



Synthesis, characterization and electrochemical studies of azo dyes derived from barbituric acid



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ABSTRACT

We have made an effort to synthesize three heterocyclic azo dyes 1(a-c) by means of diazotization of 6-methoxy-1,3-benzothiazol-2-amine, 4-(4-nitrophenyl)-1,3-thiazol-2-amine and 6-methyl-1,3-benzothiazol-2-amine by coupling with barbituric acid with high yield in basic media (pH = 9–10). Structural confirmation of the synthesized azo dyes has been accomplished by Ultra Violet-Visible, Fourier Transform Infrared, Proton Nuclear Magnetic Resonance and Mass spectrometric techniques. The electrochemical properties of above azo dyes are investigated by cyclic voltammetric technique. The effects of scan rate and concentration of sulphuric acid was studied at glassy carbon electrode. The overall electrode process is diffusion controlled. The electrode reaction mechanism was proposed.

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1. Introduction

In recent decades, organic color chemistry has undergone rapid and very exciting developments as a result of the opportunities presented by dye applications in various high technology fields. The design and synthesis of various organic chromophores as non-linear optical (NLO) materials have attracted a great deal of attention in recent years [1]. Azo dyes of organic NLO materials have many advantages over inorganic materials including large non-linear optical co-efficient, greater ease of synthetic design, easy preparation & lower cost. Azo dyes are of particular interest because they can be readily prepared with a wide range of donor & acceptor group in it. They are promising candidates for photoconductivity [2,3].

Development of azo dyes based on heterocyclic compounds of pharmacological and industrial importance is an important task for heterocyclic chemists. Nitrogen and sulphur containing five membered heterocyclic compounds are the platform to produce a substance of interest in numerous therapeutic areas. Their biological importance is well known for their use as antidiabetics [4], antiseptics [5], and other useful chemotherapeutic agents [6–8]. It

has been found that the activity of azo linkage increases on the incorporation of suitable heterocyclic moiety, amino benzothiazoles are a class of heterocycles and they are of significant interest in medicine and pesticide chemistry in a number of biological targets including anti-inflammatory agents, antibacterial, tuberculostatic and antimicrobial activity.

Recently, the reduction of azo dyes has considerable interest area because, in order to obtain a deeper insight into the ground state properties and more specially the mutual donor-acceptor electronic influence having applications in catalysis [9–11], material science [12], sensing, chromophoric and metallochromic reagents [13], photochromic materials [14], colorants and photosensitizers [15] have attracted the interest of many electrochemists. Therefore the electrochemical investigations of various heterocyclic azo dyes were reported. Because S–N containing ring compounds possess very fascinating properties and the most promising of all these is their ability to be redox-active; and show good conducting and magnetic properties. In this regard, the electrochemical behavior and electrode reaction pathways of numerous azo-dyes in various supporting electrolytes were studied and discussed [16–22]. Chemical reduction of azo compounds leads to saturate the azo group giving a hydrazo derivative and then breaks the –N=N– linkage to form two primary amine molecules. Therefore, in most of the studies, electrochemical reduction was utilized for the study of the azo dyes because electrochemistry

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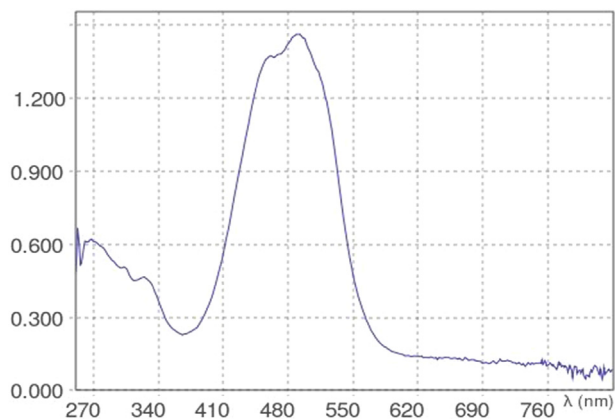


Fig. 1. UV–Visible spectrum of compound 1a in DMSO.

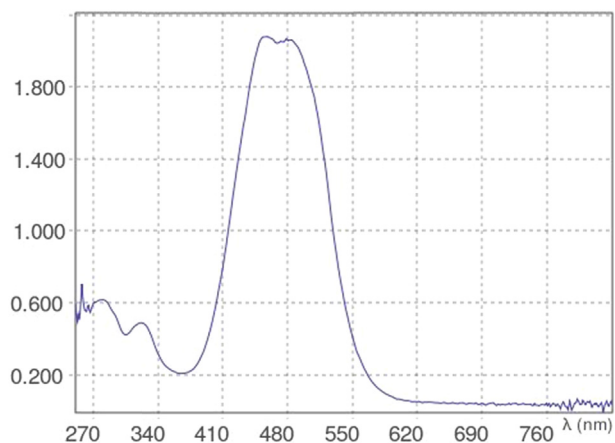


Fig. 2. UV–Visible spectrum of compound 1a in DMF.

provides convenient methods for studying their mechanism and kinetics. The introduction of substituent groups into the aromatic ring can completely change the nature of the electrode reaction because of their different sizes and orientations [23–27].

