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Analysis of the vibrational spectra of *trans-N*,*N*′-bis-salicylidene-1′,2′-cyclohexanediamine tautomers

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Abstract

The vibrational spectra of two tautomeric forms of *trans-N*,*N*′-bis-salicylidene cyclohexanediamine (OHN-sal and NHO-sal) as well as the reference compound with weak hydrogen bond (OH-sal) have been analysed using DFT and HF methods. The results have revealed the most important spectroscopic consequences of formation of the medium strength intramolecular OH···N hydrogen bond and the proton transfer in Schiff bases. The IR spectrum of OHN-sal calculated by the B3LYP/6-31G(d,p) method is in a satisfactory agreement with the experimental one. The discrepancies result from the neglect of the anharmonicity correction and intermolecular interactions. The HF/6-31G level of theory do not reproduce correctly the intramolecular hydrogen bond in the Schiff base studied.

Keywords: Schiff bases; Vibrational analysis; Hydrogen bond

1. Introduction

The di-Schiff base derivatives of *trans*-1,2-diaminocyclohexane have received considerable attention due to a wide application of their metal complexes in asymmetric synthesis [1–3]. The studies of the deuterium isotope effect on ^{13}C and ^{15}N NMR chemical shifts have shown that in some derivatives of *trans*-1,2-diaminocyclohexane and aromatic *ortho*-hydroxyaldehydes the proton transfer takes place in OH···N intramolecular hydrogen bond, leading to the existence of the two tautomeric OH– and NH-form, both in the $CHCl_3$ solution and in the solid state [4,5]. The IR spectroscopy, known to be a very efficient tool to study the hydrogen bond, has also been applied in the studies of these di-Schiff bases [3,5]. However, strong coupling of vibrations and complexity of the spectra, particularly at the equilibrium of both tautomers have made reliable assignments of the spectra impossible. Despite of numerous experimental works, the vibrational assignment for Schiff bases with the proton shifted to the nitrogen atom seems not be unequivocally established [6–8].

In this paper we have undertaken theoretical analysis of vibrational spectra of the simplest di-Schiff base of this series: *trans-N*,*N*′-bis-salicylidene-1′,2′-cyclohexanediamine (OHN-sal), its tautomer (NHO-sal) and the reference conformer (OH-sal) (Fig. 1).

Recognition of spectroscopic consequences of the proton transfer in the intramolecular OH···N hydrogen bond will be very helpful in the application of the IR spectroscopy in the investigation of the tautomerism in the whole series of derivatives of *trans*-cyclohexanediamine and other Schiff bases. Numerous properties of the Schiff bases are known to depend on this process [9]. The second purpose of this work is to give reliable band assignment of the vibrational spectrum of *trans-N*,*N*′-bis-salicylidene-1′,2′-cyclohexanediamine by comparison of the calculated and experimental IR spectra.

2. Experimental

Trans-N,*N*′-bis-salicylidene-1′,2′-cyclohexanediamine (OHO-sal) was obtained by condensation of *trans*-cyclohexanediamine with salicylaldehyde in ethanol solution [4].

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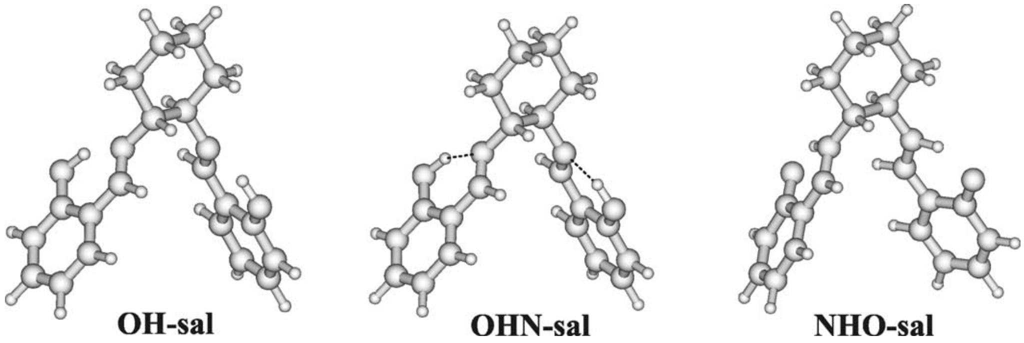

Fig. 1. The investigated tautomers of *trans-N,N′*-bis-salicylidene-cyclohexanediamine.

