Case study

Unusual effects of intramolecular hydrogen bonds and dipole interaction on FTIR and NMR of some imines

ABSTRACT

Unusual effects of intramolecular hydrogen bonds and dipole interactions are investigated using FTIR, NMR and X-Ray crystallography analyses of some imines. These phenomena affect both FTIR absorptions and chemical shifts.

Keywords: Intramolecular hydrogen bonds; Dipole interactions; FTIR; ^{1}H NMR.

1. INTRODUCTION

Organosynthetic chemistry field is important in the drug discovery, which needs some of the different analytical characterizations for identification and confirmation of the chemical structure of these compounds. A hydrogen atom in organic compounds that is bonded to oxygen O or nitrogen N can participate in hydrogen bonding. This electrophilic hydrogen can form intramolecular and intermolecular attachments with nonbonding electrons on O or N atoms.

A hydrogen bond is a strong dipole-dipole attraction. In some organic compounds, we can see that intramolecular hydrogen bonding and dipole interactions have a strong effect on the elongation of N–H and O–H bonds resulting in unusual values of FTIR and ^{1}HNMR of some organic compounds, as shown in compounds **1–5**.

The X–Ray crystallographic analyses of **1** and **2** were determined, and the intramolecular hydrogen bonds of both imines were compared. The length of the intramolecular hydrogen bonds, –C=N$^{\cdots}$H–O and –C=N$^{\cdots}$H–N in **1** are at the respective 1.77 and 2.23 *Å* [1]. So, the bond –C=N$^{\cdots}$H form weaker intramolecular hydrogen bonds than the bond –C=N$^{\cdots}$H–O because the nitrogen atom is less electronegativity than oxygen. While the intramolecular bond –C=N$^{\cdots}$H–N in **2** has two values (2.31 and 2.29 *Å*) for both stereoisomers of **2** [2]. However, imines **1** and **2** are used in synthesize of bis-Schiff base [3] and benzimidazole derivatives [4-6], which are used widely in pharmaceutical and biological applications [7-9].

2. CHEMICAL STRUCTURE AND ITS APPLICATION

The effect of N–H and O–H intramolecular hydrogen bonding can be seen in the case of an imine **1** as shown in Fig. 1. The FTIR spectrum of this compound exhibits only one spike around 3414 cm^{-1} for a single N–H stretching bond instead of two spikes of a primary amino group as in Fig. 2. This may be assigned to the intramolecular hydrogen bonding of nitrogen

atom in N=C–H and one hydrogen atom in the amino group. On another hand, the chemical shifts of hydroxyl proton and a proton that attached to carbon number seven both appear as a singlet at δ = 13.56 and 8.63 ppm respectively, Fig. 3 [10].

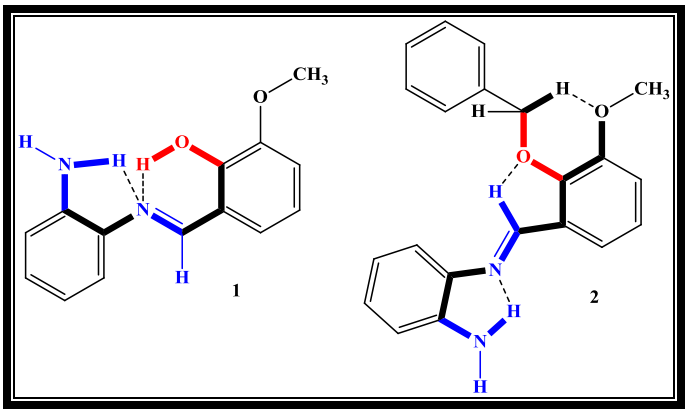

Fig. 1: Imines 1 and 2.

