

Studies of tautomerism in the azonaphthol derivatives of benzimidazoles

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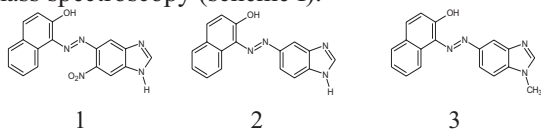
The tautomeric behaviour of three azonaphthol derivatives of benzimidazoles, 1-[(6-nitro-1*H*-benzimidazol-5-yl)diazenyl]naphthalen-2-ol, 1-[1*H*-benzimidazol-5-yl diazenyl]naphthalen-2-ol and 1-[(1-methyl-1*H*-benzimidazol-5-yl)diazenyl]naphthalen-2-ol, were studied in solution, in solid state and in gas phase using spectroscopic techniques. The results show that the ketohydrazone tautomeric form is predominant in solution and in solid state while in gas phase the tautomeric equilibrium is on the azoenol side.

Keywords: Benzimidazole, azonaphthol, tautomerism, mass spectroscopy

INTRODUCTION

Heterocycles have been extensively used as diazo or coupling components in the synthesis of azo dyes [1–3] and many of these compounds display tautomerism depending on the intramolecular proton transfer which also determines their optical and physical characteristics. Their application as disperse dyes or photosensitive and photoconductive materials provokes a considerable interest in the technology of these compounds [4]. Owing to the properties of azo dyes, such as volatility, thermal lability, *etc.*, the tautomerism of these compounds has been widely studied by various techniques [5–9] including NMR, UV-vis, IR spectroscopy, X-ray crystallography and limited mass spectrometry analysis [10–12].

This paper reports the study of the azoenol-ketohydrazone tautomerization of the benzimidazole derivatives, namely, 1-[(6-nitro-1*H*-benzimidazol-5-yl) diazenyl]naphthalen-2-ol **1**, 1-[1*H*-benzimidazol-5-yl diazenyl]naphthalen-2-ol **2**, and 1-[(1-methyl-1*H*-benzimidazol-5-yl)diazenyl]naphthalen-2-ol **3**, using ¹H NMR, UV-vis, IR and mass spectroscopy (scheme I).



Scheme I. Structures of the reported compounds

MATERIALS AND METHODS

5-Nitro-1*H*-benzimidazole, naphthalen-2-ol, nitric acid, sulfuric acid, dimethyl sulfate and the solvents were purchased from Merck. Melting points were measured on a Gallenkamp apparatus. NMR measurements were carried out on a Bruker 500 MHz spectrometer. FTIR and UV-vis spectra were recorded on a Mattson 1000 FTIR spectrometer (in KBr discs) and on a UNICAM UV2–100 series spectrometer, respectively. Mass spectra were recorded on the AGILENT 1100 MSD spectrometer. Elemental analysis performed on the LECO 932 CHNS agreed with the calculated values.

EXPERIMENTAL

The synthesis of 5(6)-amino-6(5)-nitrobenzimidazole and its azonaphthol derivative – [(6-nitro-1*H*-benzimidazol-5-diazenyl] naphthalen-2-ol **1** was reported in a previous paper of the author [13]. The compound **2** was prepared according to ref. [13] and the compound **3** was synthesized in the same way using 5-amino-1-methyl-1*H*-benzimidazole as starting material.

*Synthesis of 1-[(1-methyl-1*H*-benzimidazol-5-yl)diazenyl]naphthalen-2-ol*

5-Amino-1-methyl-1*H*-benzimidazole: A mixture of 5-nitro-1*H*-benzimidazole (10 mmol), (CH₃)₂SO₄ (5.0 mL) and 1.5 mL 1.0 N NaOH was refluxed for 30 min. After cooling, the crude product was filtered and recrystallized from water. 1-Methyl-5-nitro-1*H*-benzimidazole was obtained as a brown solid, m.p. 203°C, yield 1.5 g (82%). This nitro compound was reduced using Sn/HCl by a standard

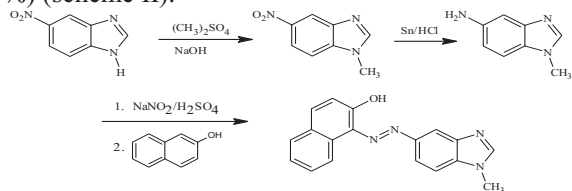
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procedure; 5-amino-1-methyl-1*H*-benzimidazole was obtained as a yellow solid after recrystallization from ethanol, m.p. 158–159°C, yield 0.98 g (67 %).

