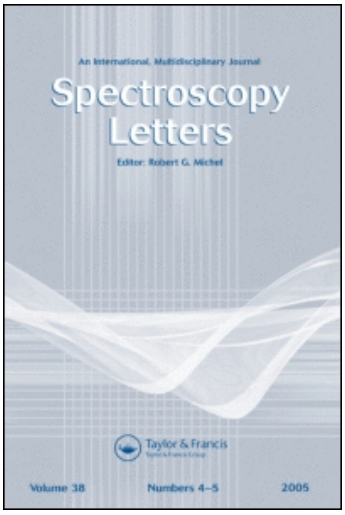

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Vibrational Spectra of Benzylidene Aniline, O-Hydroxybenzylidene O-Hydroxyaniline and its Complexes with Cu(II) and NI(II) Metal Ions

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VIBRATIONAL SPECTRA OF BENZYLIDENE ANILINE, O-HYDROXYBENZYLIDENE O-HYDROXYANILINE AND ITS COMPLEXES WITH CU(II) AND NI(II) METAL IONS

Keywords: benzylidene aniline, and o-hydroxybenzylidene o-hydroxyaniline, FTIR and FT Raman

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ABSTRACT

The FTIR and FT Raman spectra of benzylidene aniline, and o-hydroxybenzylidene o-hydroxyaniline compounds in the solid state in the wavenumber (1800-200 cm^{-1}) are recorded. An assignment for nearly all fundamentals are proposed. Comparison of the spectra of trans stilbene and benzylidene aniline reveals that ν N-Ph stretch for the latter compound is situated at 1368 cm^{-1} in the IR spectra with medium intensity. For o-hydroxybenzylidene o-hydroxyaniline, the stretching modes ν N-Ph, and ν C–Ph are observed at 1356 and 1226 cm^{-1} respectively. The two ν O-Ph are observed as intense bands in the IR spectra at 1245 and 1278 cm^{-1}, respectively. The FTIR spectra of the o-hydroxybenzylidene o-hydroxyaniline complexes with Cu(II) and Ni(II) metal ions are also recorded and assigned.

INTRODUCTION

There has been considerable interest for studying molecular systems having photo and thermochromism [1, 2]. Many studies have dealt with this topic, for example, a spectroscopic

analysis of the photochromic compound N-(2-hydroxybenzylidene aniline) and its photoproduct was achieved [2]. The complexes of this ligand with some transition metal ions are prepared and characterized [3].

Despite these previous spectroscopic studies, only a few vibrational studies have been devoted toward the analysis and attribution of the two compounds, benzylidene aniline and o-hydroxybenzylidene o-hydroxy aniline. We present here, an almost complete vibrational assignment for the two compounds, benzylidene aniline (BZA), and o-hydroxybenzylidene o-hydroxy-aniline (OHBZA) in the 1800-200 cm^{-1} range. The synthesized complexes of the ligand (OHBZA) with Cu(II) and Ni(II) ions are also demonstrated with their FTIR spectra recorded and characterized. We discuss, at first, the assignment of the (BZA) IR and Raman spectra by comparison with monosubstituted benzene derivatives [4]. Then, the IR and Raman spectra of (OHBZA) are assigned as o-substituted benzene derivatives [4]. Finally the Cu(II)–OHBZA and Ni(II)-OHBZA IR spectra are assigned in comparison with the salicylaldimine complexes of Cu(II) and Ni(II) metal ions[3].