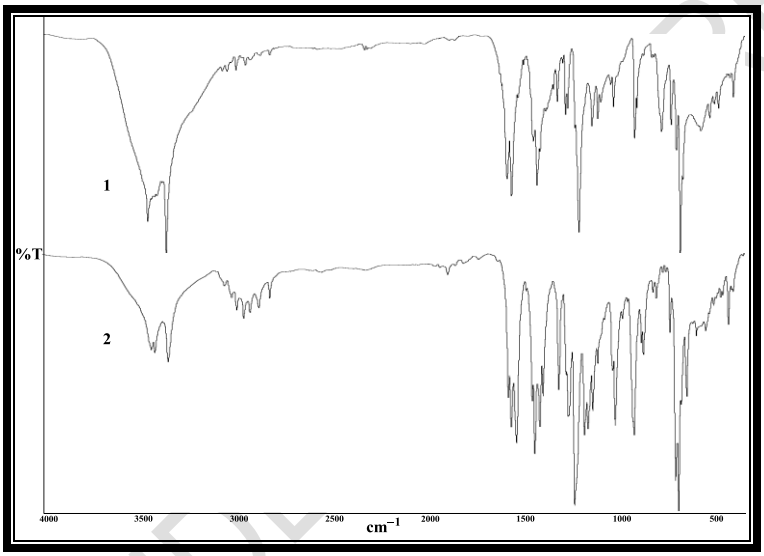

Fig. 2: FTIR spectra of imines 1 and 2.

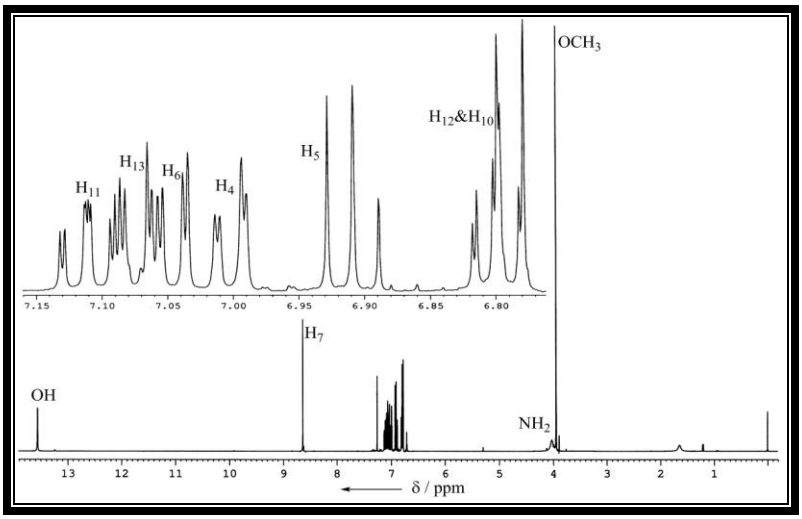

Fig. 3: ^{1}H NMR spectrum of 1.

These unexpected values can be explained by intramolecular hydrogen bonding which generates five and six ring motifs as in Fig. 1. Greater deshielding leads to unusual delta values as in Fig. 3. Imine **2** forms stronger dipole-dipole interaction. As a result, the chemical shift of a proton that attached to carbon seven appears at δ = 8.79 ppm, which is uncommon as shown in Fig. 4, similar to that from previous studies [11].

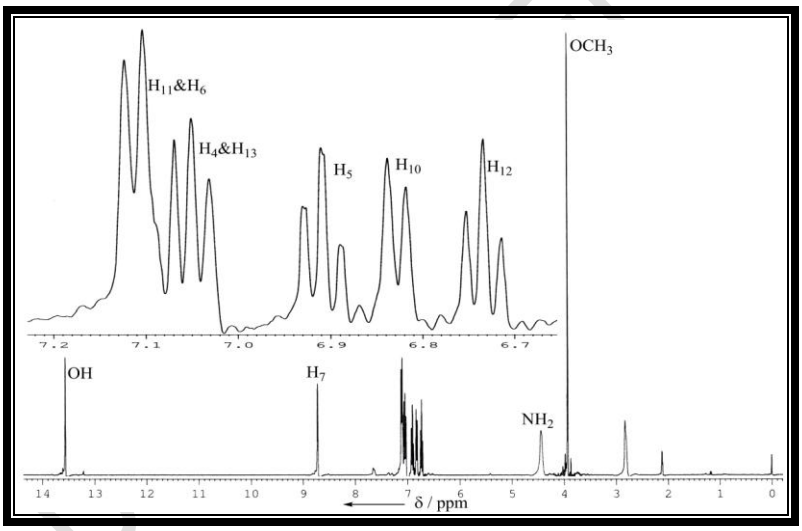

Fig. 4: ^{1}H NMR spectrum of 2.

The effect of hydrogen bonds reflects on the FTIR absorptions of diazo dyes **3**, **4** and **5**, Fig. 5. It is believed the lower symmetrical stretching of nitro groups at *ortho* position in **3** which appears at 1301 cm^{-1} due to the intramolecular hydrogen bonding and the dipole interaction between them with phenolic and aldehydic hydrogen's atoms, Fig. 5 [12].