*1-[(1-Methyl-1*H*-benzimidazol-5-yl)diazenyl]naphthalen-2-ol 3*

5-Amino-1-methyl-1*H*-benzimidazole (10 mmol) was stirred at 0–5 °C into nitrosyl sulfuric acid prepared from sodium nitrite (0.7 g) and concentrated H₂SO₄ (10 mL). After diazotizing, a 5% solution of naphthalen-2-ol in 2 N NaOH was added. By adjusting the pH to 6.0–6.5, the crude product was precipitated, filtered and recrystallized from ethanol. The compound **3** was obtained as a dark-red solid, decomp. > 340 °C, yield 2.5 g (79 %) (scheme II).



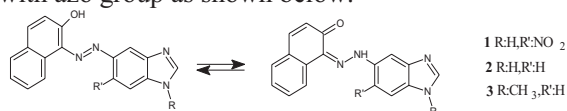
Scheme II. Synthesis of 5-amino-1-methyl-1*H*-benzimidazole and 1-[(1-methyl-1*H*-benzimidazol-5-yl)diazenyl]naphthalen-2-ol

RESULTS AND DISCUSSION

The ¹H NMR, UV-vis and IR spectra of the azonaphthol derivatives were interpreted in respect of their azoenol-ketohydrazone tautomeric behavior in solution and in solid state. The mass spectra helped to throw light on these structures in gas phase, excluding external factors like solvents and intermolecular interactions.

¹H NMR spectra

The basic structure required for tautomerism is the existence of a labile proton in the molecule. This attitude is observed as azoenol ⇌ ketohydrazone tautomerization in azonaphthol compounds containing hydroxy group conjugated with azo group as shown below.



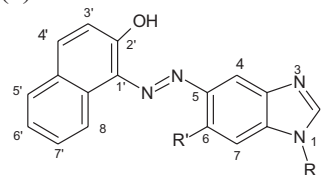
Tautomerisation of the azonaphthol derivatives of benzimidazole

The equilibrium between azoenol and ketohydrazone tautomers changed rapidly and the nature of the substituents in the phenyl ring affected the position of the equilibrium. Using ¹H NMR spectroscopy it was possible to decide the position

of the labile hydrogen atom in the molecule and determine the ratio of tautomers present at the equilibrium depending on the intensity of the signals which are proportional to the molar amounts of the compounds.

The examination of the ¹H NMR spectra of the three azonaphthol compounds, measured in *d*₆-DMSO shows that the equilibrium between azoenol and ketohydrazone tautomers is predominantly shifted to the ketohydrazone form. The analysis also revealed that the nitro group attached to C(6) in the benzimidazole ring slightly shifted the tautomeric equilibrium towards the azoenol form because of the change in π electron configuration depending on the resonance in the benzimidazole ring.

The enumeration of atoms is shown below and the chemical shifts and coupling constants are presented in Table I. Multiplicity of signals is presented as: (s) singlet, (d) doublet, (t) triplet, (m) multiplet, (b) broad.



The enumeration of atoms

Table I. ¹H chemical shifts δ/ppm, and coupling constants J/Hz of azonaphthols

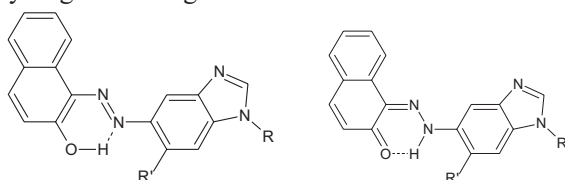
Compound	δ/ppm, J/Hz
16.36, s; 12.60, b; 9.70, b; 8.57, s; 8.49, s; 8.29, s; 7.95, d, 8 Hz;	
7.75, d, 9 Hz; 7.60–7.00, m; 6.79, d, 8 Hz	
15.35, s; 12.80, b; 12.20, b; 8.53, d, 3 Hz; 8.45, s; 8.00, d, 9 Hz;	
7.98, d, 9 Hz; 7.85, d, 9 Hz; 7.66, t, 7 Hz; 7.60–7.90, m; 7.47, t, 7 Hz;	
6.85, d, 9 Hz	
15.32, s; 13.20, b; 8.73, d, 7 Hz; 8.18, s; 7.12, d, 9 Hz; 7.99, d, 9 Hz;	
7.76, d, 9 Hz; 7.70–7.90, m; 7.68, t, 8 Hz; 7.49, t, 8 Hz; 3.92	

