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Biological active novel 2,4-dinitro phenyl hydrazones as the colorimetric sensors for selective detection of acetate ion

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ABSTRACT

Novel hydrazones such as 1-(2,4-dinitrophenyl)-2-((3-methylthiophen-2-yl)methylene)hydrazine (L_1) and 1-(6-(2-(2,4-dinitrophenyl)hydrazono)ethyl)pyridine-2-yl)ethanone (L_2) have been synthesized and explored as colorimetric sensors. Systematic studies of ionophores (L_1 and L_2) with acetate ion in DMSO revealed that they involved in H-bonding and proton transfer with acetate ion. Due to these interactions change in visible region of spectrum was observed and colour of both the ionophores changed from yellow (L_1) and orange yellow (L_2) to magenta. Further ligand–acetae ion interactions were studied with the help of ^{1}H NMR titration in DMSO and found that binding is the combined function of hydrogen bonding, electrostatic interactions and structure of binding site. Antimicrobial activities of ionophores (L_1 and L_2) were examined and tested against fungi: *Rhizoctonia solani* and *Bipolaris oryzae* using agar well diffusion method. Both ligands L_1 and L_2 were found to be exhibit antifungal activity against these strains. Antibacterial activity of L_1 and L_2 was also studied against Gram positive bacteria: *Staphylococcus aureus*, *Bacillus brevis* and Gram negative bacteria: *Escherichia coli*, *Pycnoclavella diminuta* using disc diffusion method and it was cleared that ligands were not inhibiting the growth of these strains even at higher concentration of both the ligands.

1. Introduction

Anions are ubiquitous throughout biological systems and play a significant role in the various areas such as medicinal [1], biological [2], catalysis [3] and environmental processes [4]. Selective recognition of a particular anion is an important challenge in the field of host–guest chemistry. Among several anions, acetate ion takes large attention because it is a vital component of various metabolic processes [5] and plays specific biochemical behaviours in the antibodies and enzymes. It has been widely used in the manufacturing of dyes, plastics, paper and paints and in nylon industry. The production and sedimentation rate of acetate ion has been often used as an indicator of organic decomposition in marine sediments.

Although we have many colorimetric sensors for the determination of acetate ion [6,7] but selective sensors are very limited. Most of the sensors are suffering with interfering anions like F^- ion, which has nearly equal basicity to acetate [8–10]. Thus there is a need to synthesize novel sensing units showing the potential to differentiate acetate from other anions mainly F^-. In molecular recognition, the selective sensing of acetate is reported by cooperative functions of hydrogen-bonding, electrostatic interactions and induced-fit mechanism [8]. From the literature survey, it has been found that the compounds containing the moieties such as urea [11], thiourea [12], amide [13], imidazole [14] and pyrrole [15] are able to form hydrogen bonds (N–H···A) with various anions. In recent years different types of ion sensors like potentiometric [16–20], voltammetry [21–27], fluorescence sensors have been synthesized but the growth in the field of colorimetric anion sensing becomes a point of attraction because it does not need costly apparatus and instrumentation as colour changes can be easily observed by the naked-eye. In colorimetric sensors the host compound contain a particular site known as chromophoric site, this mechanism of anion sensing will assist to accomplish

Abbreviations: DMSO, dimethyl sulfoxide; MTCC, microbial type culture collection and gene bank; L1, 1-(2,4-dinitrophenyl)-2-((3-methylthiophen-2-yl)methylene)hydrazine; L2, 1-(6-(2-(2,4-dinitrophenyl) hydrazono)ethyl)pyridine-2-yl)ethanone; *S. aureus*, *Staphylococcus aureus*; *B. brevis*, *Brevibacillus brevis*; *E. coli*, *Escherichia coli*; *P. diminuta*, *Pseudomonas diminuta*; *R. solani*, *Rhizoctonia solani*; *B. oryzae*, *Bipolaris oryzae*; PDAp, otato dextrose agar medium.

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the so-called 'naked-eyes' detection with no use of spectroscopic instrument. So, the attachment of functional group with an appropriate chromophoric site via intramolecularly or covalently as a sensor can cause to the colour changes, fluorescing or both.

Hydrazone derivatives are found to be important class of compounds in organic chemistry, draw considerable attention, due to their extensive applications in pharmaceutical and biological activities like anticancer [28], anti-inflammatory, antibacterial, antifungal [32] and anti HIV [29], antimalarial [30], antitubercular [31], activities and potential inhibitor for various enzymes [33]. Hydrazone derivatives work as multidentate ligands and also used as ink, pigments, and fluorescent materials. Phenylhydrazine containing chromophoric group like nitro and having hydrogen donor capability has been reported as good anion receptor [9,10]. In this connection, we have synthesized two novel 2,4-dinitrophenylhydrazone based ligands L_1 and L_2, which show an effective colorimetric sensing for acetate ion in dry DMSO. These anion sensors possess the suitable binding sites to adapt the anionic guest through hydrogen bonding and electrostatic interactions. Both the ligands L_1 and L_2 possess phenylhydrazone group that plays an important role for biological activity (here C=N linkage is essential for antimicrobial activity) [34]. Antimicrobial potentials of both ligands were evaluated according to their zone of inhibition against various fungal and bacterial strains and then compared with reference.

