2 δCH_{ar}
121	1347	19	δCH_{im}, δCH_2, δCH_{ar}
122	1356	232	δCH_2, δCH_{ar}, δCH_{im}
123	1377	11	δCH_{im}, δNH, δCH_2,
124	1380	1	δCH_2, δCH_{im}
125	1418	66	δCH_3, δCH_{im}
126	1418	62	δCH_3, δCH_{im}
127	1434	22	δCH_3, δNH
128	1435	26	δCH_3, δNH
129	1441	1	δCH_3
130	1443	2	δCH_3
131	1443	8	δCH_2
132	1444	2	δCH_2
133	1444	6	δCH_3
134	1444	8	δCH_3
135	1447	22	δCH_2
136	1449	43	δCH_3
137	1450	82	δCH_3
138	1460	3	δCH_2
139	1460	12	δCH_3
140	1461	17	δCH_3
141	1465	12	δCH_3
142	1466	11	δCH_3
143	1524	20	δCH_3, δCH_{ar}
144	1526	224	νCC_{ar}, νCO
145	1549	20	δNH, δCH_{im}, νCO
146	1552	557	δNH, δCH_{im}, νCO
147	1615	46	νCC_{ar}, δNH, δCH_{im}
148	1617	161	νCC_{ar}, δNH, δCH_{im}
149	1619	743	νCC_{ar}, δNH
150	1634	1799	$\nu C = N$, δCH_{im}, δNH
151	2885	162	νNH
152	2892	195	νNH
153	2908	50	νCH_3
154	2908	25	νCH_3
155	2909	86	νCH_3
156	2909	20	νCH_2
157	2909	50	νCH_2
158	2910	28	νCH_2
159	2914	4	νCH_2
160	2917	45	νCH_2
161	2918	5	νCH_2
162	2929	19	νCH_2
163	2963	61	νCH_3
164	2965	45	νCH_3
165	2971	29	νCH_3
166	2971	51	νCH_3
167	2971	13	νCH_3
168	2972	39	νCH_2
169	2972	6	νCH_2
170	2974	58	νCH_2
171	3028	27	νCH_3
172	3028	30	νCH_3
173	3031	16	νCH_3
174	3031	17	νCH_3
175	3070	0	νCH_{im}
176	3071	0	νCH_{im}
177	3115	6	νCH_{ar}
178	3116	6	νCH_{ar}
179	3126	2	νCH_{ar}
180	3126	2	νCH_{ar}

in comparison with those previously discussed, indicate a weaker hydrogen bond. The νCH_{im} mode gives a very weak absorption band at the highest wave numbers in the studied series of Schiff bases. In the imine band region, only two bands are observed. The very strong absorption band at 1634 cm^{-1} was assigned to the $\nu C=N$ vibration coupled with the δNH and δCH_{im}. In the strong band at 1619 cm^{-1}, three modes are engaged: one at 1619 cm^{-1} assigned to δNH and $\nu C=C$ and at 1617 cm^{-1} and 1615 cm^{-1} assigned to the δNH, $\nu C=C$, and δCH_{im} vibrations. The band at 1552 cm^{-1} is assigned to $\nu C=C$, δNH, and νCO. The νCO vibration also participates in the $\nu C=C_{ar}$ band at 1526 cm^{-1}. The low-intensity bands in the 1466–1380 cm^{-1} region originate from the deformation vibrations of the CH_3 and CH_2 groups. The δCH_{im} vibration predominates in the band at 1322 cm^{-1} and participates in the numerous medium and weak bands in the region between 1377 and 1220 cm^{-1}. The medium-intensity band at 1148 cm^{-1} is attributed mainly to δCH_3 and δCH_{ar} and $\nu CO(CH_3)$ groups. The γNH vibration participates in the numerous bands in the 975–874 cm^{-1} region.

