

**Stranger Values of FTIR and NMR reflect  
Intramolecular Hydrogen Bonds and Dipole  
Interaction**

---

**ABSTRACT**

Stranger values due to intramolecular hydrogen bonds and dipole interactions are studied and reported with using FTIR, NMR and X-Ray crystallography analysis of some organic compounds. Those effects are shown clearly on both values of FTIR absorptions and chemical shifts of studied compounds.

*Keywords: Intramolecular hydrogen bonds; Dipole interactions; FTIR; <sup>1</sup>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.

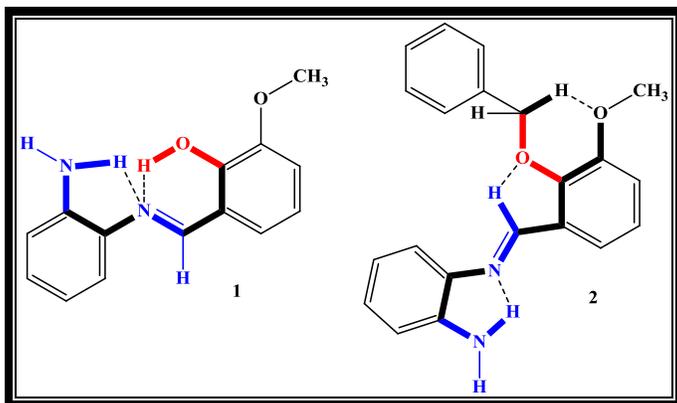
A hydrogen bond is a strong dipole-dipole attraction. In some organic compounds, we can be seen that intramolecular hydrogen bonding and dipole interactions have a large effect on the elongated of N–H and O–H bonds which reflected on the stranger values of FTIR and <sup>1</sup>HNMR of organic compounds, as shown in compounds 1–5.

The X–Ray crystallographic analysis of both 1 and 2 were determined [1-2]. The length of the intramolecular hydrogen bonds, –C=N···H–O in 1 and –C=N···H–N, –N=C–H···O–CH<sub>2</sub> in 2 were also compared. The importance of imines 1 and 2 lie in the preparation of bis-Schiff base [3] and benzimidazole derivatives [4-6], which are used widely in pharmaceutical and biological system applications [7-9].

**2. CHEMICAL STRUCTURE AND ITS APPLICATION**

The effect of N–H and O–H intramolecular hydrogen bonding can be seen in an imine 1, Fig. 1. The FTIR spectrum of this compound shows only one spike around 3414 cm<sup>-1</sup> for a single N–H stretching bond instead of two spikes of a primary amino group, 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 seven both of them appear as a singlet at  $\delta = 13.56$  and 8.63 ppm respectively, Fig. 3 [10].

