



Spectrophotometric study on the proton transfer reaction between 2-amino-4-methylpyridine with 2,6-dichloro-4-nitrophenol in methanol, acetonitrile and the binary mixture 50% methanol + 50% acetonitrile



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ARTICLE INFO

Article history:

Received 5 July 2015

Received in revised form 11 October 2015

Accepted 22 October 2015

Available online 25 October 2015

Keywords:

2-Amino-4-methylpyridine

2,6-Dichloro-4-nitrophenol

Proton transfer

Spectrophotometry

ABSTRACT

Proton transfer reaction between 2-amino-4-methylpyridine (2AMP) as the proton acceptor with 2,6-dichloro-4-nitrophenol (DCNP) as the proton donor has been investigated spectrophotometrically in methanol (MeOH), acetonitrile (AN) and a binary mixture composed of 50% MeOH and 50% AN (AN-Me). The composition of the complex has been investigated utilizing Job's and photometric titration methods to be 1:1. Minimum–maximum absorbance equation has been applied to estimate the formation constant of the proton transfer reaction (K_{PT}) where it reached high values in the investigated solvent confirming its high stability. The formation constant recorded higher value in AN compared with MeOH and mixture of AN-Me. Based on the formation of stable proton transfer complex, a sensitive spectrophotometric method was suggested for quantitative determination of 2AMP. The Lambert–Beer's law was obeyed in the concentration range 0.5–8 $\mu\text{g mL}^{-1}$ with small values of limits of detection and quantification. The solid complex between 2AMP with DCNP has been synthesized and characterized by elemental analysis to be 1:1 in concordant with the molecular stoichiometry in solution. Further analysis of the solid complex was carried out using infrared and $^1\text{H NMR}$ spectroscopy.

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1. Introduction

Recently, much attention has been given to the study of PT-complexes formed in the reactions of chemistry and biochemistry [1–4]. Proton transfer complexes play an important role in a wide variety of chemical and biological processes like stabilizing biomolecular structures [5], controlling the speed of enzymatic reactions [6] as well as constructing supramolecular structures [7]. Complexes of phenols with nitrogen bases belong to the most important investigated hydrogen-bonded complexes, may be due to the possibility of almost continuous control of the donor–acceptor properties of the interacting components. These complexes have been investigated by many techniques [8].

Aminopyridines are known to form stable proton transfer complexes with proton donors so the study of their proton transfer or hydrogen-bonded complexes is very important to explain many chemical phenomena they take part in. They have many medical and pharmacological applications, in addition to their use in analytical chemistry [9,10]. Aminopyridines are effective drugs in improving

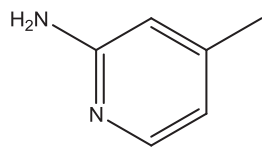
neuromuscular transmission [11]. In particular, 2-amino-4-methylpyridine is one of the potential impurities in piroxicam and teroxicam, which are non-steroidal anti-inflammatory drugs that are used in musculo-skeletal and joint disorders [12]. Moreover, aminopyridines are commonly present in synthetic and natural products [13]. They form repeated moiety in many large molecules with interesting photophysical, electrochemical and catalytic applications [14].

Nitrophenol is a useful tool in chemical and biochemical research, in the synthesis of metal-complexes characterized by strong hydrogen-bonding interactions [15], or as electron- acceptor in the synthesis of charge-transfer complexes [16]. Keeping in view the biological and pharmaceutical importance of 2AMP, and in connection with our scope of interest, charge and proton-transfer interactions [17–26], this article presents the results obtained from electronic absorption spectra on the proton-transfer reaction between 2AMP as the proton acceptor and DCNP as the proton donor in acetonitrile, methanol and binary mixture composed of 50% acetonitrile with 50% methanol (v/v) aiming to determine the reaction stoichiometry, formation constant (K_{PT}), molecular extinction coefficient (ϵ_{max}), oscillator strength, transition dipole moment and analytical parameters of the formed hydrogen bonded complex. An important goal of this work is the synthesized of the

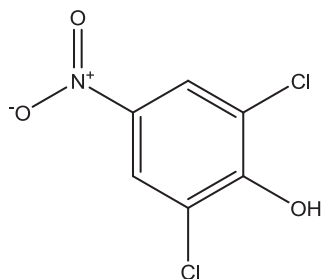
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solid complex 2AMP–DCNP and its characterization using elemental analysis, infrared and ^1H NMR studies.



2-amino-4-methylpyridine



2,6-dichloro-4-nitrophenol

2. Experimental

2.1. Chemicals

All chemicals used were of analytical grade. 2-Amino-4-methylpyridine and 2,6-dichloro-4-nitrophenol were supplied by Acros organics (Geel-Belgium). Acetonitrile and methanol were purchased from Aldrich (Sussex, England).

2.2. Spectral measurements

The electronic absorption spectra were recorded in the region 200 to 800 nm using double beams ultraviolet–visible spectrophotometer (Shimadzu UV-1650, Japan) with matched 1-cm quartz cells and personal spectroscopy software version 3.7, connected to Shimadzu TCC-ZUOA temperature controller unit (Japan). Infrared spectra were recorded as KBr disks on Bruker FTIR Tensor 37 Fourier transform infrared spectrophotometer (USA), evacuated to avoid water and CO_2 absorption. ^1H NMR (600 MHz) spectra were measured on a Bruker DPX spectrometer using $\text{DMSO}-d_6$ as solvent and TMS as an internal standard; chemical shifts are expressed as δ ppm.

