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Synthesis and Spectroscopic Properties of New Benzimidazole Schiff Bases

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Four new *ortho-hydroxy* Schiff bases of aminobenzimidazoles were synthesised and keto-enol tautomerism were studied using spectroscopic techniques such as UV-VIS, ^{1}H NMR, IR and GC-MS. The results suggest that the salicylaldimine Schiff bases exist predominantly in enol form and the naphthaldimines can coexist in the keto ⇌ enol tautomeric forms.

Key Words: Benzimidazole, Schiff base, Tautomerism, Spectroscopy.

INTRODUCTION

The *ortho-hydroxy* Schiff bases are of great interest because of their applications as photochromic, thermochromic and electronically functional materials[1-3] and biological activities[4-6]. In this respect, the syntheses, structures and the keto-enol tautomerism of these compounds have been studied extensively[7-13].

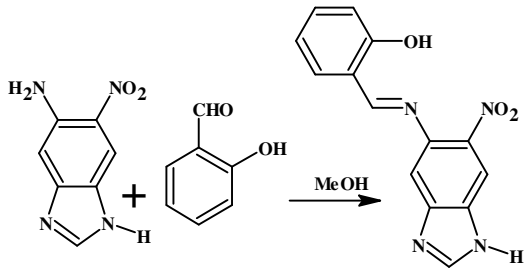
In general, using either IR and X-ray crystallography techniques, the predominance of enol tautomeric form has been shown for salicylaldimine Schiff bases in solid state and O-H···N type intramolecular hydrogen bond is observed for these compounds. Naphthaldimine Schiff bases prefer the keto tautomeric form because of resonance and delocalization energies in naphthalene ring which increase the electron density on the imino nitrogen atom[14-17] and therefore O···H-N type intramolecular hydrogen bond is observed. In solution, the results obtained using either NMR, ultra-violet or visible spectrometry suggested that the tautomeric equilibrium shifted to the side of the enol form for salicylaldimines and the keto form for naphthaldimines Schiff bases[18]. In this study, the synthesis of new *ortho-hydroxy* Schiff bases, derivatives of 5-amino-6-nitro-1*H*-benzimidazole and 1-methyl-5-amino-benzimidazole, was reported and the keto-enol tautomerism was examined in solid state, in solution and in gas phase.

EXPERIMENTAL

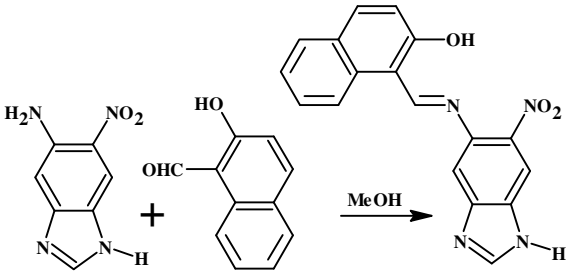
Melting points were obtained on a Gallenkamp apparatus (uncorrected). IR spectra were recorded on a Mattson 1000 FT-IR spectrophotometer in KBr discs. UV-VIS spectra were measured using a UNICAM-UV2-100 spectrometer. ^{1}H NMR spectra were obtained with a Brucker DPX-400 spectrometer. ESI mass spectra were recorded on a Waters 2695 Alliance Micromass ZQ spectrophotometer. Elemental analyses were performed on a LECO CHNS-932 analyser. Salicylaldehyde and 2-hydroxy-1-naphthaldehyde were purchased from Fluka and used without further purification. 5-Amino-6-nitro-1*H*-benzimidazole and 1-methyl-5-amino benzimidazole were synthesized as described in literature[19,20] and used as starting materials to synthesize the reported benzimidazole derivatives.

Synthesis of 2-{[(6-nitro-1*H*-benzimidazol-5-yl)imino]-methyl}phenol (1) and 1-{[(6-nitro-1*H*-benzimidazol-5-yl)imino]methyl}naphthalen-2-ol (2): A solution of salicylaldehyde (1.46 g, 12 mmol) in methanol was added slowly to a solution of the 5-amino-6-nitro-1*H*-benzimidazole (1.78 g, 10 mmol) in methanol (50 mL). (**Scheme-I**). The resulting mixture was refluxed until the completion of reaction which was checked by TLC. Then the solvent was removed and the crude product was washed with water and acetone. The compound **1** was obtained as yellow solid (2.20 g, 78 %); m.p. 270-271 ºC; UV (CH_3OH) λ_{max} 328 nm, UV (CH_2Cl_2) λ_{max} 352 nm; IR (KBr, ν_{max}, cm^{-1}) 3249, 1618, 1532, 1327; ^{1}H NMR (DMSO-d_6) δ 6.80-7.02 (m, 2H, ArH), 7.43 (t, 1H, ArH), 7.71 (t, 1H, ArH), 7.80 (s, 1H, CH=N), 8.34 (s, 1H, CH=N), 8.54 (s, 1H, ArH), 9.10 (s, 1H, ArH), 12.40 (s, 1H, Ar-OH); MS m/z: 282(M^+,100), 237, 163, 121. Anal. calcd. (%) for $C_{14}H_{10}N_4O_3$: C 59.58, H 3.55, N 19.86. Found (%): C 59.52, H 3.49, N 19.80.

