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Structure investigation of three hydrazones Schiff's bases by spectroscopic, thermal and molecular orbital calculations and their biological activities

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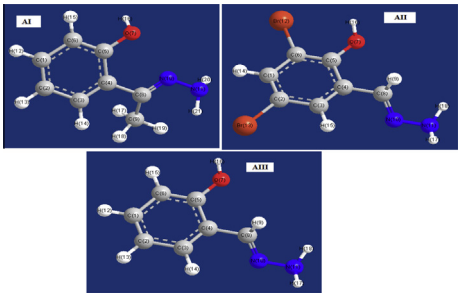
HIGHLIGHTS

- Three important hydrazone Schiff bases (AI–AIII) were prepared and characterized.
- Active groups and bonds responsible for their biological activities were checked.
- They of important capacity to bind and transport metal ions from environmental media.
- Thermal and mass practical results are confirmed by semi-empirical MO-calculations.
- Their biological activities were tested to assess their anti-microbial potential.

GRAPHICAL ABSTRACT

Important biologically active Schiff's bases AI–AIII were prepared and characterized based on elemental analysis, mass, FT-IR, ^{1}H NMR spectra and thermal analyses in comparison with molecular orbital calculations.



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ABSTRACT

Three Schiff's bases AI (2(1-hydrazonoethyl)phenol), AII (2, 4-dibromo 6-(hydrazonomethyl)phenol) and AIII (2(hydrazonomethyl)phenol) were prepared as new hydrazone compounds via condensation reactions with molar ratio (1:1) of reactants. Firstly by reaction of 2-hydroxy acetophenone solution and hydrazine hydrate; it gives AI. Secondly condensation between 3,5-dibromo-salicylaldehyde and hydrazine hydrate gives AII. Thirdly condensation between salicylaldehyde and hydrazine hydrate gives AIII. The structures of AI–AIII were characterized by elemental analysis (EA), mass (MS), FT-IR and ^{1}H NMR spectra, and thermal analyses (TG, DTG, and DTA). The activation thermodynamic parameters, such as, ΔE^*, ΔH^*, ΔS^* and ΔG^* were calculated from the TG curves using Coats–Redfern method. It is important to investigate their molecular structures to know the active groups and weak bond responsible for their biological activities. Consequently in the present work, the obtained thermal (TA) and mass (MS) practical results are confirmed by semi-empirical MO-calculations (MOCS) using PM3 procedure. Their biological activities have been tested in vitro against *Escherichia coli*, *Proteus vulgaris*, *Bacillissubtilies* and *Staphylococcus aurous* bacteria in order to assess their anti-microbial potential.

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Introduction

Hydrazones, RR′C═N—NR″R″, were used as intermediates in synthesis [1], as functional groups in metal carbonyls [2], in organic compounds [3,4] and in particular in hydrazones Schiff base ligands [5–8], which are among others employed in binuclear catalysts [9]. Furthermore, hydrazones exhibit physiological activities in the treatment of several diseases such as tuberculosis. This activity is attributed to the formation of stable chelate complexes with transition metals which catalyze physiological processes [10–12]. They also act as herbicides, insecticides, nematocides, rodenticides, plant growth regulators, sterilants for houseflies, among other applications [10,11,13]. In analytical chemistry; hydrazones find applications as multidentate ligands for transition metals in colorimetric or fluorimetric determinations [14,15].

Schiff's bases are important class of compounds, due to their variety of applications including biological, clinical, analytical and industrial in addition to their important roles in catalysis and organic synthesis [16–20]. Schiff bases [21] were still regarded as one of the most potential group of organic compounds for facile preparations of metallo-organic hybrid materials. In the past two decades, the properties of Schiff base stimulated much interest for their noteworthy contributions to single molecule-based magnetism, material science [22], catalysis of many reactions like carbonization, oxidation, reduction [23], their industrial applications [24], complexing ability towards some toxic metals [25]. The interest in Schiff base compounds as analytical reagents is increasing since they enable simple and inexpensive determinations of different organic and inorganic substances [26]. The importance of the present work stems from preparation of three novel hydrazones Schiff bases (AI–AIII), its characterization and its hopeful applications in different industrial and life sides applications.