EXPERIMENTAL

The compounds (BZA) and (OHBZA) were prepared and purified as described before [5]. The two complexes Cu(II)–OHBZA and Ni(II)-OHBZA are prepared via a procedure similar to that of ref. [3] only using methanol as a solvent. The C, H, N elemental analysis indicates that the two ions form 1:1 complexes having the formula $MOHBZA{\bullet}3H_2O$ where M represents the metal ions Cu(II) or Ni(II). The two compounds BZA and OHBZA were sublimed under reduced pressure before recording the IR and Raman spectra. Infrared spectra were recorded in the solid state as KBr pellets on Mattson 1000 FTIR spectrometer or dispersed as a nujol mull between two CsI (cesium iodide) plates on a Perkin Elmer 983 spectrometer. Elemental analysis was done using a Perkin Elmer 2400 apparatus. Raman spectra were recorded on a Perkin Elmer FT Raman 2000R spectrometer equipped with a

Nd:YAG laser source of wavelength = 1064 nm. The samples were inserted in tubes of small diameter and excited using a laser power of about 100 mw. The spectra were also recorded as micro samples using the xy Dilor spectrometer, having laser lines of wavelengths equal to 632. 816, 514. 532 and 457. 94 nm of ionized Krypton and argon lasers. The laser power was about 0. 240 mw.

RESULTS AND DISCUSSION

The IR and Raman spectra (1800-200 cm^{-1}) of (BZA) and (OHBZA) compounds are displayed in Figs. 1 and 2, respectively. The FTIR spectra of the two complexes Cu(II) – OHBZA and Ni(II)-OHBZA are given in Fig. 3. The IR and Raman wavenumbers are listed together with their proposed assignments in Tables I and II for (BZA) and (OHBZA), respectively. Table II also contains the IR spectra of Cu(II) –OHBZA and Ni(II)-OHBZA. In the absence of x-ray studies of the two molecules (BZA) and (OHBZA), we assume here that the symmetry is nearly C_s. For molecules of C_s type the vibrations are of types A' and A'', both are IR and Raman active. The assignment notations are those of Wilson [6] as adapted for substituted benzene derivatives [4].

Vibrational assignment of (BZA)

According to the C_s point group, (BZA) spans the following representation: 47 A + 22 A''. The spectra of this compound can be safely attributed by comparison with those of trans stilbene [7] and N, N-dimethyl aniline [8]. The ν N-Ph is assigned to the IR band at 1368 cm^{-1} and the Raman line at 1367 cm^{-1}. This mode was found at 1366 cm^{-1} for N-(2-hydroxybenzylidene) aniline [2] and at 1348 cm^{-1} for N, N-dimethyl aniline [8]. For stilbene, no bands were observed at this wave number confirming our assignment [7]. The ν_a C= N is localized at 1627 cm^{-1} in the Raman and 1630 cm^{-1} in the IR spectra as previously found [10]. For stilbene ν C=C is observed at 1639 cm^{-1} in the Raman spectra [7] indicating some

