



Critical assessment of the intramolecular hydrogen bonding (IMHB) interaction in two isomeric hydroxynicotinic acids: A computational approach



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ARTICLE INFO

Article history:

Received 25 April 2014

Received in revised form 6 June 2014

Accepted 30 June 2014

Available online 8 July 2014

Keywords:

Density functional theory

Intramolecular hydrogen bonding

Atoms-In-Molecule

Bond critical point

Natural Bond Orbital

Resonance assisted hydrogen bond

ABSTRACT

Density Functional Theory (DFT) based computational study has been performed to characterize intramolecular hydrogen bonding (IMHB) interaction in two isomeric hydroxynicotinic acids viz. 3-hydroxyisonicotinic acid (3HINA) and 4-hydroxynicotinic acid (4HNA). The IMHB interaction has been analyzed by the calculation of electron density $\rho(\mathbf{r})$ and Laplacian $\nabla^2\rho(\mathbf{r})$ at the bond critical point using Atoms-In-Molecule (AIM) theory. Topological features and energy densities based on $\rho(\mathbf{r})$ through the perturbation of the IMHB distances suggest that at equilibrium geometry the IMHB interaction develops certain characteristics typical of a covalent interaction. Concomitantly, the role of charge transfer interaction in the IMHB has been critically addressed under the provision of Natural Bond Orbital (NBO) analysis. The assistance of resonance in the IMHB interaction present in these molecular systems is also delineated from quantum chemical calculations. The comparatively greater IMHB energy for 4HNA with respect to its isomer has also been attempted to address critically along with the argument about the superiority of quantum chemical criteria over geometrical criteria for the assessment of IMHB interaction in the studied compounds.

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1. Introduction

Despite being characterized as a weak interaction, Hydrogen bonding (HB) has always been a key element to a plethora of activities in nature. By virtue of its unique properties like directionality, specificity and transience, this non-covalent interaction plays pivotal roles in providing specific shapes to biomolecules and maintaining their functionality which in turn advocates for its inevitability in sustaining life-cycle on this planet [1,2]. Hydrogen bonding (HB) also plays a crucial role in defining the crystal packing of molecules and is the source of specific properties of associated liquids like water and thus crops up as a demanding topic of research [1–3].

A classical hydrogen bond is formed by two heteroatoms, X and Y (having already saturated valencies), with a hydrogen atom bonded to one of them and located approximately in between (X–H...Y). Mostly, H-bonding has been considered as an electrostatic attraction between the positive end of the bond dipole of X–H and the center of negative charge on Y (generally a lone pair

of electrons) [4]. Unlike typical chemical bonds, the H-bond ranges over a large scale of energy, from very weak ones to very strong ones depending upon the nature of the groups involved [5]. A particular type of H-bonding interaction is the one often found in association with excited state intramolecular proton transfer (ESIPT) reaction, i.e., the intramolecular hydrogen bond (IMHB) which is a particular case of the interaction occurring within the same molecular architecture. The IMHB interaction is well-documented to have its crucial impact on the feasibility and rate of ESIPT process [6].

Vitamin B₃ or Nicotinic acid is an essential human nutrient known for its involvement in repairing damaged DNA, producing steroid hormones in adrenal gland, lowering of plasma lipids and so on and so forth [7]. Nicotinic acid and its derivatives (especially hydroxy derivatives) are not only biologically and pharmaceutically important, but are also frequently used in crystallographic studies involving metal organic frameworks (MOFs) and in the synthesis of microporous coordination polymers [8,9]. So, a meticulous understanding of the structure and the H-bonding property of such systems is a must from scientific perspective. Following the aforesaid points, in the present contribution, we have focused on a thorough exploration of IMHB interaction in two isomeric hydroxynicotinic acids viz., 3-hydroxyisonicotinic acid (3HINA) and 4-hydroxynicotinic acid (4HNA) from

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computational perspectives. Particular emphasis has been delivered on the application of different quantum chemical tools for detection and evaluation of the IMHB interaction in the studied molecules. The topological properties of IMHB interaction are assayed under the provision of Atoms-In-Molecule (AIM) [10] methodology, while a critical evaluation of the role of hyperconjugative charge transfer interaction is deduced from the Natural Bond Orbital (NBO) analysis [11]. The possibility for the resonance assisted hydrogen bond (RAHB) interaction is also scrutinized from geometrical criteria as well as quantum chemical analysis. Further, the interplay between aromaticity and RAHB has also been explored in this context. Finally, the geometrical and quantum chemical criteria have been directly compared in an endeavor to provide a picture arguing the origin of and then to find reliable criteria for the evaluation of H-bond strength.

2. Computational procedures

2.1. Geometry optimization

The structural calculations have been performed on Gaussian 03W suite of programs [12]. The ground-state structure for various possible low energy conformations of both 3-hydroxyisonicotinic acid (3HINA) and 4-hydroxynicotinic acid (4HNA) have been computed at the Density Functional Theory (DFT) level using the celebrated B3LYP hybrid functional [13]. For this purpose 6-311++G(d,p) basis set has been chosen because this basis set is of triple- ζ quality for valence electrons with diffuse functions which are useful in calculations for anions and structures with lone pair electrons [14]. The characteristic of local minimum corresponding to the optimized geometries has been verified by establishing that the matrices of the second derivative of energy (Hessian) have no imaginary frequency.