Trans-N,N′-bis-(3,5-Dichlorosalicylidene)-cyclohexanediamine) (IV)

The nonequivalence of the salicylidene moieties is greater than in the other compounds of the series. The νNH stretching vibration of 2896 cm^{-1} corresponds with the longer hydrogen bond (2.5619 Å) and that of 2788 cm^{-1} to the shorter one (2.5293 Å) (Table 4). The first νNH stretching vibration also contributes to the weak bands at 2913 and 2911 cm^{-1} assigned to νCH_2 of the cyclohexyl ring. The very weak absorption bands at 3065 and 3044 cm^{-1} are assigned to the stretching vibrations of the imine groups. The $\nu C=N$ vibrations coupled with δNH and δCH_{im} give rise to the very strong bands at 1635 cm^{-1} and the weaker one at 1622 cm^{-1}. The mixed δNH, νCO, and $\nu C=C_{ar}$ vibrations absorb at 1599 cm^{-1}. These vibrations also give rise to the bands at 1551 and 1531 cm^{-1}. $\nu C=C$ coupled with δNH absorbs at 1491 and 1488 cm^{-1}. The weak bands in the 1417–1348 cm^{-1} region are assigned to the δCH_{im} vibrations mixed with those of δCH_{ar}, δCH_2, and δNH. Comparison of the 1350–1000 cm^{-1} region of the spectra of the nondeuterated and the NH and CH deuterated compounds (Fig. 5) shows the extensive coupling of the δCH_{im} vibration with the deformation vibrations of the aromatic and aliphatic CH

TABLE 4 **Calculated Frequencies (cm^{-1}) and Intensities (km/mol) for *trans-N,N′*-bis-(3,5-Dichlorosalicylidene)-1′,2′-cyclohexanediamine**

Mode	ν (cm^{-1})	A (km/mol)	Assignment
26	358	2	$\tau C=N$, $\alpha CC=N$
27	360	3	τ_{ar} ring, γCH_{im}, γNH
28	374	6	$\alpha CC=N$, γNH
29	381	4	$\alpha C=NC$, $\alpha CC=N$
30	386	6	δ_{ar} ring, $\alpha CC=N$, δ_{al} ring
31	388	10	δ_{al} ring, $\tau C=N$
32	405	12	δ_{ar} ring, δ_{al} ring
33	430	2	δ_{al} ring
34	452	9	δ_{al} ring, γCH_{im}, δCO
35	460	3	$\tau C=N$
36	467	9	δ_{al} ring,
37	483	2	τ_{ar} ring, γCH_{ar}, γCH_{im}, γNH
38	514	3	τ_{ar} ring, γCH_{ar}, γCH_{im}, γNH
39	533	4	δ_{ar} ring, δCH_{im}, δ_{al} ring
40	534	3	δ_{ar} ring δCH_{im}, δ_{al} ring
41	539	1	δ_{ar} ring
42	544	5	δ_{al} ring, δCH_{im}, δ_{ar} ring, γNH
43	561	1	δ_{al} ring, δCH_{im}, δ_{ar} ring
44	591	3	τ_{ar} ring, γCH_{ar}
45	608	1	δ_{ar} ring, γNH, γCH_{im}
46	658	8	δ_{ar} ring, γNH, γCH_{im}
47	709	1	τ_{ar} ring, γCO, γCH_{im}, γCH_{ar}
48	719	63	δ_{ar} ring, δCH_{im}
49	743	16	τ_{ar} ring, γCO, γCH_{im}
50	745	25	τ_{ar} ring, γCO, γCH_{im}
51	769	15	δCH_2
52	791	24	γCH_{ar}, γCH_{im}
53	796	9	δ_{ar} ring, δCH_{im}
54	822	75	δ_{ar} ring, δCH_{im}
55	825	3	δCH_2
56	835	26	γCH_{ar},γCH_{im}, δNH
57	837	13	γCH_{ar}, γCH_{im}, δNH
58	842	8	δCH_2, γNH
59	871	8	γNH, γCH_{im}, γCH_{ar}
60	877	23	γNH, γCH_{im}, γCH_{ar}
61	879	0	δCH_2
62	900	19	γNH, γCH_{im}
63	917	20	γCH_{im}, γNH, δCH_2
64	921	33	γCH_{im}, γNH, δCH_2
65	935	101	γNH, γCH_{im}, δCH_2
66	937	6	δCH_2, δCH_{im}, νCC_{im}
67	977	79	γCH_{im}, γNH
68	983	23	γCH_{im}, γNH
69	1012	6	δCH_2
70	1016	45	δCH_2, γNH, γCH_{im}
71	1033	82	δCH_{im}, γNH, γCH_{ar}, δCH_2
72	1049	80	γCH_{ar}, δCH_2, δCH_{im}, γNH
73	1053	5	δCH_2
74	1068	20	δCH_{ar}, δNH
75	1077	16	δCH_{ar}, δNH