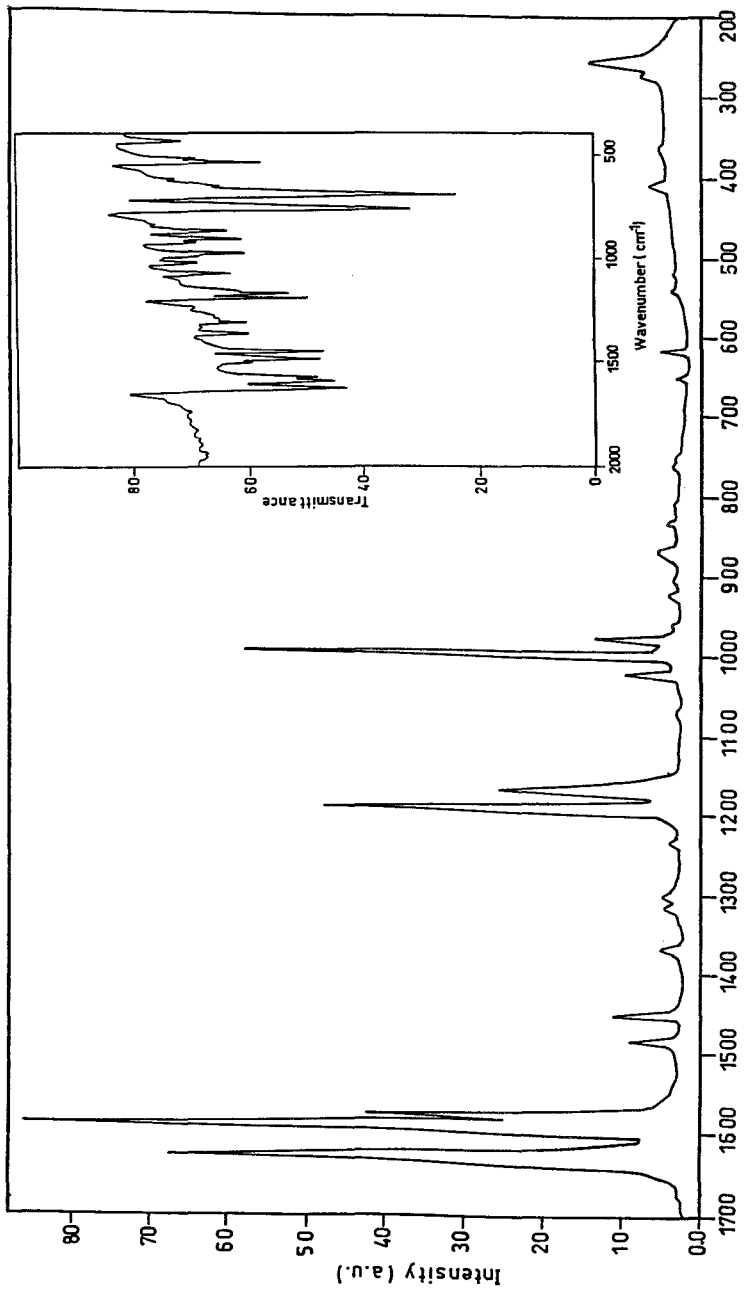

FIG 1. IR and Raman spectra of BZA (IR, above and Raman below).