2.3. Synthesis of the solid PT-Complex

The solid PT-Complex between 2AMP and DCNP was prepared by mixing of 5 mL saturated solutions of both 2AMP (0.11 g, 1 mmol) and DCNP (0.21 g, 1 mmol) in acetonitrile. The resulting complex solution was allowed to evaporate slowly at room temperature where the complex was isolated as yellow crystals. The isolated complex was filtered and washed well with acetonitrile to remove the residual reactants and dried over calcium chloride for 24 h. Anal. Calc. for (2AMP–DCNP) $\text{C}_{11}\text{H}_{10}\text{N}_2\text{O}_4$ Complex: C, 45.57%; H, 3.48%; N, 13.29%. Found: C, 45.39%; H, 3.45%; N, 13.14%. MP = 206 °C.

3. Result and discussion

3.1. Electronic absorption spectra

Fig. 1 shows the electronic absorption spectra of the proton transfer complex of 2AMP with DCNP in MeOH, AN and AN-Me, respectively. Although neither of the reactant spectra displays any measurable absorption above 400 nm, the absorption spectra of mixed donor–acceptor solution are characterized by the appearance of new absorption band above 400 nm. This new absorption band is attributed to the π – π^* transition of the resulting yellow colored PT-complex and is centered at 395.5, 423.0 and 402.5 nm in Me.... in MeOH, AN and AN-Me solutions, respectively. It is worthy to report that all spectra of mixtures containing the acceptor and donor were recorded against the corresponding donor as reference in order to eliminate a possible overlap that may arise between PT complex and DCNP bands.

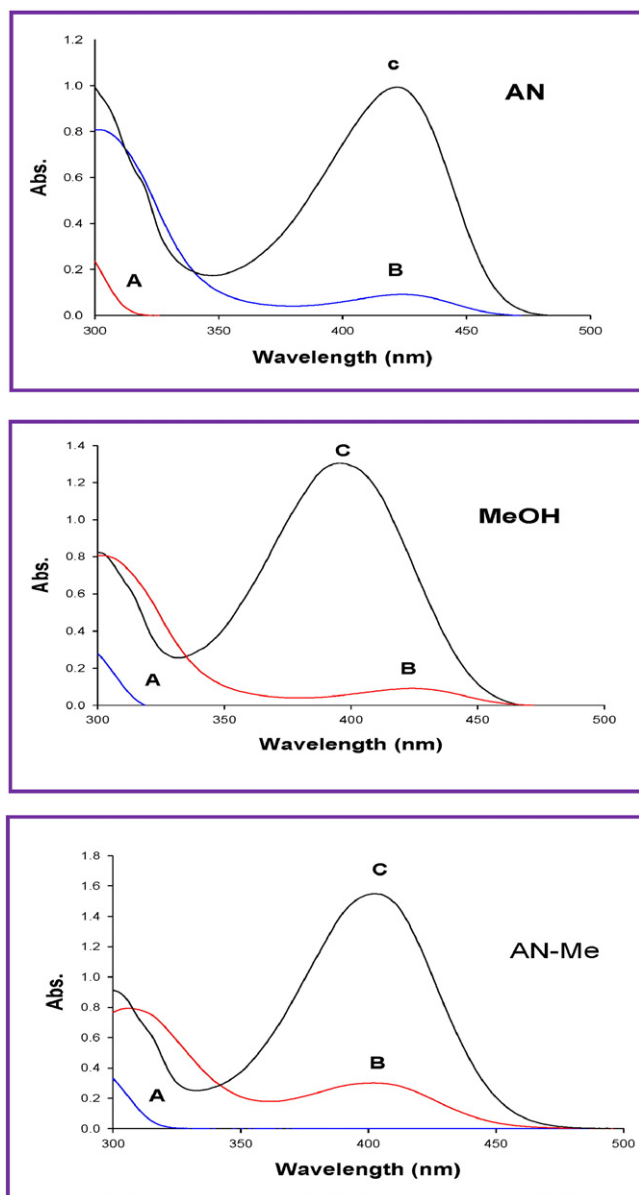


Fig. 1. Electronic spectra: (A) 1×10^{-4} M (2AMP), (B) 1×10^{-4} M (DCNP) and (C) [1×10^{-4} M (2AMP) + 1×10^{-4} M (DCNP)] in different solvents.

Fig. 2 shows the effect of 2AMP concentration on the PT complex absorption, it has been recorded that the increase in 2AMP concentration led to the increase in the intensity of absorbance of the complex suggesting that the concentration of the complex increases by increasing the acceptor concentration with the formation of a stable complex. An important finding from Fig. 2 is the constancy of the PT complex absorbance at 5×10^{-5} mol L^{-1} 2AMP in all solvents under studied. It has been recorded that the increase of 2AMP concentration more than the last value has no effect on the absorbance of the complex.

3.2. Optimization of the proton transfer reaction condition

3.2.1. Effect of reaction time

The effect of time on the PT reaction was monitored by following the absorbance of the complex resulting by mixing 1×10^{-4} mol L^{-1} from both donor and acceptor. The absorbance was followed within two hours period, Fig. 3. It has been found that the change in absorbance recorded 0.01, 0.12 and 0.07 in AN, MeOH and AN-Me, respectively. This

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