(*Continued*)

TABLE 4 Continued

Mode	ν (cm^{-1})	A (km/mol)	Assignment
76	1107	25	δCH_2, δCH_{ar}
77	1120	57	δCH_{im}, δCH_2, δCH_{ar}
78	1130	43	δCH_{ar}, δNH, δCH_{im}
79	1138	49	δCH_{ar}, δNH
80	1183	1	δCH_2
81	1197	30	δCH_{im}, δCH_{ar}
82	1211	117	δCH_{im}, δCH_{ar}, δNH, δCH_2
83	1225	11	δCH_2, δCH_{im}
84	1230	7	δCH_2, δCH_{im}
85	1249	24	δCH_{im}, δNH, δCH_2, $\delta CHar$
86	1265	27	δCH_{im}, δNH, δCH_2, δCH_{ar}
87	1275	26	δNH, δCH_{ar}, δCH_2
88	1286	0	δCH_2, δCH_{im}, δCH_{ar}
89	1293	12	δCH_2, δCH_{im}, δCH_{ar}
90	1300	26	δCH_2, δNH
91	1312	105	δCH_{im}, δCH_2
92	1318	2	δCH_{im}, δCH_2
93	1323	33	δCH_{im}, δCH_2
94	1326	12	δCH_{ar}, δNH, δCH_{im}, νco
95	1332	45	δCH_2, δCH_{im}
96	1339	17	δCH_2, δCH_{im}
97	1344	4	δCH_2
98	1348	20	δCH_2, δCH_{im}
99	1359	47	δCH_{im}, δCH_{ar}, δNH
100	1368	44	δCH_{im}, δCH_{ar}, δNH
101	1398	50	δCH_{ar}, δNH, δCH_{im}
102	1417	46	δCH_{ar}, δNH, δCH_{im}
103	1442	0	δCH_2
104	1444	3	δCH_2
105	1448	9	δCH_2
106	1460	2	δCH_2
107	1488	223	νCC_{ar}, δNH
108	1491	90	νCC_{ar}, δNH
109	1531	104	νCC_{ar}, δNH
110	1551	173	νCC_{ar}, δNH
111	1599	319	νCC_{ar}, δNH
112	1605	4	$\nu C=N$, νCO, δNH, νCC_{ar}, δCH_{im}
113	1622	559	$\nu C=N$, νCO, δNH, $\nu C=C$, δCH_{im}
114	1635	1195	$\nu C=N$, δNH, δCH_{im}, νCO
115	2788	147	νNH
116	2896	116	νNH
117	2911	21	νNH, νCH_2
118	2913	19	νNH, νCH_2
119	2915	8	νCH_2
120	2920	5	νCH_2
121	2922	28	νCH_2
122	2934	34	νCH_2
123	2970	48	νCH_2
124	2972	34	νCH_2
125	2975	14	νCH_2
126	2979	36	νCH_2
127	3044	1	νCH_2
128	3065	0	νCH_{im}
129	3079	1	νCH_{im}
130	3099	0	νCH_{ar}
131	3114	0	νCH_{ar}
132	3127	3	νCH_{ar}

(*Continued*)

groups. δNH also participates in numerous bands in this region. γNH coupled with γCH and δCH_2 give rise to several bands in the 983–720 cm^{-1} range. These vibrations also contribute to very weak absorption bands in the 700–300 cm^{-1} region.