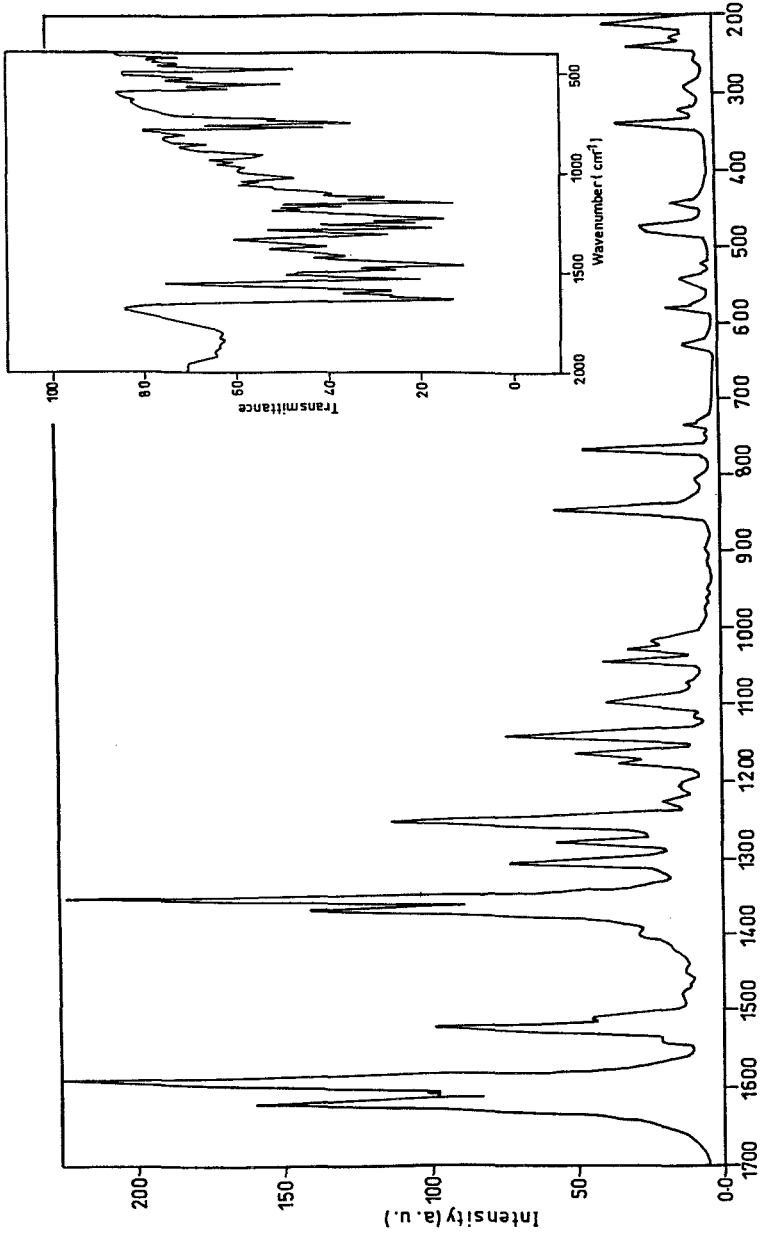

FIG 2. IR and Raman spectra of OHBZA (IR, above and Raman, below).

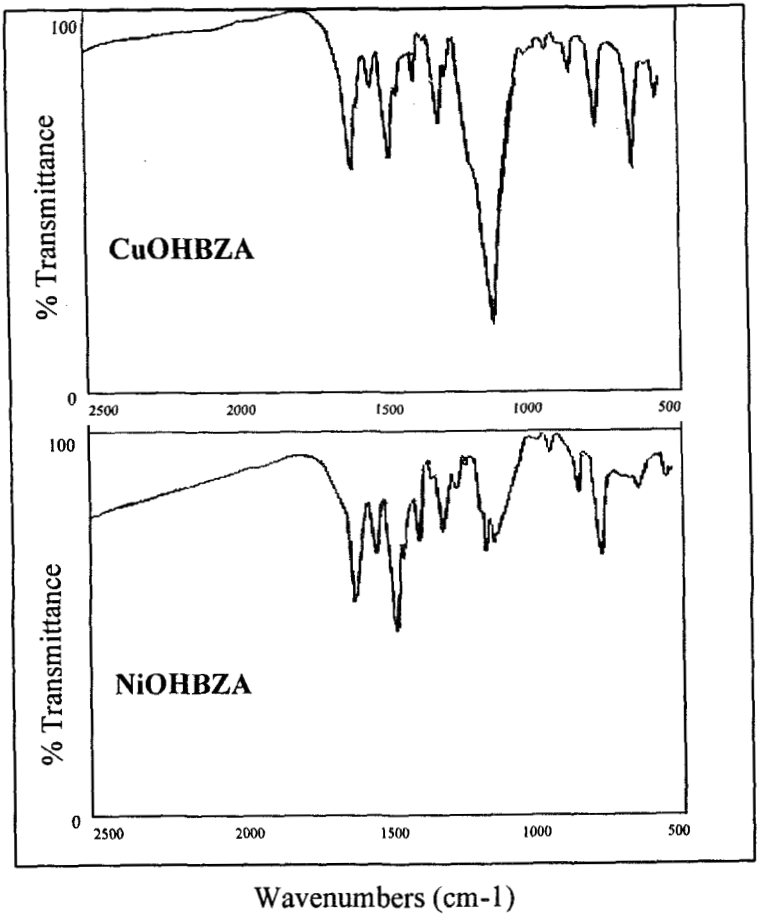

FIG 3. IR of Cu(II)-OHBZA(above) and of Ni(II)-OHBZA(below).

more conjugation in the (BZA) molecule. The ν C-Ph corresponds to the strong IR and Raman peaks at 1193 cm^{-1}. For stilbene, it was observed at 1193 cm^{-1} in the Raman and at 1218 cm^{-1} in the IR spectra. The other vibration modes lie in the expected region as for monosubstituted benzene [4, 7, 8]. However, it is difficult to differentiate between the δCH of the ring (number 3) and δCH of the imine group which are probably coupled. The γ CH of the imine group is assigned to the IR band at 871 cm^{-1} and the Raman line at 868 cm^{-1}. This

TABLE 1

IR and Raman band wavenumbers (cm^{-1}) and assignments of Benzylidene aniline(BZA) *.

