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Relationship between calculated NMR data and intermolecular hydrogen bond properties in X-pyridine···HF

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ABSTRACT

The effect of different substituents in para and metapositions on the NMR data of X-pyridine···HF complex has been studied at B3LYP/6-311++G(d,p) level of theory. The relationship between NMR data and electron donation of substituents has been investigated. The results of topological properties of electron charge density calculated using atoms in molecules (AIM) analysis can be used to predict some NMR data. The magnetism-based indices, nucleus independent chemical shift NICS(1) and its z component $NICS(1)_{ZZ}$, were used to investigate the ring aromaticity changes on complexation. A linear correlation between Hammett coefficients and some NMR data could be found with a good correlation coefficient.

1. Introduction

The investigation on hydrogen bond (HB) is an interesting subject from theoretical and experimental view points [1–6]. The study of the intermolecular interactions of six membered nitrogenated aromatic rings is of particular importance since they are known to constitute key building blocks of proteins, nucleotides, and many other important compounds [7–9]. For example, Boenigk and Mootz [10] investigated the formation of solid complexes at low temperatures in pyridine–hydrogen fluoride system using difference thermal analysis and X-ray powder diffraction. With regard to obtained melting diagram, they proved the existence of as many as eight intermediary compounds $C_2H_5N \cdot n$HF (n = 1–8) with melting points between −1 and −124 °C. Harmon and Pillar [11] examined a number of 1:1 hydrogen fluoride compounds of tertiary amines, including monocyclic, bicyclic, aromatic, and trialkyl examples using infrared spectral studies. This technique demonstrates that tertiary amines with considerable rang in structure and basicity form stable adducts with hydrogen fluoride that contain covalent three center NHF hydrogen bonds. Also, Rusa et al. [12] characterized hydrogen-bonded complexes between hydrogen fluoride as proton donor and aromatic azines (pyridine, pyrimidine, pyridazine, pyrazine, 1,3,5-triazine, and 1,2,4-triazine). The H-bond strength was dependent on both the number of nitrogen atoms as well as the position of these atoms in aromatic ring. The binding energies of azines–HF with or without BSSE and ZPE corrections decreased with the increasing number of nitrogen atoms in the ring. With respect to position of the nitrogen atom in the aromatic ring, the more pronounced effect was verified when it was at meta position relative to the pyridine ring. Panek and Jezierska [13] carried out a detailed investigation into the interaction energy decomposition in dimers and trimers containing N···HX bonds of different types. Their studies were performed using the symmetry-adapted perturbation theory (SAPT) [14]. Also, Campodonico et al. [15] used two classical tools, the intermolecular stretching force constants of H-bonded and the molecular electrostatics potential to purpose a nucleophilicity index evaluated for a series of pyridines.

A new and important area of both experimental and computational research is the investigation of NMR spin–spin coupling constants across hydrogen bonds [16–22]. MR data reflect the electronic structure in a molecule and therefore can be a powerful tool in identifying and characterizing hydrogen bond. The formation of hydrogen bonds shifts electron density from the proton acceptor to the proton donor resulting in deshielding of the bridging atom [23–25].

The values of chemical shift in the ^{1}H NMR spectra of complexes with the strongest quasi-symmetrical hydrogen bond $A^{\delta-}\cdots H\cdots B^{\delta+}$ with a minimal A···B distance have theoretically been analyzed by Shenderovich [26]. The maximum of the chemical shift was somewhat displaced from the shift of mentioned structure toward that of limiting structure (free acid or protonated base) in which the proton was less shielded, but the value of this displacement was insignificant and did not correlate directly with the difference between the chemical shifts of the limiting structures. Spin–spin

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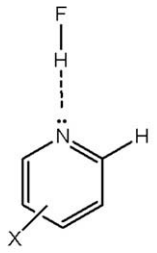

$X = NH^-, O^-, S^-, N(CH_3)_2, NH(CH_3), NH_2, C_2H_5, CH_3, OH, OF, F, Cl, Br, NO_2, NH_3^+$

Scheme 1.

coupling constants have been measured by Limbach et al. [27,28] for the FH···collidine complex in solution as a function of temperature. They observed that whereas the one-bond $^1J_{F-H}$ and $^{1h}J_{H-N}$ coupling constants changed over the range of investigated temperatures, the two-bond $^{2h}J_{F-N}$ coupling constant across the $^{15}N\cdots H-^{19}F$ hydrogen bond was constant to within 5 Hz. They suggested that as a function of temperature and therefore changing dielectric constant of the solvent, the hydrogen-bonded proton moved from its position closer to the F atom at higher temperature, through a quasi-symmetric hydrogen bond, to a position closer to N atom at lower temperature. They described these changes in terms of changing hydrogen bond type, from traditional, to proton-shared, to zwitterion pair. Also, an experimental (extrapolated value) of $^{2h}J_{F-N} = -97.5$ Hz for collidine···HF was obtained by Limbach et al. [29], in which the geometry of HB was considerably affected by solvent. Del Bene et al. examined these coupling constants in two model systems, $FH-NH_3$ and FH–pyridine as a function of the F–H and F–N distances [30]. The absolute value of $^1J_{F-H}$ decreased and that of $^{1h}J_{H-N}$ increased rapidly along the proton-transfer coordinate, even in the region of the proton-shared F–H–N hydrogen bond. In contrast, $^{2h}J_{F-N}$ remained essentially constant in this region. In addition, the changes of $^{2h}J_{F-N}$ values in terms of hybridization of nitrogen atom have been evaluated by Del Bene et al. [20].

