

Intramolecular hydrogen bonding in N-salicylideneaniline: FT-IR spectrum and quantum chemical calculations



Zainab Moosavi-Tekyeh*, Najmeh Dastani

Chemistry Department, Shahrood University, Shahrood, 3619995161, Iran

ARTICLE INFO

Article history:

Received 15 July 2015

Received in revised form

31 August 2015

Accepted 3 September 2015

Available online 8 September 2015

Keywords:

N-salicylideneaniline (SAn)

Intramolecular hydrogen bonding

Vibrational assignment

FT-IR spectra

DFT calculations

CPCM

ABSTRACT

FT-IR and FT-Raman spectra of N-salicylideneaniline (SAn) and its deuterated analogue (D-SAn) are recorded, and the theoretical calculations are performed on their molecular structures and vibrational frequencies. The same calculations are performed for SAn in different solutions using the polarizable conductor continuum model (CPCM) method. Comparisons between the spectra obtained and the corresponding theoretical calculations are used to assign the vibrational frequencies for these compounds. The spectral behavior of SAn upon deuteration is also used to distinguish the positions of OH vibrational frequencies. The hydrogen bond strength of SAn is investigated by applying the atoms-in-molecules (AIM) theory, natural bond orbital (NBO) analysis, and geometry calculations. The harmonic vibrational frequencies of SAn are calculated at B3LYP and X3LYP levels of theory using 6–31G*, 6–311G**, and 6–311++G** basis sets.

The AIM results support a medium hydrogen bonding in SAn. The observed $\nu_{\text{OH}}/\nu_{\text{OD}}$ and $\gamma_{\text{OH}}/\gamma_{\text{OD}}$ for SAn appear at 2940/2122 and 830/589 cm^{-1} , respectively.

© 2015 Elsevier B.V. All rights reserved.

1. Introduction

Among β -Enaminones and β -ketoenamines, N-salicylideneaniline (SAn) belong to the large family of aromatic Schiff's bases, which have heteronuclear intramolecular hydrogen bonds (IHBs). Several asymmetric prototropic tautomers of SAn can exist according to any factor that can alternate the π -electronic state of this molecule such as the temperature, nature of solvent, electronic and steric characteristics of substituents, and light irradiation.

The intramolecular proton transfer (PT) between the enol-imine (O–H) and keto-enamine (N–H) tautomers is called the photo- and thermo-chromism. The chromism behavior and non-linear optical properties [1–14] make SAn useful for potential applications in the field of technological areas such as optical processing and switching devices [12,15–24]. SAn derivatives have also been used in various fields such as biology [25–27], coordination chemistry [28–31], and liquid crystal [32,33].

The photo- and thermo-chromism behaviors of SAn, and some substituent effects on the tautomeric equilibrium responsible for the above-mentioned behaviors have been extensively studied

experimentally on the basis of fluorescence [1–12,34–45], ^1H (^{15}N , ^{18}O)-NMR, Raman, and IR spectroscopic data, and theoretical methods [46–63].

The fact that a rapid PT plays a key role in chromism is related to the existence of IHB that is assisted by resonance in the pseudo six-membered or chelate ring formed by the O–H \cdots N=C and N–H \cdots O=C tautomers [64]. Despite the experimental studies carried out using IR and Raman spectroscopy in order to describe the photo- and thermo-products of SAn, the nature of IHB in SAn has been much less investigated.

Also, the vibrational frequencies of IR and Raman spectra have been assigned tentatively in the region of 1000–1700 cm^{-1} , in different solutions [9,49]. Although recently, density functional theory at B3LYP/6–311++G** has been applied to study the vibrational frequencies in the region of 1700–67 cm^{-1} in the solid state of SAn [52], without considering isotopic deuterium shifts of deuterated SAn, the assignments have been related to the vibrational modes of O–H bond cannot be reliable.

In this work, our attention was focused on the estimation of the strength of IHB in SAn, and determination of the positions of its vibrational OH frequencies by the experimental methods and theoretical calculations. The vibrational frequencies of SAn and its deuterated analogue (D-SAn) are calculated by means of density

* Corresponding author.

E-mail address: ztmoosavi@gmail.com (Z. Moosavi-Tekyeh).

functional theory (DFT), and investigated by the observed IR and Raman spectra.

2. Experimental

SAn (Fig. 1) was prepared according to the Schiff's base condensation procedure [65], refluxing equimolar quantities of salicylaldehyde and aniline in methanol. For purification of the title compound, recrystallization was carried out on it using methanol (mp, 51 °C; ^1H NMR (CDCl_3): δ 6.95 (t, 1H, $J = 0.02$, CH Arom.), δ 7.04 (d, H, $J = 0.01$, CH Arom.), δ 7.27–7.30 (m, 3H, CH Arom.), δ 7.37–7.44 (m, 4H, CH Arom.), and δ 13.26 (s, 1H, OH), the ^1H NMR spectrum of SAn was presented in Fig. 2.

Deuterated SAn (D-SAn) was prepared by adding D_2O (99.78%) to a freshly-dried CCl_4 solution of SAn (3:1), and leaving the solution overnight at room temperature. The organic layer including D-SAn was separated and dried over anhydrous sodium sulfate [66].

The Mid-IR and Raman spectra of SAn and D-SAn were obtained on a Bomem MB-154 Fourier Transform Spectrophotometer. The Far-IR spectra were collected employing a Thermo Nicolet NEXUS 870 FT-IR spectrometer. The ^1H NMR spectrum of SAn was recorded on an FT-NMR Bruker DRX 500 spectrometer operating at 500 MHz at 25 °C. More details about instrumentation is placed in supplementary material.