Using 2-hydroxy-1-naphthaldehyde (2.06 g, 12 mmol) in state of salicylaldehyde, the same reaction procedure yielded the compound **2** (**Scheme-II**) as red solid (1.8 g, 53 %); m.p. > 300 ºC dec.; UV (CH_3OH) λ_{max} 362 nm, 462 nm, UV (CH_2Cl_2) λ_{max} 362 nm; IR (KBr, ν_{max}, cm^{-1}) 3100, 1620, 1521, 1327; ^{1}H NMR (DMSO-d_6) δ 7.12 (d, 1H, ArH), 7.40 (t, 1H,



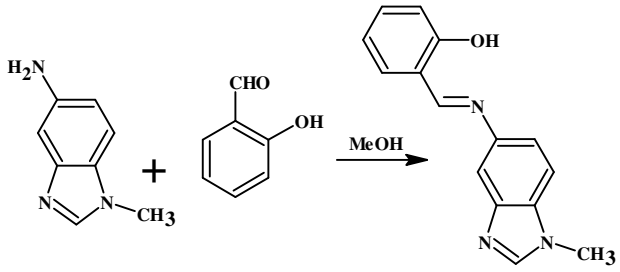
Scheme-I: Synthesis of 2-{[(6-nitro-1*H*-benzimidazol-5-yl)imino]methyl}-phenol (**1**)



Scheme-II: Synthesis of 1-{[(6-nitro-1*H*-benzimidazol-5-yl)imino]methyl}-naphthalen-2-ol (**2**)

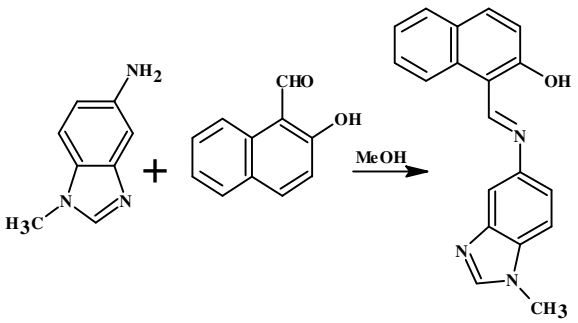
ArH), 7.60 (t, 1H, ArH), 7.86 (d, 1H, ArH), 8.00 (m, 2H, ArH), 8.38 (s, 1H, CH = N), 8.60-8.70 (m, 2H, ArH), 9.78 (s, 1H, CH-NH), 9.82 (s, 1H, CH=NH), 13.20 (s, 1H, Ar-OH), 14.10 (d, 1H, CH-NH···ONO); MS m/z: 332 (M^+, 100), 287, 171. Anal. calcd. (%) for $C_{18}H_{12}N_4O_3$: C 65.06, H 3.62, N 16.87. Found (%): C 65.00, H 3.59, N 16.83.

Synthesis of 2-{[(1-methyl-benzimidazol-5-yl)imino-methyl}phenol (3) and 1-{[(1-methyl-benzimidazol-5-yl)imino]methyl}naphthalen-2-ol (4): Addition of a solution of salicylaldehyde (1.46 g, 12 mmol) in methanol to a solution of the 1-methyl-5-aminobenzimidazole (1.47 g, 10 mmol) in methanol (50 mL) yielded 1.68 g (67 %) of the compound **3** as light yellow solid (**Scheme-III**); m.p. > 300 ºC dec.; (1.68 g, 67 %); UV (CH_2Cl_2) λ_{max} 344 nm; IR (KBr, ν_{max}, cm^{-1}) 3118, 1620, 1481; ^1H NMR ($CDCl_3$) δ 3.80 (s, 3H, CH_3), 7.00-8.20 (m, 8H, ArH), 8.90 (s, 1H, CH=N), 11.00 (s, 1H, Ar-OH); MS m/z: 251 (M^+), 237, 121, 118. Anal. calcd. (%) for $C_{15}H_{13}N_3O$: C 71.71, H 5.18, N 16.73. Found (%): C 71.69, H 5.11, N 16.43.