Experimental

Materials and reagents

All chemicals used in this study were of the analytical reagent grade and of highest purity available. The spectroscopic pure organic solvents used were purchased from British Drug House (BDH). They included absolute ethyl alcohol, dimethylformamide (DMF), duterated chloroform and dimethylsulphoxide (DMSO). De-ionized water collected from all glass equipments were used in all studies in aqueous solutions. The other materials included 2-hydroxy acetophenone, hydrazine hydrate (Sigma), Salicylaldehyde and 3,5-dibromo-salicylaldehyde were purchased from (Aldrich).

Instruments

Elemental microanalyses (EA) of the prepared hydrazone Schiff's bases for C, H, and N were performed in the microanalytical center at Cairo University. The analyses were repeated twice to check the accuracy of the data. Infrared spectra were measured using a Perkin–Elmer FT-IR type 1650 spectrophotometer in the wave number region 4000–400 cm^{-1} as KBr disks. The ^1H NMR spectra were recorded using a varian-300 MHz in DMSO-*d6* as solvent; whereas the chemical shifts were determined relative to the solvent peaks. The thermal analyses (TG and DTG and DTA) were carried out in dynamic nitrogen atmosphere (20 mL min^{-1}) with a heating rate of 10 °C min^{-1} using Shimadzu combined TG and DTA-60H thermal analyzer. The mass spectrum (MS) was recorded by the electron impact (EI) technique at 70 eV using MS-5988 GS–MS Hewlett–Packard instrument.

Procedures for the synthesis of hydrazones Schiff's bases

Preparation of AI

AI was prepared by slow dropwise of 6.0 ml (0.05 mol) from 2-hydroxy acetophenone solution during 3 h to stirring 15 ml of hydrazine hydrate (0.3 mol) at room temperature. Pale yellow crystal began precipitate after half an hour from the beginning of the addition of 2-hydroxy acetophenone solution to hydrazine solution. The formed compound was filtered off and washed with water to remove the excess of hydrazine hydrate. The material was recrystallized from ethyl alcohol and then dried in a vacuum desiccator over anhydrous calcium chloride.

Preparation of AII

AII was prepared by dissolving 2.8 g (0.01 mol) from 3,5-dibromo-salicylaldehyde in 10 ml ethyl alcohol and slow dropwise this solution during 1 h to stirring 10 ml of hydrazine at room temperature. Yellowish-white crystal precipitated with the addition of 3,5-dibromo-salicylaldehyde solution to hydrazine hydrate solution. The formed white crystals were filtered off and washed with water to remove excess hydrazine hydrate. The material was recrystallized from ethyl alcohol and then dried in a vacuum desiccator over anhydrous calcium chloride.

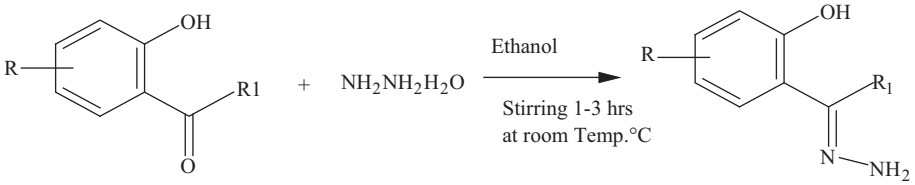
Preparation of AIII

AIII was prepared by slow dropwise ethanol solution 5.2 ml (0.05 mol) of salicylaldehyde solution during 1 h to stirring 15 ml of hydrazine hydrate (0.3 mol) at room temperature. White crystals precipitate with the addition of salicylaldehyde solution to hydrazine hydrate solution. The formed white crystals were filtered off and washed with water. The material was recrystallized from ethyl alcohol and then dried in a vacuum desiccator over anhydrous calcium chloride.

The preparation of these Schiff's bases is given by Scheme 1:

Biological activity of Schiff's bases studies

The test was done using the diffusion agar technique. Spore suspension (0.5 mL, 10^{-6}–10^{-7} sporem L^{-1}) of each of the investigated organism (Two Gram-positive *Bacillus subtilis* ATTC 6051 and *Staphylococcus pyogones* ATTC 12600) and two Gram-negative



R = H (AI, AIII), 2,4-dibromo (AII),
R1 = H (AII,AIII), CH_3 (AI)

Scheme 1. Preparation of Schiff's bases.