In all cases, in the spectra there is a signal in the range of 15.32–16.36 ppm corresponding to the –NH–N= hydrazone protons. The broad peaks appearing at 12.60–13.20 ppm indicate –OH protons. The peaks observed between ca. 6.79 and 9.70 ppm are related to aromatic protons and their integration agrees with the number of protons for each compound.

UV-vis spectra

The UV spectra of the azonaphthol derivatives **1**, **2** and **3** show that ketohydrazone tautomers

predominantly exist in methanol solution. The strong band appearing at 480–500 nm indicates the presence of the ketohydrazone form while the band related to the azoenol form apparently disappeared. Using dichloromethane as a solvent with corresponding decrease in polarity, no absorption band about 400 nm was observed which proves that these compounds exist in azoenol form in non-polar solvents. It is suggested that the tautomerism strongly depends on solvent polarity causing intermolecular or intramolecular hydrogen bonding. Therefore, the ketohydrazone form can be stabilized by hydrogen bonding with polar solvents and when hydrogen bonding is not possible, the azoenol form is stabilized by intramolecular hydrogen bonding as shown below.



Intramolecular hydrogen bond in O-H.....N and N-H.....O forms IR spectra

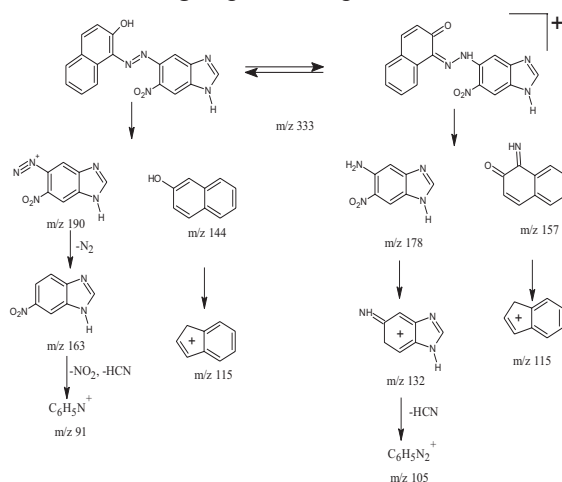
In all cases, the $\nu_{\text{O-H}}$ absorption bands observed around $3200\text{--}3000\text{ cm}^{-1}$, are shifted to lower values as a result of the intramolecular hydrogen bond in the O-H..N form. This bonding favors the shift of the tautomeric equilibrium on the ketohydrazone side. The observation of $\nu_{\text{C=O}}$ phenolic absorption bands at 1320 , 1300 and 1342 cm^{-1} for the compounds **1**, **2** and **3**, respectively, supported the existence of a ketohydrazone tautomer including an intra- molecular hydrogen bond in the N..O in the solid state. $\nu_{\text{C=O}}$ absorption bands confirming this structure are not distinguishable because of the overlapping with $\nu_{\text{C=N}}$ imine absorption band of the benzimidazole ring.

Mass spectra

Mass spectra of the azonaphthol derivatives of benzimidazoles were also interpreted in respect of their tautomeric behavior. The spectra resemble each other revealing the preference of the azoenol tautomeric form in the equilibrium. The formation of a ketohydrazone tautomer by the hydroxy group in *ortho* position affected the fragmentation pathways in mass spectrometry [14–17]. The ketohydrazone tautomer shows a cleavage of the single HN-N= bond, whereas the =N-C(napht) bond in the azoenol form should be preferably broken. The proposed fragmentation pathways are given in schemes III, IV and V.

