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ORIGINAL ARTICLE

Synthesis and antitumor evaluation of thiophene based azo dyes incorporating pyrazolone moiety

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Abstract A series of thiophene incorporating pyrazolone moieties **5a–f** and **6a–c** were synthesized *via* diazo coupling of diazonium salt of 3-substituted-2-amino-4,5,6,7-tetrahydrobenzo[*b*]thiophenes **1a–c** with 3-methyl-1*H*-pyrazol-5(4*H*)-one, 3-methyl-1-phenyl-1*H*-pyrazol-5(4*H*)-one or 3-amino-1*H*-pyrazol-5(4*H*)-one, respectively. Newly synthesized dyes were applied to polyester fabric as disperse dyes in which their color measurements and fastness properties were evaluated. These dyes showed generally red to blue shifted color with high extinction coefficient in comparison with aniline-based azo dyes. The antitumor activity of the synthesized dyes was evaluated. The results showed clearly that most of them exhibited good activity and compounds **5c** and **5d** exhibited moderate activity.

1. Introduction

It has been known for many years that the azo compounds are the most widely used class of dyes due to their versatile application in various fields such as the dyeing of textile fibers, the coloring of different materials, in biological–medical studies and advanced applications in organic synthesis (Waring & Halas, 1990; Zollinger, 2003; Bhatti and Seshadri, 2004; Tanaka et al., 1984; Towns, 1999; Dickey et al., 1959). In recent years, the use of heterocyclic intermediates in the synthesis of azo disperse dyes is well established, and the resultant dyes exhibit good tinctorial strength and brighter dyeing than those aniline-based components (Penchev et al., 1991; Peters and Gbadamosi, 1992; Kraska and Sokoowska-Gajda, 1987; Sokolowska-Gajda, 1991, 1992). Furthermore, 2-aminothiophene and its benzo analogs are very useful compounds as intermediates in the dyestuff industry and find a wide range of pharmaceutical applications (Lutjens et al., 2003; Nikolakopoulos et al., 2006; Pillai et al., 2005). Thiophene based azo dyes showed generally red to blue color with a high extinction coefficient in comparison with aniline-based azo dyes. On the other hand, pyrazole nucleus has pronounced pharmacological applications as anti-anxiety, antipyretic (Yamaguchi and Ishikawa, 1981), analgesic and anti-inflammatory drugs (Georgiadou and Tsatsaroni, 2002; Yen and Wang, 2004). To our knowledge 2-aminothiophene derivatives incorporated pyrazole moiety are little known in the literature (Abu-Hashem et al., 2010; El Bialy and Gouda, 2011; Gouda et al., 2010).

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Therefore, our aim in this work is to synthesize some new pyrazole derivatives incorporating thiophene moiety, starting from 2-amino-4,5,6,7-tetrahydrobenzo[*b*]thiophene derivatives in order to evaluate their dyeing behavior as dyestuff on polyester fabric and their biological activity as antitumor agents.

2. Results and discussion

2.1. Chemistry

The synthetic routes adopted to obtain the target compounds are described in Scheme 1. 3-Substituted-2-amino-4,5,6,7-tetrahydrobenzo[*b*]thiophene derivatives **1a–c** were prepared *via* multicomponent condensation of cylohexanone with ethyl cyanoacetate, malononitrile or cyanoacetamide and elemental sulfur containing morpholine as a catalyst following a procedure described by Gewald (1965).

Treatment of **1a–c** in HCl with sodium nitrite solution afforded the corresponding diazonium salts which coupled with pyrazoles **3a** or **3b** or **4** in pyridine or ethanol containing sodium acetate to afford the corresponding hydrazones **5a–f** and **6a–c**, respectively. Assignment of the newly synthesized compounds was based on elemental analyses and spectral data (IR, ^{1}H NMR and mass spectra) (*cf.* Section 4).