The IR spectrum of OHO-sal in KBr pellets was recorded on a Perkin–Elmer SPECTRUM ONE spectrometer. Raman spectrum of OHO-sal of a powdered sample was recorded on a Nicolet Magna 860 FT Raman spectrometer. A diode-pumped Nd:YAG laser was excitation source, with a power of ca 200 mW. The resolution was set up 2 cm^{-1}, 512 scans were measured.

The optimization and frequencies calculation of investigated compounds were performed by using the Gaussian 1998 program with HF, DFT B3LYP methods at 6-31G and 6-31G(d,p) levels [10]. The lowest energy structures with restricted geometry were used to calculate the force constants using the Gamess package [11].

3. Results and discussion

3.1. Geometrical parameters

The structures of studied di-Schiff base tautomers shown in Fig. 1, have been optimized using the HF and B3LYP method with 6-31G(d,p) and 6-31G basis sets. The selected bond lengths and bond angles are collected in Table 1. Atom labelling is given in Fig. 2. The optimization of OHN-sal with B3LYP/6-31G(d,p) method reproduces the molecular structure determined by X-ray analysis [12]. Two phenyl groups are inclined to each other. However, the differences in bond lengths and angles between two salicylidene moieties are smaller in comparison with the experimental values. The N···O distance is a bit longer and the length of the CO bonds are a bit shorter than the experimental values of 2.604 and 1.347 Å (1.348 Å) [12]. Optimization of the same molecule at the HF/6-31G level gives as a result the structure of the same configuration but with the O···N distance of 2.684 Å and the OHN angle 139.98° (OH-sal) that suggests the existence of very weak OH···N intramolecular hydrogen bond [13]. This structure has been taken as reference to show the influence of the hydrogen bond strength on the geometric parameters and spectroscopic properties of the Schiff base studied. Comparison of the data for OH-sal and OHN-sal (Table 1) shows that a shortening of the O···N distance and an increase in the OHN angle lead to the changes in all geometrical parameters in the chelate ring formed by HOCCC=N atoms, particularly

Table 1
Calculated bond length [Å] and angles [deg] for OH-sal, OHN-sal and NHO-sal and NHO-sal

Bond/angle	OHsal	OHNsal	NHOsal		OHsal	OHNsal	NHOsal
N8···O24	2.684	2.619	2.537	N15···O23	2.684	2.619	2.550
O24–H46	0.964	0.999	1.608	O23–H37	0.964	0.999	1.633
N8–H46	1.873	1.714	1.058	N15–H37	1.873	1.714	1.054
O24H46N8	139.98	148.61					
C9–C10	1.540	1.551	1.557				
C9–N8	1.458	1.454	1.451	C10–N15	1.458	1.454	1.451
N8–C7	1.268	1.286	1.323	N15–C16	1.268	1.286	1.323
C7–C2	1.464	1.455	1.404	C16–C17	1.464	1.455	1.402
C1–O24	1.358	1.342	1.274	C22–O23	1.358	1.342	1.270
C1–C2	1.401	1.422	1.464	C17–C22	1.401	1.422	1.466
C9N8C7	121.68	119.83	126.21	C10N15C16	121.68	119.81	125.36
N8C7C2	123.56	122.47	121.94	N15C16C17	123.56	122.47	122.03
C7C2C1	122.10	120.85	118.95	C16C17C22	122.10	120.85	119.27
C1O24H46	112.18	106.85	103.12	C22O23H37	112.18	106.85	103.47
H44C7N8	120.80	121.03	117.66	H43C16N15	120.80	121.03	117.74
C10C9N8C7	115.63	114.79	119.15	C9C10N15C16	115.64	114.85	87.22
C9N8C7C2	−179.96	−179.97	−173.84	C10N15C16C17	−179.96	−179.93	−178.01
H46O24C1C2	−0.32	−0.46	−2.99	H37O23C22C17	−1.01	−0.46	−0.42
N8C7C2C3	179.86	−179.91	−177.85	N15C16C17C18	179.86	−179.83	−179.58