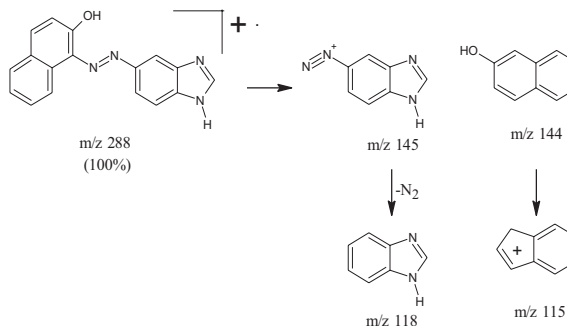
Electron-impact (EI) fragmentation of this azonaphthol derivatives gives rise to the major ions $\text{M}^+ \rightarrow (\text{m/z } 190)^+ \rightarrow (\text{m/z } 163)^+ \rightarrow (\text{m/z } 144)^+ \rightarrow (\text{m/z } 115)^+$ for the compound **1** (scheme III) and $\text{M}^+ \rightarrow (\text{m/z } 145)^+ \rightarrow (\text{m/z } 115)^+$ for **2** (scheme IV) which corresponds to cleavage of the =N-C(napht) single bond.

The existence of the azoenol form of **1** was particularly supported by the (M-190)⁺ ion of the major decomposition. The cleavage of the (benz) – N=N-C(napht) bonds occurred as indicated above depending on the electron donating power of the naphthalene ring [18–21]. On the other hand, the ion peaks (m/z 178)⁺ → (m/z 132)⁺ and (m/z 157)⁺ in the mass spectra of **1** point to a minor fragmentation process of the ketohydrazone form due to the nitro group at *ortho* position.



Scheme III. Proposed fragmentation pathway for compound **1**

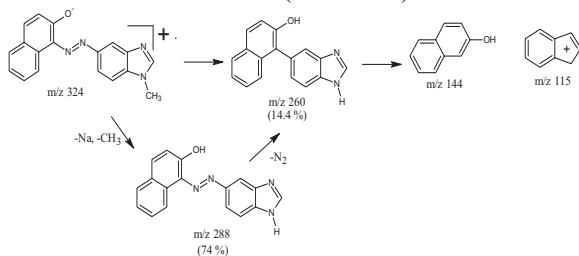
In addition, the comparison of the abundances of the ion (m/z 144)⁺ in the spectra of these compounds suggested that the azoenol tautomer dominates in the gas phase for **2** rather than for **1**, probably due to the resonance effect.



Scheme IV. Proposed fragmentation pathway for compound **2**

The main reaction observed in the mass spectra of the compound **3** is $(\text{M}+23)^+ \rightarrow (\text{m/z}$

288)⁺→(m/z 260)⁺→(m/z 144)⁺→(m/z 115)⁺. The major ion at (m/z 288) corresponds to the loss of Na and -CH₃. The ion peak at (m/z 260) may be attributed to the proposed azoenol type fragmentation including N₂ loss. The ion peak (m/z 115) dominates in the spectrum and the ion peak observed at (m/z 144) confirms the cleavage of the azoenol tautomeric form (scheme V).



Scheme V. Proposed fragmentation pathway for compound 3

CONCLUSION

Three azonaphthol derivatives of benzimidazole were studied in respect of azoenol ⇌ ketohydrazone tautomerism using ¹H NMR, UV-vis, IR and mass spectroscopy. The results show that the ketohydrazone tautomeric form is predominant in solution and in solid state while the tautomeric equilibrium is on the azoenol side in gas phase.

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ИЗСЛЕДВАНИЯ ВЪРХУ ТАВТОМЕРИЯТА НА АЗОНАФТОЛОВИ ПРОИЗВОДНИ НА БЕНЗИМИДАЗОЛА

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Тавтомерните отношения на три азоафтолови производни на бензимидазола 1-[(6-нитро-1H-бензимидазол-5-ил)дiazенил]нафтален-2-ол, 1-[1H бензимидазол-5-ил-дiazенил]нафтален-2-ол и 1-[(1-метил-1H-бензимидазол-5-ил)дiazенил]нафтален-2-ол са изследвани в разтвор, в твърдо състояние и в газова фаза, were studied in solution, in solid state and in gas с помощта на спектроскопска техника. Резултатите показват, че кетохидразоновата тавтомерна форма преобладава в разтвор и в твърдо състояние, докато в газообразно състояние равновесието е изтеглено към азо-енолната форма.