3. Chemical quantum calculations

The molecular structure of SAn was optimized in its isolated phase, and the frequencies as well as the band intensities of its vibrational spectrum was calculated at the B3LYP/6–311++G(d,p) level of theory [67,68]. The same calculations were performed for the CCl_4 , CH_2Cl_2 , CH_3CN and CH_3OH solutions of SAn by using conductor-like polarizable continuum model (CPCM) [69] method.

The ^1H NMR spectrum of SAn was also calculated using the GIAO approach [70,71] at the same level and basis set. The chemical shift of protons (δ_{H}) were determined by subtracting the calculated absolute shieldings of the proton nuclei of SAn from that of the proton in tetramethylsilane (TMS). All the above-mentioned calculations were carried out using the G03W package program [72]. The vibrational non-harmonicities inherent to the computational level were corrected using the scaling factors method, to the calculated wave numbers, for a better comparison with the experimental values. The geometric parameters and vibrational frequencies of the most stable conformer of SAn were re-calculated by the X3LYP functional [73] (extended hybrid functional combined with Lee–Yang–Parr correlation functional) using the 6–31G**, 6–311G**, and 6–311++G** basis sets. It has been shown this extended functional improved the accuracy for hydrogen-bonded (HB) systems over the most popular and accurate method, B3LYP (Becke

three-parameter hybrid functional combined with Lee–Yang–Parr correlation functional [67,68]). The X3LYP functional was able to predicting absolute HB strengths, relative energies, HB distances and vibrational frequencies of HB complexes, accurately [74–77]. The GaussView 4.1.2 graphical interface [78] was used for visualization of the vibrational normal modes, and the Lorentzian function was utilized for de-convolution of the IR spectra using the Origin 5.0 software [79]. To obtain a deeper insight into the nature of IHB in SAn, AIM analysis was performed using AIM2000 [80–84]. The bond critical points (BCPs) of the $\text{H}\cdots\text{N}$ bond as well as the $\text{H}\cdots\text{O}$ interactions were found. Furthermore, natural bond orbital (NBO) analysis was performed using the NBO 5.0 program [85–87] to analyze the charge distribution.

4. Results and discussion

4.1. Conformational stability

The most stable geometry of SAn along with the atom numbering system is shown in Fig. 1, and the six possible structures for the fully-optimized SAn with the calculated energy difference relative to the most stable conformer (O–H form) at the B3LYP/6–311++G** level is presented in Fig. S1 (Supplementary material). As shown in Fig. 1, there are three rings in this compound including the salicyliden (Sa), aniline (An), and pseudo six-membered rings.

The six conformers shown in Fig. S1 are either in the *cis* or *trans* form, in which two phenyl rings have either a *cis* or *trans* configuration relative to each other for the C=N bond. Three of these conformers, i.e. *A-I*, *B-I*, and *B-II* have a very important role in the thermo-chromis and photo-chromis processes. The full optimization of SAn shows that the *cis*-enol conformer (*A-I*) has a non-planar structure. The *cis*-keto form (*B-I*) and the *trans*-keto form (*B-II*) are almost planar. The former, in which PT is from O to N, is due to the temperature-induced shift of the tautomeric equilibrium (*A-I* \leftrightarrow *B-I*), and the latter, in which a geometric change is accompanied with PT, is a photo-induced product (*A-I* \leftrightarrow *B-II*) [1,3]. As it is shown in Fig. S1, the *A-I* and *B-I* forms have two types of IHB, namely O–H \cdots N in imine-enol and O \cdots H–N in keto-amine. The O–H tautomer is 4.64 kcal mol $^{-1}$ more stable than the N–H one [88,89]. The relative energies for the four remaining structures are above 9 kcal mol $^{-1}$, and from the viewpoint of thermal equilibrium, their populations can be neglected in the sample. The energy difference between the *cis* and *trans* forms ($\Delta E_{\text{cis-trans}}$) for the *A-I*, *A-II* and *B-I*, *B-II* conformers is about 10 kcal mol $^{-1}$, and that for *C-I*, *C-II* is 4 kcal mol $^{-1}$. This discrepancy can be explained by considering IHB in the *A* and *B* forms, which is absent in the *C* form.

To take the solvent effects into account, the N–H and O–H conformers were then fully re-optimized using the CPCM in different solvents. Comparison of these two forms of SAn, also revealed more stability for O–H form than N–H one (see Table S1).

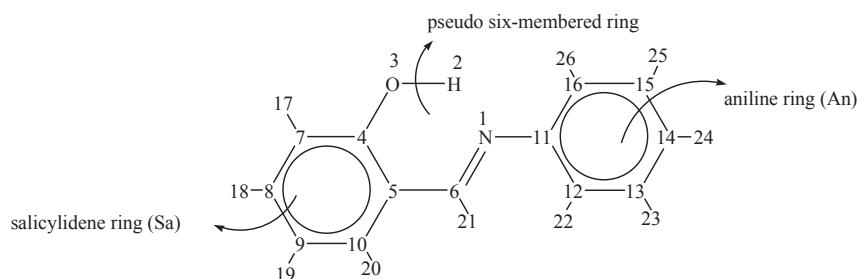


Fig. 1. Atomic numberings for SAn, three rings in this compound including the salicyliden (Sa), aniline (An), and pseudo six-membered rings. Reproduced from Ref. [89].

Download English Version:

<https://daneshyari.com/en/article/1401656>

Download Persian Version:

<https://daneshyari.com/article/1401656>

[Daneshyari.com](https://daneshyari.com)