IR(Nujol)	IR(KBr)	Raman(solid)	Symmetry	Assignment
1627s	1630s	1627s	A′	ν C=N
1591m	1591m	1590vs	A′	8a
1576m	1581m	1579s	A′	8b
1482m	1487m	1484m	A′	19a
1450s	1451s	1451s	A′	19b
1365m	1368m	1367w	A′	νN-Ph
1338m	1328m		A′	14
1312m	1310vw	1314w	A′	δCH imine
1300w	1293m	1300w	A′	3
1241w	1257w	1238w	A′	
1191s	1194s	1193s	A′	ν C-Ph
1170m	1170m	1171m	A′	9a
1157w	1150m	1155s	A′	9b
1072m	1074m	1075vw	A′	18b
1025m	1030m	1024m	A′	18a
988m	998w	999s	A′	12
975s	978m	979w	A"	17a
960w		962w	A"	17a
925m		923w	A"	17b
906s		908m	A"	17b
871m	882m	868w	A"	γCH imine
	846w	851vw	A"	10a
852vw				
832w	834w	834w	A"	10a
765vs	762vs	762w	A"	11
697vs	696vs	693vw	A"	4
665m			A"	4
652m	654m	651w	A′	δCCN
617m	620m	617w	A′	6b
540s	543m	541vw	A′	δ CCN
530m	532m		A′	6a
518m	520m	520vw	A"	16b
436s	438m		A"	16a
402m		409w	A′	15
364m		362w	A′	15
273m		273w	A"	t C=N
250m		258m	A′	δCCN
224w			A"	10b

*/ v:very, s:strong m:medium and w:weak

TABLE 2
IR and Raman band wavenumbers and assignments for o-hydroxybenzylidene o-hydroxy aniline(OHBZA), CuOHBZA and NiOHBZA.

IR (Nujol)	IR (KBr)	Raman (solid)	CuOHBZA	NiOHBZA	Symmetry	Assignment
1628 vs	1634vs	1624 s	1610 s	1613 s	A′	ν C=N
1611m	1611m		1590 m		A′	8b
1594m	1593m	1599vs	1554 m	1538 m	A′	8a
1528s	1533s	1524s	1469 s	1467 s	A′	19b
1495m	1485m			1383 m	A′	19b
1413m	1416m			1435 m	A′	δOH asso.
	1370m	1370s	1377 m		A′	14(ring A)
1356m		1356s	1410 w		A′	νN-Ph
1306s	1308m	1306w			A′	δ CH imine
1278s	1278s	1278m	1330 w	1332 w	A′	νC-O, dOH
1245m	1245s	1253s	1255 w	1248 w	A′	νC-Ph
1226s	1225s	1226w	1295 s	1300 s	A′	ν C-O, δOH
1177w	1177w	1177w	1204 w	1202 w	A′	9a (ring B)
1162m	1162m	1165m	1150 sh	1150 s	A′	9a (ring A)
1141s	1140s	1141s			A′	18a (ring B)
1118m	1116m		1112 vs	1110 m	A′	18a(ring A)
1098w		1098m				11+10a
1045w	1045w	1045m			A′	18b (ring A)
1028w	1028m	1028w			A′	18b (ring B)
1018w		1018w			A"	5
970w			983 w	980 vw	A"	5
945w			940 vw	942 vw	A"	17b
922w					A"	17b
905w	905m		910 w	920 w	A"	γ CH imine
855w	855w	848m	833 m	828 m	A"	17a
805w	805w	807w			A′	12
768s	765s	769m			A"	11
742s	743s	736w	748 s	746 s	A"	11
726w		726vw			A′	1
630vw		620w	618 s	614 s	A′	δ CCN, νM-O
573w	581m	581w			A"	16a
549m	550s	542w	535 m	534 m	A′	δ CCN
477s	480s	475m			A′	6b
452w	443w	443w			A′	6b
420w	430w		417 w	412 w	A′	9b
342w		340m			A"	10a
292sh		292w			A"	10a
284m					A"	t C=N
242m		240m			A′	15
		230w			A′	15
		212m			A"	10b