2.2. NBO and AIM calculations

The Natural Bond Orbital (NBO) analysis has been employed to evaluate the direction and magnitude of donor–acceptor interactions. The necessary computations for NBO analysis has been performed on Gaussian 03W software package [12] at the same level of calculation as mentioned earlier. The contour plot for visualization of the NBO result is constructed on NBO View (Version 1.1) software package using the standard keywords implemented therein. Similarly, the AIM calculation has also been performed on Gaussian 03W software at B3LYP/6-31+G(d,p) level using the standard keywords implemented therein.

2.3. Calculation of aromaticity indices

The Harmonic Oscillator Model of Aromaticity (HOMA) [15] and the Nucleus Independent Chemical Shift (NICS) indices [16] have been employed as the criteria of local aromaticity. For the NICS calculations, we have adopted the gauge-independent atomic orbital (GIAO) formalism using the “Bq” probe atom to designate the positions for evaluation. NICS (0) is defined as the negative value of the absolute shielding computed at a ring center determined by the non-weighted average of the heavy atoms’ coordinates in the ring. Following the literature arguments about spurious contributions from the in-plane tensor components arising from σ -bonding that are not related to aromaticity in NICS (0) analysis [17], NICS(1) as well as NICS (1)_{zz} values have also been calculated as the negative values of absolute shielding measured at 1 Å above the center of the ring (and the corresponding zz tensor component) which have been postulated to better reflect the aromaticity patterns because of diminution of the local σ -bonding contributions.

3. Results and discussion

3.1. Geometrical criteria and theoretical IR spectra for assessing the presence of IMHB interaction

As seen in Table 1a, the lengthening of the proton donating bond (H_1-O_d distance) in the closed form compared to that in the open form is in consensus with the occurrence of IMHB interaction in both the molecular systems under investigation [2,3]. Apart from this, some modulations in the geometry parameters surrounding the entire IMHB site in the studied molecules, e.g., lengthening of $C_4=O_a$ and $C_2=C_3$ bonds along with shortening of C_3-C_4 and O_d-C_2 distances in the closed form with respect to that in open form can be corroborated to the presence of resonance assistance in the IMHB interactions concerned [2,3]. Interestingly, we observed the $O_a \cdots H_1$ bond length to be smaller in case of 4HNA (1.772 Å) as compared to that in 3HINA (1.797 Å) which has been corroborated to the presence of heteroatom in the aromatic nucleus. Unlike benzene, in pyridine system the C–C and N–C bond lengths are unequal, resulting in an unsymmetrical structure which leads to an increasing spatial separation between the *m*- and *p*-substituents. This fact is in harmony with a comparatively shorter HB distance in salicylic acid (1.76 Å, calculated at the same level of computation, as mentioned earlier). Now, comparing the bond lengths of C=O (1.23 Å, a portion of the –COOH group, the *m*- substituent for 4HNA) and O–H moieties (0.98 Å, *m*- substituent for 3HINA), it is expected that in the latter the effect of spatial separation would be comparatively more leading to a relatively longer $O_a \cdots H_1$ bond length which in turn will account for a weaker IMHB interaction. To further validate the aforesaid point, we have evaluated the energy of the IMHB interactions in the molecular systems under study using three well-admired methods viz. (i) the energy difference between closed and open form [3], (ii) empirical energy-geometry correlations as proposed by Musin and Mariam [18] and (iii) potential energy density at the corresponding BCP [19], a glance at which (*vide* Table 1b, corresponding energies are designated as $E_{HB}^{(1)}$, $E_{HB}^{(2)}$ and $E_{HB}^{(3)}$ respectively) immediately suggests a stronger IMHB interaction in 4HNA.

Typically, the formation of IMHB in a molecule is characterized via a hyperconjugative charge transfer from the lone pair of the acceptor atom (in the present case, O_a) to the σ^* orbital of the donor bond (O_d-H_1), which is essentially accompanied with some decrement in the O_d-H_1 bond order as reflected in weakening of the O_d-H_1 bond in the closed form compared to that in the open form [3] and thereby accounts for the observed shift in the corresponding IR stretching frequency (*vide* Table 2, the O_d-H_1 IR stretching frequency, on moving from the open form to the H-bonded closed form, undergoes red-shifts of 292 cm^{-1} for 3HINA and 352 cm^{-1} for 4HNA stating the fact that the latter compound comprises of a stronger IMHB interaction). Interestingly, the $C_4=O_a$ bond stretching frequency also undergoes a substantial red shift of $\sim 65 cm^{-1}$ for both the studied systems. This can be rationalized invoking the fact that due to resonance assistance, the non-bonding molecular orbital of the acceptor atom (O_a) probably attains some bonding character and thus during the hyperconjugative charge transfer, a decrement of the $C_4=O_a$ bond order takes place which in turn is responsible for the aforementioned red shift.

3.2. Topological analysis: Atoms-In-Molecule (AIM) study

3.2.1. Electron density and electronic energy density at the critical points (CPs)

According to AIM theory (which is mainly based on an analysis of electron density at specific points $\rho(\mathbf{r})$), identification of a

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