In this work, a systematic study was undertaken to investigate the electro reduction of three heterocyclic azo dyes derived from barbituric acid at different concentrations of sulphuric acid media and the effect of scan rate was also studied at glassy carbon electrode by using cyclic voltammetric technique. The results showed

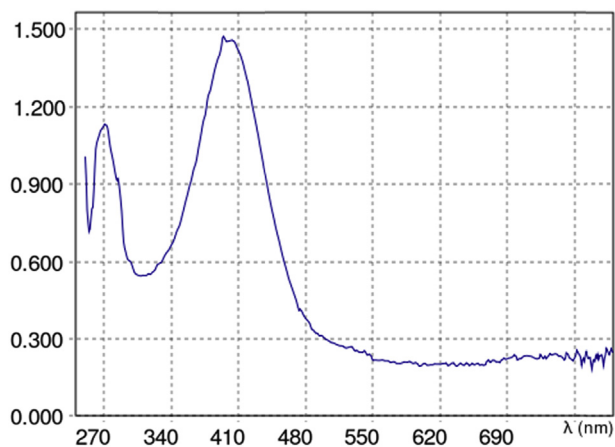


Fig. 3. UV–Visible spectrum of compound 1b in DMSO.

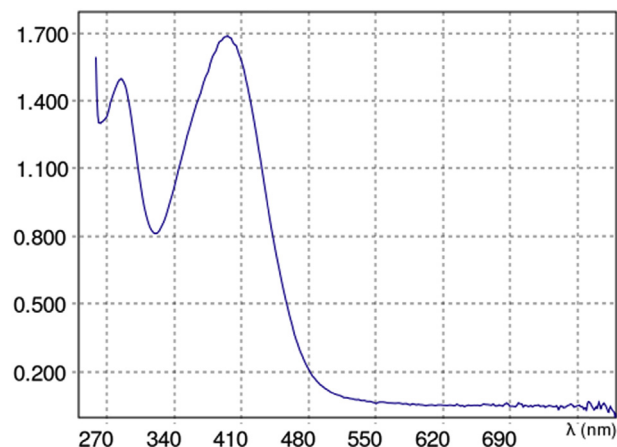


Fig. 4. UV–Visible spectrum of compound 1b in DMF.

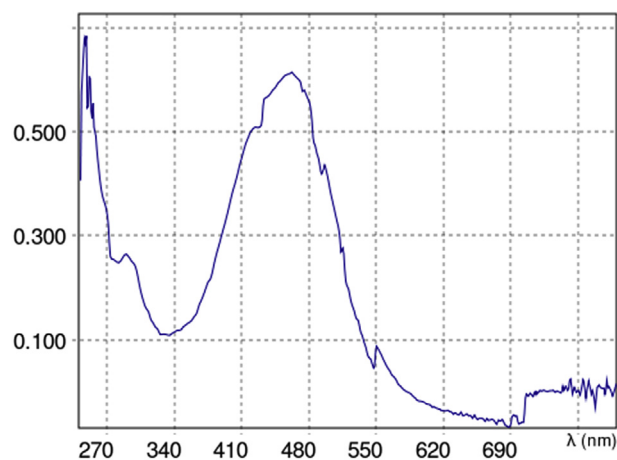


Fig. 5. UV–Visible spectrum of compound 1c in DMSO.

that reduction of azo dye occurs through two irreversible reduction peaks and the reduction mechanism was proposed and discussed.

2. Method and materials

2.1. General

All the chemicals, reagents and solvents used for the synthesis are purchased from Sigma Aldrich, SD-fine, Hi-Media Company of

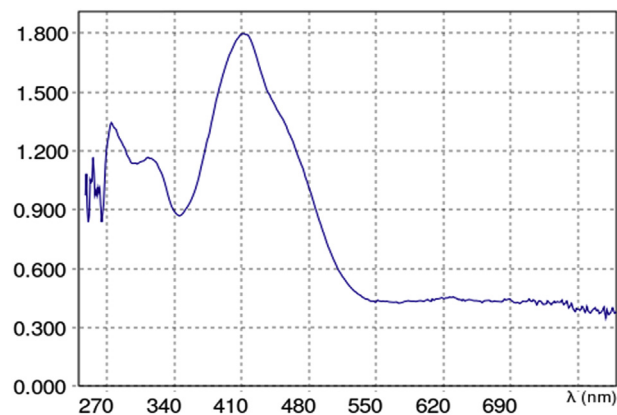


Fig. 6. UV–Visible spectrum of compound 1c in DMF.

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