assignment was previously given for this compound in the IR spectra [9]. The assignment of bands below 650 cm^{-1} are tentative despite its agreement with those of monosubstituted benzene derivatives [4, 7]. It is worth noting that the imine group in (BZA) binds two phenyl groups, hence we have two kinds of substituted rings (phenyl-C and phenyl-N). It is expected that the vibration modes of each ring may be observed [2, 4]. For example, for vibration number 11 (γ CH ring) two bands are observed at 750 and 765 cm^{-1} for this mode for BZA molecule (Table 1).

Vibrational assignment of (OHBZA)

The compound (OHBZA) has the following representation 51 A' + 24 A''. The assignment in Table 2 has been established from the comparison with vibrational results for salicylaldehyde oxime (SAO), orthoamino phenol (OAP) [7] and the recent assignment of N-(2-hydroxybenzylidene) aniline [1, 2]. For the latter compound and based on isotopic substitution νN-ring was localized at 1366 cm^{-1}. For (OHBZA), this mode is observed at 1356 cm^{-1} as a very strong band. The two bands at 1279 and 1245 cm^{-1} are assigned to the νO-Ph and νC-Ph respectively [4]. The other νO-Ph is observed at 1225 cm^{-1} (IR, Raman). The two stretches νO-Ph and νC-Ph for (SAO) were found at 1262 and 1200 cm^{-1} respectively [4]. As for (BZA), we have for (OHBZA) two types of o-disubstituted benzene [4]. The splitting of the vibrational modes of the two sorts is observed especially for the modes 9a, 18a, 18b, 17b and 11 as shown in table 2. The γCHimine can be attributed to the IR bandat 905 cm^{-1}as for N-(2-hydroxybenzylidene) aniline [1, 4]. The remaining vibrations are localized in the regions expected for o-disubstituted benzene derivatives [1, 4].

The FTIR spectra of the two complexes Cu(II) –OHBZA and Ni(II)-OHBZA

The analogy between the vibrational wavenumbers of the two complexes indicate that they have a similar structure. The ν_a C=N of the ligand OHBZA is shifted to lower

wavenumbers for the two complexes, see Table II [3]. The ν N-Ph stretch at 1356 cm^{-1} moves to higher wavenumbers and are observed at 1410 and 1435 cm^{-1} [3] for the two complexes Cu(II)-OHBZA and Ni(II)-OHBZA, respectively. The two νC-O stretches of the ligand at 1225 and 1278 cm^{-1} disappear and two new bands arise at 1295 and 1330 cm^{-1} for Cu(II)-OHBZA and at 1300 and 1332 cm^{-1} for Ni(II)-OHBZA, respectively. This observation confirms the assignment of the two bands at 1245 and 1278 cm^{-1} as νC-O stretches. Similar behavior was observed for salicylaldimine [3] and azine complexes [11]. It is of interest to note that a new strong band is observed at 618 and 614 cm^{-1} for Cu(II)-OHBZA and Ni(II)-OHBZA, respectively, which characterize the chelate ring [5]. This band may have contribution from the δCCN and νM-O motions. The previous assignment indicate that the ligand OHBZA is coordinated with the two metal ions Cu (II) and Ni(II) through the two oxygen atoms of the O-Ph groups and the nitrogen atom of the imine group, as previously proposed for the complexes of the same ligand with Al(III) ion [5]. The IR spectra also a strong and broad band at 3433 and 3431 cm^{-1} for CuOHBZA and NiOHBZA, respectively, due to the coordination with water molecules[5]. The deformation mode of water is observed as a very weak band at about 1640 cm^{-1}.

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