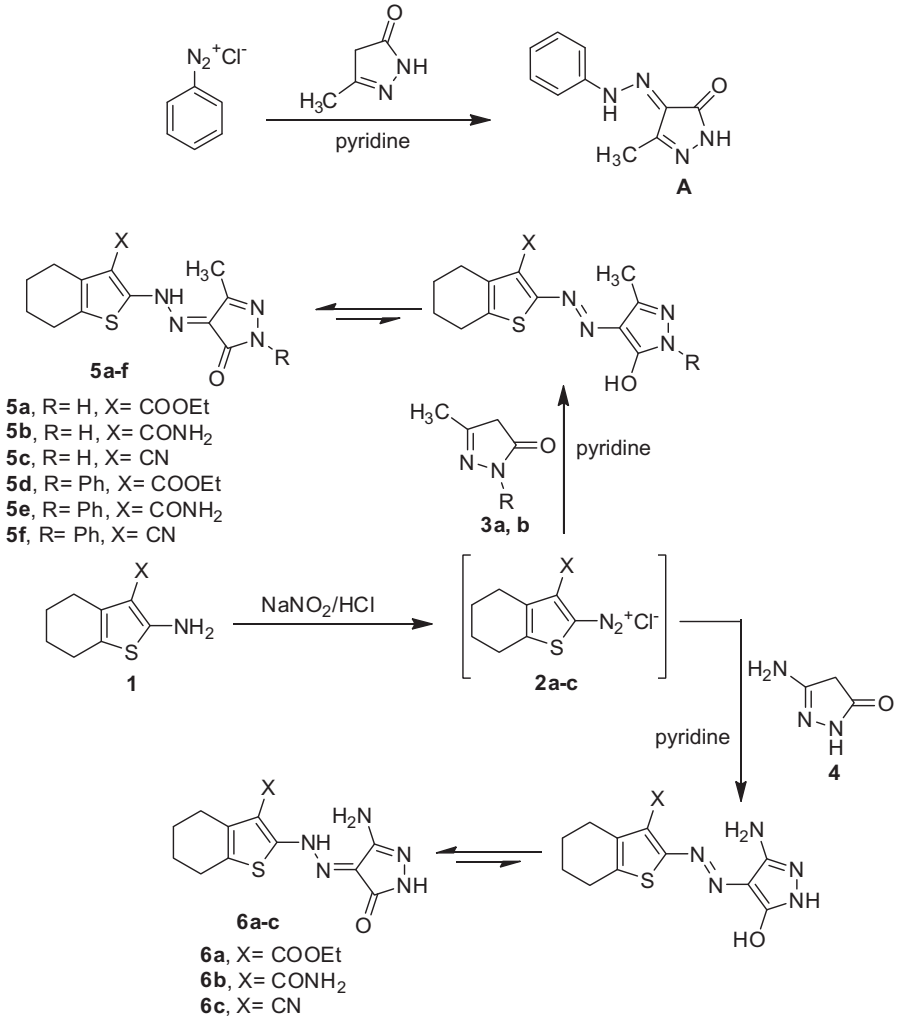
2.2. Dyeing of polyester fabrics and dyeing properties

2.2.1. Color measurement

The effect of the nature of different substituents on dyeing behavior, color hue and depth was discussed. This investigation depends on some spectral data of the dyed materials. The most commonly used function f(R) is the one developed theoretically by *Kubelka* and *Munk*. In their theory, the optical properties of a sample are described by two values "K" is the measure of the light absorption and "S" is the measure of the light scattering. On textiles, "K" is determined primarily by the dyestuffs and "S" only by the substrate. From the wave-length *Kubelka* and *Munk* calculate the following relationship for reflectance R of thick, opaque samples with the constant of "K" and "S":

$$K/S = (1 - R)^2/2R \quad (1)$$

In this equation R is used as a ratio, *e.g.* 32% reflectance as 0.32. The K/S value at λ_{max} was taken as a measure of color depth.



Scheme 1 Synthesis of substituted-4-{2-[(or 3-phenyl-)4,5,6,7-tetrahydrobenzo[*b*]thiophen-2-yl]hydrazono}-1*H*-pyrazol-5(4*H*)-one derivatives **5** and **6**.