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INVESTIGATIONS ON ANION RECOGNITION OF ACETATE IONS USING 2-HYDRAZINO PYRIDINE-2 IMINOTHIAZOLIDINE- 4-CARBOXYLIC ACID

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ABSTRACT

The synthesis and anion recognition properties of the 2-hydrazino pyridine-2-iminothiazolidine-4-carboxylic acid (HPIC) has been reported. It contains one NH group of pyridyl hydrazine and other of thiazolidine structure that could function as anion binding moieties.

Key words: Anion recognition, Acetate.

INTRODUCTION

Anions are ubiquitous throughout biological systems. It is believed that they carry genetic information (like DNA, a polyanion) and participate in 70% of all enzymatic reactions[1-3]. The design and synthesis of functionalized receptors for the development of potential chemosensors has recently gained considerable attention due to their low detection limits[4-6]. The binding of anionic species to the recognition sites leads to changes in certain properties of the receptors (such as colour change) enabling them to serve as indicators for guest association. This sensing function is generally achieved by the coupling of two well-defined parts. One is the anion- binding part employing various combinations of pyrroles, guanidiniums, lewis acids, amides and urea/ thioureas[7-10]. The other is the signaling subunits. The second component makes binding- induced changes into optical signals[11] (i. e. colour changes or fluorescence quenching or enhancement). Sensing molecules showing those changes can be built by attaching chromogenic units or fluorescent signaling subunits[12], near the binding sites[13].

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EXPERIMENTAL

All anions in the form of tetrabutylammonium salts (BDH) were stored in a desiccator under vacuum containing self indicating silica and used without any further purification. Solvents were purified prior to use and stored under nitrogen. Dimethyl sulfoxide was dried with calcium hydride and distilled at reduced pressure.

For synthesizing 2-hydrazine pyridine-2-iminothiazolidine-4-carboxylic acid (HPLC), a solution of 2-oxothiazolidine-4- carboxylic acid (1.183 g) in methanol (20 mL) was added dropwise to a solution of 2- pyridyl hydrazine (1.09 g) in methanol (60 mL) with stirring and refluxed for 10h. Then the solvent was removed by evaporation. Recrystallization using DMF yielded reddish brown crystals.

The experiments were carried out at 298 ± 1 K. The ^{1}H NMR spectra were recorded on a Hitachi Perkin-Elmer using TMS as an internal standard. UV–Vis spectra were recorded on a Hilger's Uvispek H-700-8 spectrophotometer.

Absorption titration studies

The binding ability of receptor **1**(R-**1**) for $CH_3\ CO_2^-$, $H_2PO_4^-$, OH^- and halide ions (as tetrabutyl ammonium salts) was investigated by UV- vis spectroscopy in DMSO solution using a constant host concentration (2.5×10^{-5} mol dm^{-3}) and increasing concentration of anions (0-10 equiv). The change in absorbance at 505 nm for (**1**) was plotted against anion concentration and fitted by the equation as described by Connors[13].