2. Experimental

2.1. Apparatus

IR spectra were taken with Perkin Elmer FT-IR 1000 spectrophotometer as films between KBr. The UV–vis titration experiments were performed on Specord S600 PC single beam spectrophotometer with quartz cuvette having path length 1 cm. ^{1}H NMR spectra along with titration experiments were carried out on a Bruker DRX 500 MHz spectrophotometer by using tetramethylsilane (TMS) as an internal standard.

2.2. Reagents

All reagents used for the synthesis work viz. 2,4-dinitrophenylhydrazine, 3-methyl-2-thiophenecarboxaldehyde and 2,6-diacetylpyridin were purchased from Sigma–Aldrich chemical. These reagents were stored under vacuum condition and were used without further purification. All the anions were taken in the form of tetra-*n*-butyl ammonium salts purchased from Merck. DMSO (dimethyl sulphoxide) used for the preparation of stalk solutions of different concentrations were dried by the help of drying agent and distilled under reduced pressure.

For biological activities pure cultures of experimental fungi and bacteria were obtained from microbial type culture collection and gene bank (MTCC) Chandigarh. Potato dextrose agar medium (PDA) and nutrient agar medium were purchased from Hi Media.

2.3. Synthesis

The 2,4-dinitrophenylhydrazine based hydrazones 1-(2,4-dinitrophenyl)-2-((3-methylthiophen-2-yl)methylene)hydrazine (L_1) and 1-(6-(2-(2,4-dinitrophenyl)hydrazono)-ethyl)pyridine-2-yl)ethanone (L_2) were synthesized as follows (Scheme 1).

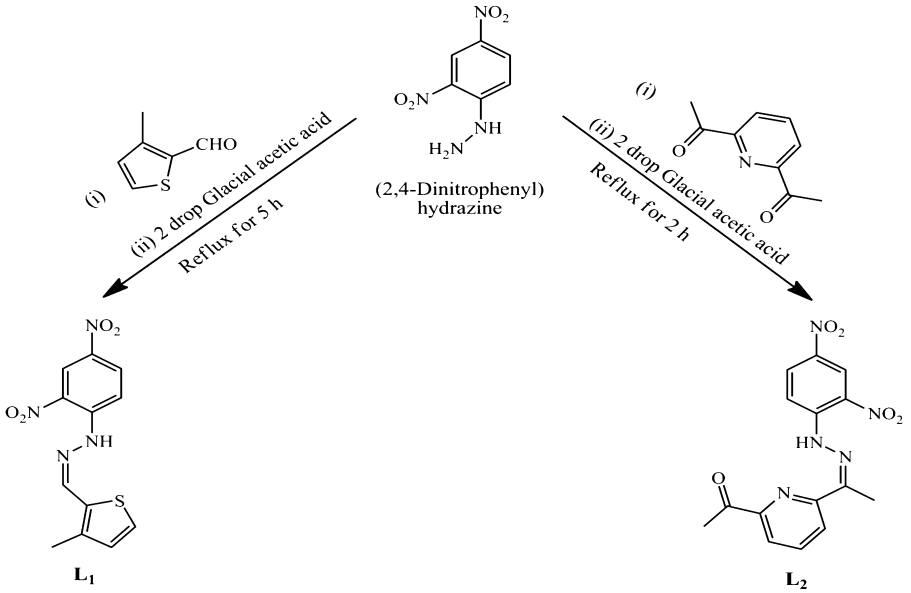
2.3.1. Synthesis of 1-(2,4-dinitrophenyl)-2-((3-methylthiophen-2-yl)methylene)hydrazine (L_1)

To a 15 mL of ethanolic solution of 2,4-dinitrophenylhydrazine (0.19 g, 1 mmol), 15 mL of ethanolic solution of 3-methyl-2-thiophene-carboxaldehyde (0.13 g, 1 mmol) was added and stirred for 30 min. To this solution two drops of glacial acetic acid was added and refluxed for 5 h. A red coloured precipitate was obtained which was then filtered and washed with hot ethanol.

Yield: 90%. IR (KBr, cm^{-1}): 1615 cm^{-1} (C=N). UV–vis: 265 nm (aromatic system), 416 nm (azomethine group). ^{1}H NMR (δ, DMSO-d_6): 11.698 (s 1H), 9.06 (s 1H), 8.86 (d 1H), 8.41 (d 1H), 7.90 (d 1H), 7.90 (d 1H), 7.65 (d 1H), 7.01 (d 1H), 2.37 (s 3H).

2.3.2. Synthesis of 1-(6-(2-(2,4-dinitrophenyl)hydrazono)ethyl)pyridine-2-yl)ethanone (L_2)

0.17 g (1 mmol) of 2,6-diacetyl pyridine was dissolved in 20 mL of ethanol, to this 15 mL of ethanolic solution of 2,4-dinitrophenylhydrazine (0.19 g, 1 mmol) was added. To the reaction mixture two drops of glacial acetic acid was added and



Scheme 1. Synthetic route to hydrazine based ionophores, 1(2,4-dinitrophenyl)-2-((3-methylthiophen-2-yl)methylene)hydrazine (L_1) and 1-(6-(2-(2,4-dinitrophenyl)hydrazono)ethyl)pyridine-2-yl)ethanone (L_2).