DISCUSSION

Analysis of the geometric parameters (Table 1) of *trans-N,N′*-bis(R-salicylidene)-cyclohexanediamine I–IV permits drawing conclusion concerning the influence of the aromatic ring substituent on the hydrogen bond strength. The N···O distances of 2.53–2.55 Å indicate the presence of a medium-strength hydrogen bond. The partially ionic character of the NH+···O$^-$ hydrogen bond can be suggested on the basis of the C–O distances.[14] For I, an about 50% zwitterionic structure (Scheme 1) has been proposed.[9] The differences in bond length between the two salicylidene moieties are observed in all the compounds but III. In the series of OH tautomers, differentiation of the two moieties was observed only in IV. Comparison of the calculated N···O distances for the respective NH and OH tautomers[6] shows that proton transfer leads to a shortening of the hydrogen bond N···O bridge and increases the nonequivalence of the moieties. In IV, the N···O distances in the two moieties differ considerably. One of the N···O distance is the longest one, and the other is the shortest in the series of NH tautomers studied. This difference in N···O length in the two moieties of these compounds cannot be explained, as for the OH tautomers, by mesomeric and steric effects only. In these di-Schiff bases, the inductive and field effects of the C=NH$^+$ groups have to be taken into account. The NMR results indicated interrelations between the two hydrogen bonds in the Schiff base derivatives of 1,2-diaminocyclohexane.[6,8,15] Comparison of the distances in I and II shows that introduction of the NO_2 group to the salicylidene ring causes elongation of the N···O bridge and differentiation of the N···O bond in the two salicylidene moieties. The NO_2 group in *para* position to phenolic oxygen causes a decrease in its proton acceptor properties, which causes a decrease in the hydrogen bond strength. The unfavorable electrostatic interactions between the two NH^+ groups additionally influences the N···O distances in the two moieties. The presence of two electron-donor OCH_3 groups in III leads to an increase in the charge density on the N atoms, which explains the relatively long N···O distance similar in both salicylidene moieties.

The calculated νNH frequencies in the range 2913–2730 cm^{-1} are in agreement with the N···O bond length and confirm the presence of the moderately strong hydrogen bonds. It should be noted that the calculated νNH frequencies are generally higher than the experimental values due to neglecting the intermolecular interactions and the anharmonicity of these vibrations. The νNH frequency indicates that the $NH^+ \cdots O^-$ hydrogen bonds are stronger than the OH···N ones.[9] Comparison of the νNH frequencies of the investigated compounds shows, similarly as their distances, that the introduction of the electron donor and electron withdrawing substituents leads to weakening of the hydrogen bond. The stretching vibration of the NH groups for all the compounds but III gives rise to double bands, in accordance with the two different N···O distances in the molecules (Figs. 2–5).

The stretching vibration of the imine CH group νCH_{im} gives rise to weak absorption bands in the 3126–3023 cm^{-1} region whose frequencies decrease in inverse range in comparison with the νNH.

Comparison of the 1700–300 cm^{-1} region shows that other vibrations of the NH form of *trans-N,N'*-bis-(R-salicylidene)-cyclohexanediamine are sensitive to the substituents on the aromatic ring.

The most characteristic vibrations of the Schiff bases are those of the C = N imine group, strongly coupled with the other vibration that influence several bands in the region of 1640–1605 cm^{-1}. The appearance of the band at 1640–1635 cm^{-1} sensitive to NH and CH deuteration confirms a contribution from the resonance zwitterionic structure of tautomeric NH form. The origin of the absorption in the 1650–1630 cm^{-1} region of the IR spectra of the NH tautomers of Schiff bases has been the subject of discussion.[15–17] Assignment to νCO and $\nu C = NH^+$ vibrations has been proposed. Unequivocal assignment of the νCO vibration is difficult due to the complicated nature of the normal modes and overlapping of the bands. For OH tautomers, the νCO vibration participates in the bands in the 1290–1215 cm^{-1} region.[9,10] For the NH form of the Schiff bases under study, this vibration is substituent sensitive and participates in the bands in the 1635–1552 cm^{-1} region. For all compounds, absorption bands at 1530–1550 cm^{-1} are observed. This mode is assigned to coupled δNH and $\nu C = C$ vibrations, and for I and III also to νCO ones. This band was recognized to be very characteristic for NH tautomers and Schiff base complexes.[15,17–19] Yuzawa[15] assigned it to the vibration of the $^-O–C = C–C = N^+ \leftrightarrow O = C–C = N$ group. The deformation vibrations of the imine group are difficult to assign due to a strong coupling with the other vibration. The 1350–1100 cm^{-1} region is characteristic for each compound of the series due to the presence of the absorption bands of the substituents (NO_2, OCH_3) and the differences in the coupling of the vibrations. γNH coupled with γCH_{im} is associated with the bands in the 980–930 cm^{-1} region. The very weak absorption bands in the region below 700 cm^{-1} are related mainly to the deformation vibration of the aromatic and aliphatic rings and to skeletal deformations.

The vibrations of the cyclohexyl absorb at the characteristic regions, strongly mixed with the δCH_{im}, δCH_{ar}, and δNH vibrations. The deformation vibrations of the aromatic CH group are difficult to assign due to strong mixing with the other vibrations.