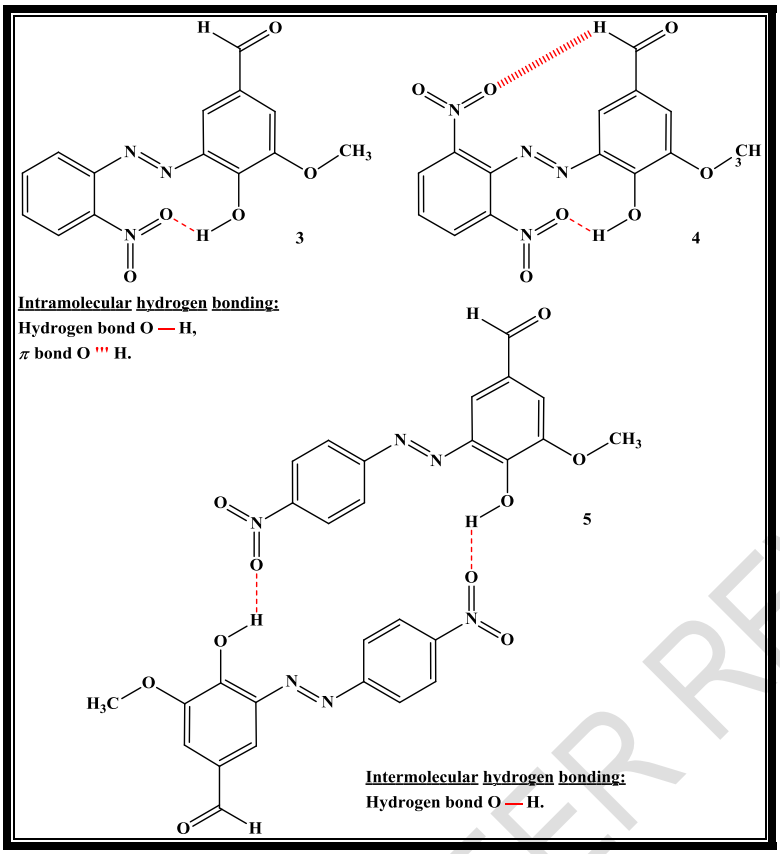

Fig. 5: The dipole interaction and intramolecular hydrogen bonding in both 3 and 4, and intermolecular hydrogen bonding in 5.

These overlaps leave these bonds to have a little electron density, a little less stiff. As a result, they vibrate a little more slowly. The O–H stretching frequency in **3** reflects the stronger intramolecular hydrogen bonding as a very broad absorption around 3277 cm^{-1} shown in Fig. 6. However, the IR spectra of both **4** and **5** display slightly lower asymmetrical stretching frequencies of $–NO_2$ and O–H due to intramolecular and intermolecular hydrogen bonding, respectively as in Fig. 6 and the results previously reported [12].

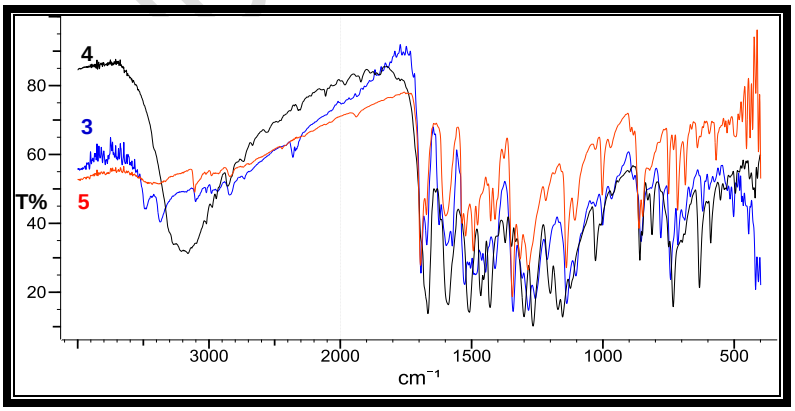

Fig. 6: The FTIR spectra of diazo dyes 3, 4 and 5.

4. CONCLUSION

In this work, we have reported some imines that have strong effects on intramolecular hydrogen bonding and dipole interaction which leads to the unexpected FTIR absorptions and the stranger values of chemical shifts in ^{1}HNMR.

CONFLICTS OF INTEREST

The authors declare that there is no conflict of interest regarding the publication of this article.

COMPETING INTERESTS

Authors have declared that no competing interests exist.

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