We previously reported [31] the results of an ab initio study on hydrogen-bonded complexes between HF and a series of para and meta substituted pyridines. In the present study, the characteristics of intermolecular hydrogen bonds in terms of NMR data, also, the influence of hydrogen bonds on the aromaticity of the substituted pyridine and the relation between Hammett constants [32] and NMR data have been investigated by density functional theory (DFT) for those complexes (see Scheme 1). DFT methods has been shown to be successful in predicting various molecular properties, often giving results of a quality comparable or even better than MP2 [33–35] for a cost that is substantially less than that of traditional correlation techniques. Especially, the DFT methods have significantly reduced computer cost for the calculation of NMR data, thus, the tremendous progress made by DFT-based methods for these calculations [36–42].

2. Methods

All calculations have been implemented in the Gaussian 03 suite of programs [43] at the spin-restricted level. The geometries were optimized using hybrid B3LYP [44] functional and Pople's 6-311++G(d,p) [45] basis set. Frequency calculations have been performed for complexes at the same level of theory. The absence of imaginary frequencies verified that all structures were true minima.

Herein, NICS, $^{2h}J_{F-N}$, $^1J_{F-H}$, isotropic value of the proton shielding tensor, and the anisotropy of the proton tensor have been calculated. The isotropic shielding values, defined as: $\sigma_{iso} = \frac{1}{3}(\sigma_{11} + \sigma_{22} + \sigma_{33})$ (σ_{ii} being the principal tensor components) were used to calculate the isotropic chemical shift δ with respect to TMS, $\delta^x_{iso} = (\sigma^{TMS}_{iso} - \sigma^x_{iso})$. In nuclear magnetic resonance (NMR), the chemical shifts describe the dependence of nuclear magnetic energy levels on the electronic environment in a molecule [46]. The NICS index is one of the most widely employed indicators of aromaticity [47–49]. It is defined as the negative value of the absolute shielding computed at a ring center or at some other interesting point of a system. Rings with large negative NICS values are considered aromatic. As shown by Lazzeretti and Aihara [50–52], NICS values at the geometrical center of the ring (NICS(0)) contain important spurious contributions from the in-plane tensor components that are not related to aromaticity. NICS(1) (1 Å above/below the plane of the ring) essentially reflects π-effects and it is a better indicator of the ring current than the value at the center, because at this point the effects of the local σ-bonding contributions are diminished [50,53,54]. The NMR calculations were performed using SPINSPIN formalism.

The topological electron charge density was analyzed by the atoms in molecules (AIM) method [55], using AIM2000 program [56] on the obtained wave functions at B3LYP/6-311++G(d,p) level. The population analysis has also been performed by the natural bond orbital method [57] at same level of theory using NBO program [58] under Gaussian 03 program package.

3. Results and discussion

3.1. NMR analysis

As can be seen, some NMR data calculated at B3LYP/6-311++G(d,p) level are gathered in Table 1. The substituents could affect on anisotropy of the proton tensor and isotropic value of the proton shielding tensor of fluoric acid. The electron-donating substituents decrease isotropic value of the proton shielding tensor, whereas the electron-withdrawing substituents increase that. The isotropic value of the proton shielding tensor is higher for meta substituted rings (with the exception of C_2H_5). The minimum and maximum isotropic value of the proton shielding tensor corresponds to NH^- and NH_3^+ at para and meta positions, respectively. This trend is reversed for anisotropy of the proton tensor. In addition, calculated isotropic chemical shifts for hydrogen atom of fluoric acid are gathered in Table 1. For a proton involved in hydrogen bond, these data indicate that the increasing isotropic chemical shift is accompanied with increasing hydrogen bond strength. The isotropic chemical shift of H atom is higher for para substituted rings (with the exception of C_2H_5). The minimum and maximum isotropic chemical shifts correspond to NH_3^+ and NH^- at meta and para positions, respectively.

Herein, the substituent effect on the two-bonded spin–spin coupling constant ($^{2h}J_{F-N}$) across $^{15}N\cdots H-^{19}F$ hydrogen bond has been investigated (see Table 1). The calculated $^{2h}J_{F-N}$ value with CH_3 substituent at para and meta positions is equal to −53.19 and −53.82 Hz, respectively. The difference between these values and the value estimated by Limbach et al. for collidine···HF (−95.5 Hz) does not correspond to the additional CH3 substituents of collidine. The calculated value is equal to −59.45 Hz for collidine···HF at B3LYP/6-311++G** level of theory.

With regard to Table 1, the absolute values increase by electron-donating substituents. The behavior is reversed by electron-withdrawing substituents. The absolute value is higher for para substituted rings and the minimum and maximum values correspond to NH_3^+ and NH^- at meta and para positions, respectively.

These behaviors could be attributed to increasing π-electron cloud of ring by electron-donating substituents that consequently