Scheme-III: Synthesis of 2-{[(1-methyl-benzimidazol-5-yl)iminomethyl} phenol (**3**)

Using 2-hydroxy-1-naphthaldehyde (2.06 g, 12 mmol), the compound **4** was obtained as orange solid, (**Scheme-IV**), m.p. > 300 ºC dec.; (1.63 g, 54 %) UV (CH_2Cl_2) λ_{max} 386 nm,



Scheme-IV: Synthesis of 1-{[(1-methyl-benzimidazol-5-yl)imino]methyl} naphthalen-2-ol (**4**)

464 nm; IR (KBr, ν_{max}, cm^{-1}) 3269, 1620, 1321; ^1H NMR ($CDCl_3$) δ 3.80 (s, 3H, CH_3), 7.20-8.60 (m, 10H, ArH), 9.44 (s, 1H, CH-NH), 9.58 (s, 1H, CH=N), 10.80 (s, 1H, Ar-OH), 15.70 (s, 1H, CH-NH); MS m/z: 301 (M^+), 287 (100), 171, 118. Anal. calcd. (%) for $C_{19}H_{15}N_3O$: C 75.75, H 4.98, N 13.95. Found (%): C 75.70, H 4.90, N 13.90.

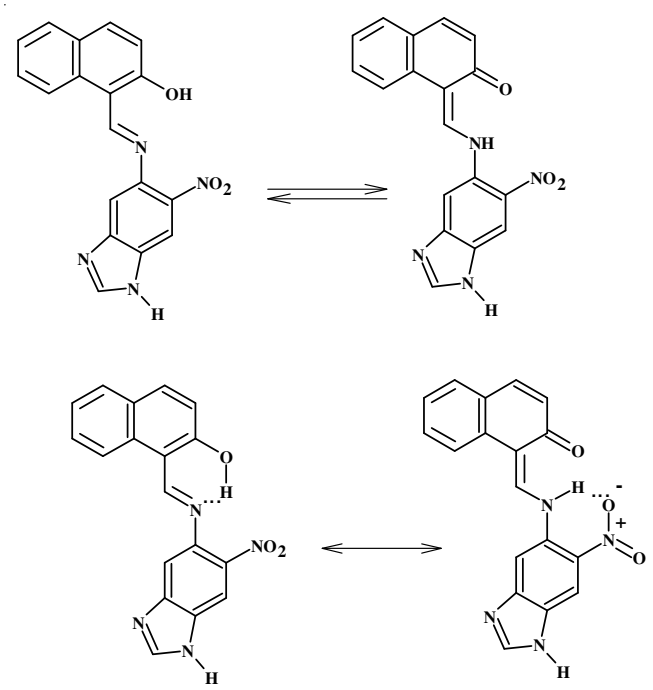
RESULTS AND DISCUSSION

IR spectra: C=N and OH groups are the functional groups in the molecules of Schiff bases to take into consideration concerning the keto-enol tautomerism. The IR spectra of the reported compounds reveal clearly the enol form in solid state. The assignments of the ν(C=N) stretching vibration are observed at 1620-1618 cm^{-1}. The shifted at lower wave numbers may be attributed to an association between C=N and OH groups. The bands appeared at 3249, 3100, 3118 and 3269 cm^{-1} are assigned to the ν(O-H) stretching vibration for the compounds **1**, **2**, **3** and **4**, respectively. The O-H absorption band is broad and shifted towards lower wavenumbers confirming also the presence of the O-H···N intramolecular hydrogen bond. Additionally, the absorption bands at 1532-1327 and 1521-1327 cm^{-1} are assigned to the nitro group of the compounds **1** and **2**.

UV-VIS spectra: In the UV-VIS spectra, the significant absorption bands at 352, 362, 344 and 386 nm in CH_2Cl_2 are attributed to C=N group, respectively for the compounds **1**, **2**, **3** and **4** proving the predominance of the enol form for the reported benzimidazole Schiff bases. In the spectra of the compounds **2** and **4**, the weak bands at 462 nm in CH_3OH and 464 nm in CH_2Cl_2 reveal the coexistence of two tautomeric forms with the preference on the enol form for naphthaldimine Schiff base.