CONCLUSIONS

DFT analysis of the *trans-N,N'*-bis-(R-salicylidene)-1,2-cyclohexanediamines shows that proton transfer leads to differentiation of the N···O bridges in the salicylidene moieties, which depends on the substituent in the aromatic ring. Comparison of the IR spectra of compounds I–IV and their analogues deuterated in the NH and CH imine groups provides evidence of the complicated nature of the normal modes. Vibrational analysis of the NH tautomers of the *trans-N,N'*-bis-(R-salicylidene)-1,2-cyclohexanediamines (R = H, 5-NO_2, 4,6-di-OCH_3, 3,5-diCl) permitted postulating some generalities concerning the IR spectra of these compounds as well as offering some possibilities of investigation of the substituent effect on $NH^{+}\cdots O^{-}$ hydrogen bond strength. The theoretical analysis of the pure OH and NH forms of *trans-N,N′*-bis-(R-salicylidene)-1,2-cyclohexanediamines suggested in this paper can be useful in the interpretation of experimental IR spectra in which both these forms coexist.

ACKNOWLEDGMENT

We thank the Wrocław Center for Networking and Supercomputing and for generous computer time.

REFERENCES

1. Dziembowska, T. *Pol. J. Chem.* **1998**, *72*, 193–209.
2. Hadjoudis, E.; Mavridis, I. M. *Chem. Soc. Rev.* **2004**, *33*, 579–588.
3. Calligaris, M.; Randaccio, L. In *Comprehensive Coordination Chemistry*; Vol. 2, Wilkinson, G., Ed.; Pergamon Press: Oxford, 1987; 715–738.
4. Canali, L.; Sherington, D. C. *Chem. Soc. Rev.* **1999**, *28*, 85–93.
5. Larrow, J. F.; Jacobsen, E. N. In *Topics Organometalic Chemistry 6*; Larsen, R. D., Ed.; Springer-Verlag: Berlin, 2004; 123–152.
6. Ambroziak, K.; Rozwadowski, Z.; Dziembowska, T.; Bieg, B. *J. Mol. Struct.* **2002**, *615*, 109–120.
7. Ambroziak, K.; Pelech, R.; Milchert, E.; Dziembowska, T.; Rozwadowski, Z. *J. Mol. Catal. A* **2004**, *211*, 9–16.
8. Dziembowska, T.; Ambroziak, K.; Rozwadowski, Z.; Schilf, W.; Kamieński, B. *Magn. Reson. Chem.* **2003**, *41*, 135–138.
9. Majerz, I.; Dziembowska, T.; Ambroziak, K. *J. Mol. Struct.* **2007**, *828*, 166–173.
10. Dziembowska, T.; Ambroziak, K.; Majerz, I. *J. Mol. Struct.* **2005**, *738*, 15–24.
11. Rozwadowski, Z.; Ambroziak, K.; Dziembowska, T.; Kotfica, M. *J. Mol. Struct.* **2002**, *643*, 93–100.
12. Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Scuseria, G. E.; Robb, M. A.; Cheeseman, J. R. Gaussian 1998, Revision A.9. Gaussian, Inc.: Pittsburgh, PA, 1998.
13. Lautie, A.; Froment, F.; Novak, A. *Spectrosc. Lett.* **1976**, *9*, 289–299.
14. Filarowski, A.; Koll, A.; Głowiak, T.; Majewski, E.; Dziembowska, T. *Ber. Bunsenges. Phys. Chem.* **1998**, *102*, 393.
15. Yuzawa, T.; Takahashi, H.; Hamaguchi, H. *Chem. Phys. Lett.* **1993**, *202*, 221–226.
16. Turbeville, W.; Dutta, P. K. *J. Phys. Chem.* **1990**, *94*, 4060–4066.
17. Berkesi, O.; Kőrtvélyesi, T.; Hetényi, C.; Németh, T.; Pálinkó, I. *Phys. Chem. Chem. Phys.* **2003**, *5*, 2009–2014.
18. Percy, G. C.; Thronton, D. A. *J. Inorg. Nucl. Chem.* **1972**, *34*, 3357–3367.
19. Gluvchinsky, P.; Mockler, G. M.; Sinn, E. *Spectrochim. Acta* **1977**, *33A*, 1073–1077.