46



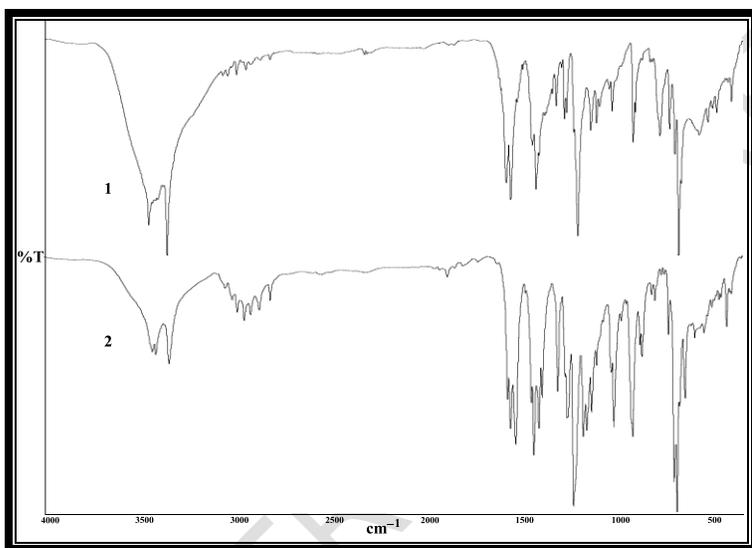
47

48

49

50

**Fig. 1: Imines 1 and 2.**



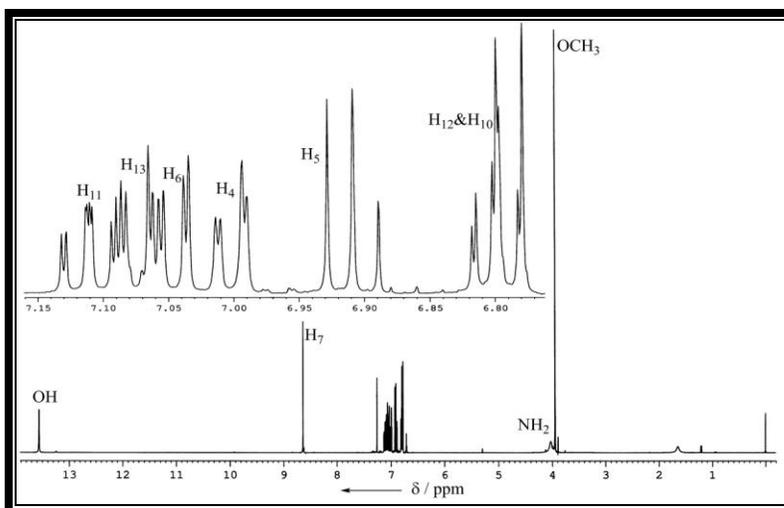
51

52

53

54

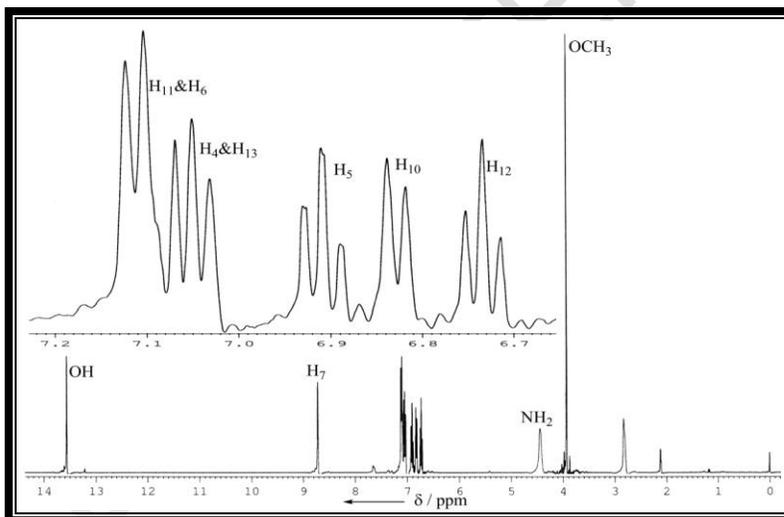
**Fig. 2: FTIR spectra of imines 1 and 2.**



55  
56  
57  
58  
59  
60  
61  
62  
63  
64  
65

**Fig. 3:  $^1\text{H}$  NMR spectrum of 1.**

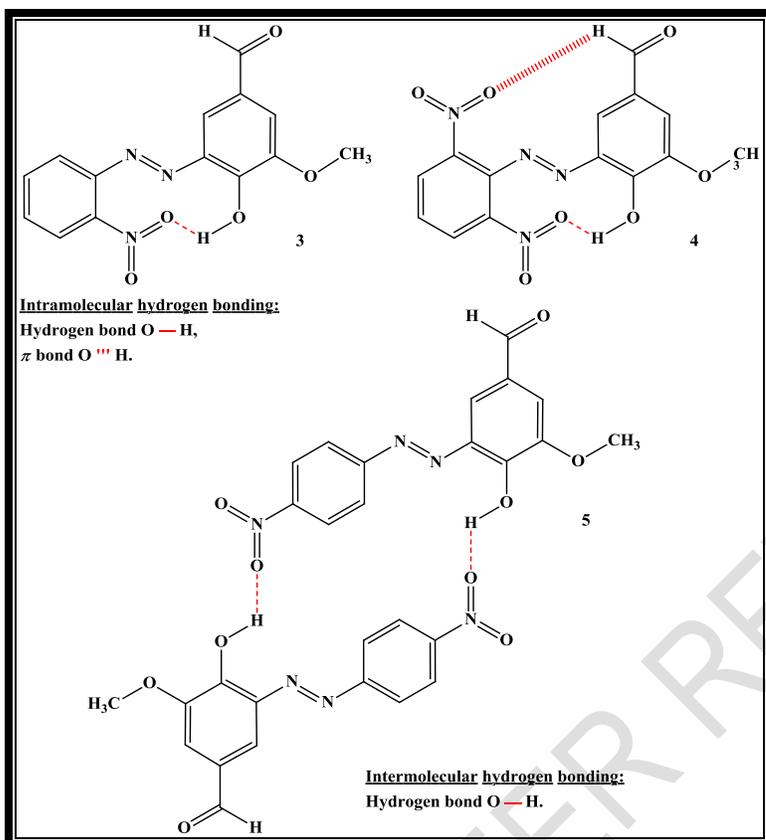
These unexpected values can be explained by intramolecular hydrogen bonding which generate five and six ring motifs, Fig. 1. So, it makes more deshielding and leads to stranger delta values, Fig. 3. Imine **2** forms stronger dipole-dipole interaction. Thus C-H $\cdots$ O and N-H $\cdots$ N interactions generate five and six ring motifs, Fig. 1. As a result of the stronger dipole-dipole interaction, the chemical shift of a proton that attached to carbon seven appears at  $\delta = 8.79$  ppm, which is the stranger value, Fig. 4 [11].