^1H NMR spectra: The ^1H NMR data confirms that the salicylaldimine Schiff bases **1** and **3** exist in only enol form while both enol and keto forms have been observed for the naphthaldimines **2** and **4**. The protons CH=N observed at δ 8.34, 9.82, 8.90, 9.58 ppm and the signals of Ar-OH protons at 12.40, 13.20, 11.00, 10.80 ppm, respectively for the compounds **1**, **2**, **3** and **4** indicate enol form for all compounds. In the spectrum of the compounds **2** and **4**, the appearance of the peaks at δ 9.78 and 9.44 ppm indicating CH-NH protons and the CH-NH peaks observed at δ 14.10 and 15.70 ppm confirm the existence of the keto for the compounds **2** and **4**, respectively. Additionally, in the nitro derivative **2**, the upfield shift of CH-NH proton signal is also due to a possible intramolecular

hydrogen bonding between the proton of the CH-NH and NO_2 groups (**Scheme-V**).



Scheme-V: Keto-enol tautomerism and intramolecular hydrogen bonding in **2**

MS spectra: The peaks at m/z 282, m/z 332, m/z 251 and m/z 301, attributed to the M^+ of **1**, **2**, **3** and **4** confirm that the reported compounds have a molecular formula $C_{14}H_{10}N_4O_3$, $C_{18}H_{12}N_4O_3$, $C_{15}H_{13}N_3O$ and $C_{19}H_{15}N_3O$, respectively. The preference on the enol form in gas phase is confirmed by the major product-ions $(m/z\ 237)^+$, $(m/z\ 163)^+$, $(m/z\ 121)^+$ for the compound **1**; $(m/z\ 287)^+$, $(m/z\ 171)^+$, $(m/z\ 163)^+$ for the compound **2**; $(m/z\ 237)^+$, $(m/z\ 121)^+$, $(m/z\ 118)^+$ for the compound **3**, $(m/z\ 287)^+$, $(m/z\ 171)^+$ and $(m/z\ 118)^+$ for the compound **4**. The mass spectra of the compounds share a common feature, the diagnostic peak at m/z 121 for the salicylaldimines and at m/z 171 for naphthaldimines. These fragment ions resulted from the cleavage of the C=N imine bond support the formation of a heterocyclic species which is characteristic of the mass spectra of the *ortho*-hydroxy Schiff bases[21]. The proposed fragmentation pathways are given below (**Schemes VI** and **VII**) for the reported compounds.

Conclusion

The new *ortho*-hydroxy Schiff bases derived from the aminobenzimidazoles were synthesized and the keto-enol tautomerism were investigated using IR, UV-VIS, ^{1}H NMR and mass spectroscopy. The results revealed that in solid state, in solution and in gas phase, the salicylaldimine Schiff bases exist preferentially in the enol form while the naphtaldimine Schiff bases showed the coexistence of the enol and keto tautomeric forms.