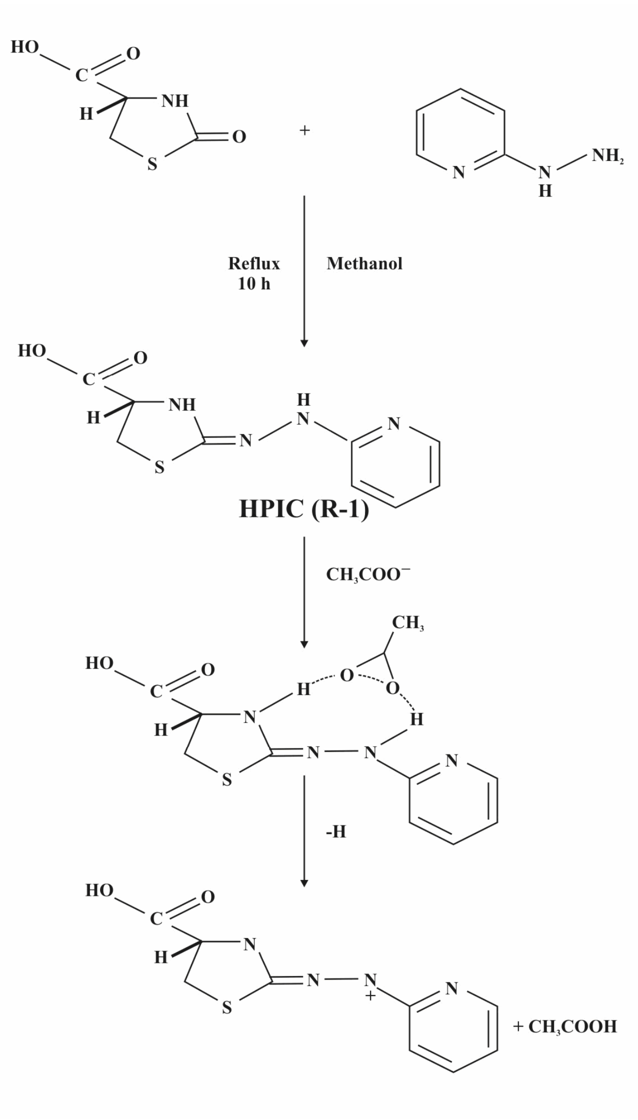
^{1}H NMR titrations

Receptor (**1**) (2.5×10^{-3} mol dm^{-3} in DMSO- d_6) was titrated against anions (tetrabutyl ammonium salts) by incremental addition of the anion solution in DMSO-d_6 such that, at the end of the titration, [receptor (**1**)] : [anions] = 1 : 2.

RESULTS AND DISCUSSION

UV – Vis titrations

The changes in the UV – Vis spectra of R-**1** upon addition of CH_3COO^- in DMSO solution show that the absorbance changes stem from anion complexation. Peaks at 310 nm and 420 nm of R-**1** decreases while one new peak at 505 nm (owing to charge transfer band, CT band) is formed.



Scheme 1

Thus, the light red colour of the receptor solution turns dark purple-red. The colorimetric properties of the receptor **(1)** can be ascribed to the anion- induced proton transfer. R-1 exhibits the best curve- fitting to the plot of change in absorbance against [CH_3COO^-]. In all cases, a 1 : 1 reaction stoichiometry is exhibited[14]. The resulting curves were analyzed by nonlinear regression methods and the obtained equilibrium constants ($LH + X^- = L^- + HX$) are given in Table 1.

Table 1.The equilibrium constants (logarithmic values) for receptor 1 in DMSO determined by UV- Vis absorbance titration measurements at 298 K

Species	CH_3COO^-	$H_2PO_4^-$	OH^-	F^-	Cl^-	Br^-	I^-
Receptor 1	5.82	4.60	5	5.02	-	-	-

Table 1 shows receptor **(1)** to exhibit best selectivity for $CH_3CO_2^-$ over other anions. It shows that receptor **(1)** recognizes anions based on their sizes. Boiocchi et al.[15] reported that the log K values ($CH_3CO_2^- > H_2PO_4^-$) should reflect the decreasing intrinsic basicity of the anions. These results reflect that higher is the negative change of anion, the higher is the tendency of forming H-bond of anion with receptor. The possible process for anion recognition is depicted in **Scheme 1**.

^{1}H NMR Studies

^{1}H NMR was used to investigate the nature of anion coordination and experiments were carried out in DMSO-d_6. Addition of tetrabutyl ammonium salt of CH_3COO^- to the solution of receptor **1** in DMSO- d_6 resulted in ^{1}H NMR spectral changes, while no spectral changes were observed upon addition of tetrabutyl ammonium salt of Cl^-, Br^- or I^-. Also the resonance ascribable to the NH proton of thiophenyl group (ppm) disappears upon successive addition of tetrabutyl ammonium salt of CH_3COO^-. It shows that the deprotonation takes place after receptor **(1)** binds to CH_3COO^-. In addition, new peak of the new species from the deprotonation of the NH group is not observed from the spectral window (+3.0 to +5.5 ppm)[16]. Upon binding CH_3COO^-, a broadened–NH resonance signal on the thiophenyl rings is noticed during the initial stages of titration. Thus, the protons of the thiophenyl rings of receptor **(1)** were resonating at 8.25 and 8.23 ppm as two separate doubles in the absence of CH_3COO^- slowly broadens and resonate at ~ 7.85 and 7.62 ppm in the presence of excess of CH_3COO^-. In fact, two effects are expected to derive from the deprotonation, viz : (i) the increase of electron density in the thiophenyl rings causes a shielding effect and should promote an upfield shift, which is expected to come from the deprotonation and (ii) the polarization of the C-H bonds, induced by through space effect[17-20].

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