66  
67  
68  
69  
70  
71  
72  
73  
74

**Fig. 4:  $^1\text{H}$  NMR spectrum of 2.**

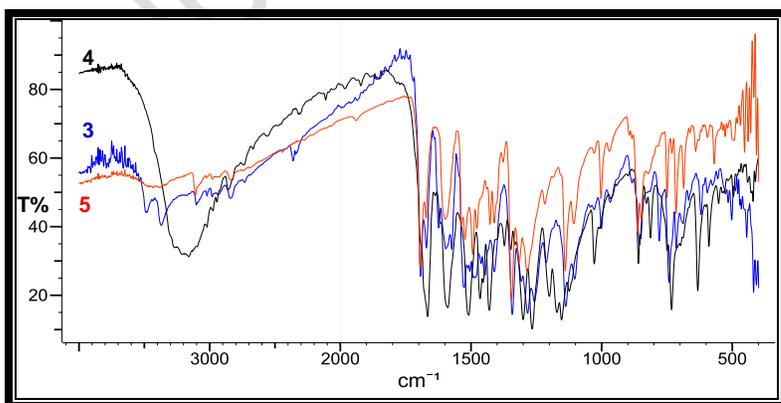
The effect of hydrogen bonds reflects on the FTIR absorptions of diazo dyes **3**, **4** and **5**, Fig. 5. It is believed the lower symmetrical stretching of nitro groups at *ortho* position in **3** which appears at  $1301\text{ cm}^{-1}$  due to the intramolecular hydrogen bonding and the dipole interaction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



75  
 76  
 77  
 78  
 79  
 80  
 81  
 82  
 83  
 84  
 85  
 86

**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, and as a result, vibrate a little more slowly. The O–H stretching frequency in **3** reflects the stronger intramolecular hydrogen bonding showing a very broad absorption around  $3277\text{ cm}^{-1}$ , Fig. 6. However, the IR spectra of both **4** and **5** display slightly lower asymmetrical stretching frequencies of  $\text{--NO}_2$  and O–H due to intramolecular and intermolecular hydrogen bonding, respectively, Fig. 6 [12].



87  
 88  
 89

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

90

#### 91 4. CONCLUSION

92

93 In this work, we have reported some organic compounds that have the large effect of  
94 intramolecular hydrogen bonding and dipole interaction which lead to the unexpected FTIR  
95 absorptions and the stranger values of chemical shifts in <sup>1</sup>HNMR.

96

#### 97 CONFLICTS OF INTEREST

98

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

101

102

#### 103 COMPETING INTERESTS

104

105 Authors have declared that no competing interests exist.

106

107

#### 108 REFERENCES

109

110 [1] Al-Douh MH, Hamid SA, Osman H, Kia R, Fun HK. 2-Amino-*N*-(2-hydroxy-3-  
111 methoxybenzylidene) aniline. Acta Crystallogr. E. 2008;64(7):o1201–o1202. DOI:  
112 10.1107/S1600536808016292.

113 [2] Al-Douh MH, Hamid SA, Osman H, Kia R, Fun HK. 2-Amino-*N*-(2-benzyloxy-3-  
114 methoxybenzylidene) aniline. Acta Crystallogr. E. 2008;64(7):o1290–o1291. DOI:  
115 10.1107/S1600536808017844.