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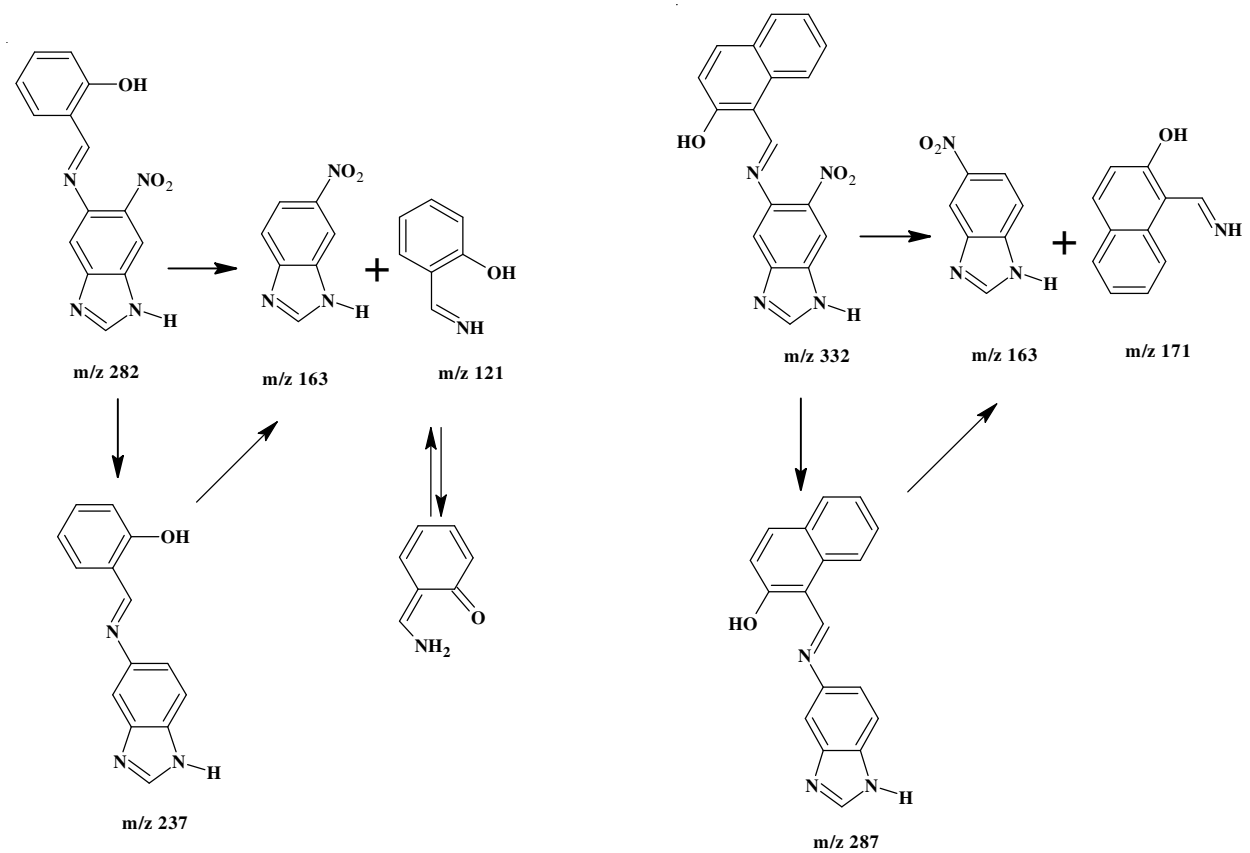
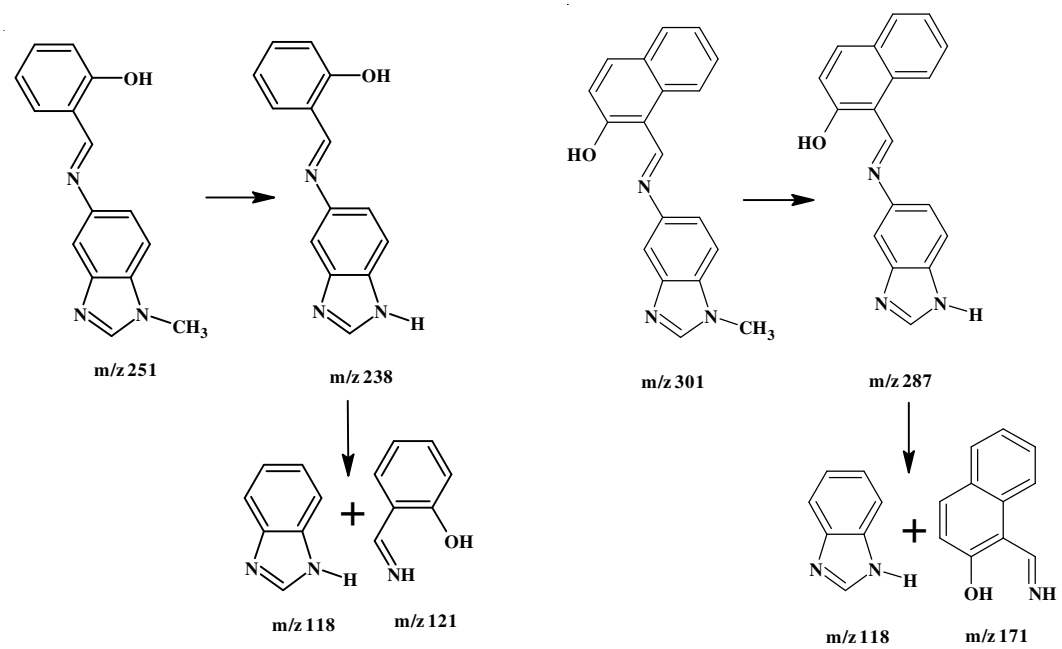


Scheme-VI: Proposed fragmentation pathways for the compound **1** and **2**



Scheme-VII: Proposed fragmentation pathways for the compounds **3** and **4**

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