116 [3] Al-Douh MH, Hamid SA, Osman H. Synthesis, spectroscopic and crystal structures  
117 studies of *N,N*-bis(2-hydroxy-3-methoxybenzylidene) diaminobenzene derivatives.  
118 University of Aden Journal of Natural and Applied Sciences. 2010;14(2):325–347. ISSN:  
119 1606-8947.

120 [4] Al-Douh MH, Osman H, Hamid SA. Synthesis and characterization of *N*-1-(2-hydroxy-3-  
121 methoxybenzyl)-2-(2-hydroxy-3-methoxyphenyl)-1*H*-benzimidazole. Hadhramout  
122 University Journal of Natural and Applied Sciences. 2011;8(1):11–32. ISSN: 2227-9164.

123 [5] Al-Douh MH, Osman H, Hamid SA. Synthesis and characterization of novel  
124 benzimidazole: *N*-1-(2-benzyloxy-3-methoxybenzyl)-2-(2-benzyloxy-3-methoxyphenyl)-  
125 1*H*-benzimidazole. University of Aden Journal of Natural and Applied Sciences.  
126 2011;15(2):375–393. ISSN: 1606-8947.

127 [6] Al-Douh MH, Osman H, Hamid SA. Synthesis and characterization of 2-(2-hydroxy-3-  
128 methoxyphenyl)-1*H*-benzimidazole. Hadhramout University Journal of Natural and  
129 Applied Sciences. 2012;9(1):49–64. ISSN: 2227-9164.

130 [7] Al-Douh MH, Sahib HB, Osman H, Hamid SA, Salhimi SM. Anti-proliferation effects of  
131 benzimidazole derivatives on HCT-116 colon cancer and MCF-7 breast cancer cell lines.  
132 Asian Pacific Journal of Cancer Prevention. 2012;13(8):4075–4079. DOI:  
133 10.7314/APJCP.2012.13.8.4075.

134 [8] Helal MH, Al-Douh MH, Hamid SA, Osman H, Salhimi SM, Majid AM. Diaminobenzene  
135 Schiff Base induces caspase 9-dependent apoptosis in U937 Leukemia cells.  
136 Webmedcentral. 2010;WMC001081:1–13. ISSN: 2046-1690,  
137 [http://www.webmedcentral.com/article\\_view/1081](http://www.webmedcentral.com/article_view/1081).

138 [9] Helal MH, Al-Mudaris ZA, Al-Douh MH, Osman H, Wahab HA, Al-Najjar BO, Abdallah  
139 HH, Majid AM. Diaminobenzene Schiff Base, A Novel Class of DNA Minor Groove  
140 Binder. International Journal of Oncology. 2012;41(2):504–510. DOI:  
141 10.3892/ijo.2012.1491.

- 142 [10] Al-Douh MH, Osman H, Hamid SA. Synthesis, NMR spectroscopy and crystal structures  
143 studies of 2-amino-*N*-(2-hydroxy-3-methoxybenzylidene) aniline. Proceeding of  
144 International Conference on Instrumentation, Communication, Information Technology  
145 and Biomedical Engineering (ICICI BME 2009), 247-253. ISBN 978-979-1344-67-8,  
146 IEEE CFP0987H-CDR, Aula Timur, Bandung Institute of Technology, Ganesha 10,  
147 Bandung 40132, Indonesia, November 23-25, 2009.
- 148 [11] Al-Douh MH, Osman H, Hamid SA. Synthesis, NMR spectroscopy and crystal structures  
149 studies of novel 2-amino-*N*-(2-benzyloxy-3-methoxybenzylidene) aniline. Proceeding of  
150 International Conference on Instrumentation, Communication, Information Technology  
151 and Biomedical Engineering (ICICI BME 2009), 438-443. ISBN 978-979-1344-67-8,  
152 IEEE CFP0987H-CDR, Aula Timur, Bandung Institute of Technology, Ganesha 10,  
153 Bandung 40132, Indonesia, November 23-25, 2009.
- 154 [12] Al-Douh MH, Bin-Selim EA, Al-Haik WM, Bin-Mahram SM, Al-Bakri AK, Al-Nohey DS,  
155 Sonbol KS. Synthesis and antimicrobial activity of some compounds derived from diazo  
156 dyes. 2019;3(4): (accept). ISSN: 2581-348X.  
157

UNDER PEER REVIEW