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Synthesis and Characterization of Arylazopyrazolopyrimidines Dyes and Studying their Antibacterial Activity

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Abstract

The purpose of this research is to synthesize several new pyrazolopyrimidine containing an arylazo function containing electron with drawing groups and benzothiazole moiety, the substituted 5-arylazopyrazolopyrimidine were prepared by reaction of aryl azopyrazole with airelidene of 2- cyanomethyl benzothiazole under basic condition in boiling ethanol. The structure of arylazopyrazolopyrimidine dyes were established by their element analysis and spectral data (MS, IR and ^{1}H-NMR). The antibacterial properties of these dyes have been investigated.

Keywords: pyrazolopyrimidine – benzothiazole – antibacterial activity

1. Introduction

Innovations in azo dye based on heterocyclic systems have been made as a result of intensive studies stimulated by the mounting need for bright dyes. Generally many of heterocyclic azodyes show dramatic bathochromic shifts combined with brilliance of shade and high tinctorial strength compared with conventional anthraquinone dyes and aminobenzene azodyes[1-4]. In spite of the large number of arylazopyrazol dyes reported in literature, only very few condensed pyrazole derivatives carrying arylazo functions on the pyrazole ring have been reported. In continuation of the increasing interest in synthesis of condensed arylazopyrazole new dyestuffs [3], the present work deals with novel synthesis of condensed arylazopyrazolopyrimidines derivatives and studying their printing properties using silk screen and heat transfer printing techniques on polyester and polyamide fabrics. The antibacterial activity of these dyes was also studied, where recently in the textile industrial sector [5], there has been increasing interest in the manufacture of clothing and products with antibacterial properties. Clothing of textile can act as carrier for microorganisms such as pathogenic or odor –generating bacteria and moulds [6]. The textile material is known to be susceptible to microbial attack, in contact with the human body it offers an ideal environment for microbial growth providing oxygen, water and warmth, and nutrients from spillages and body exudates [7]. This often leads to objectionable odor, dermal infection product deterioration, allergic responses and other related diseases which necessitate the development of clothing products with antimicrobial properties [8].

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2. Experlmental

2.1. Synthesis of dyes

Preparation of 3,5 diamino-4-arylzopyrzole (1)

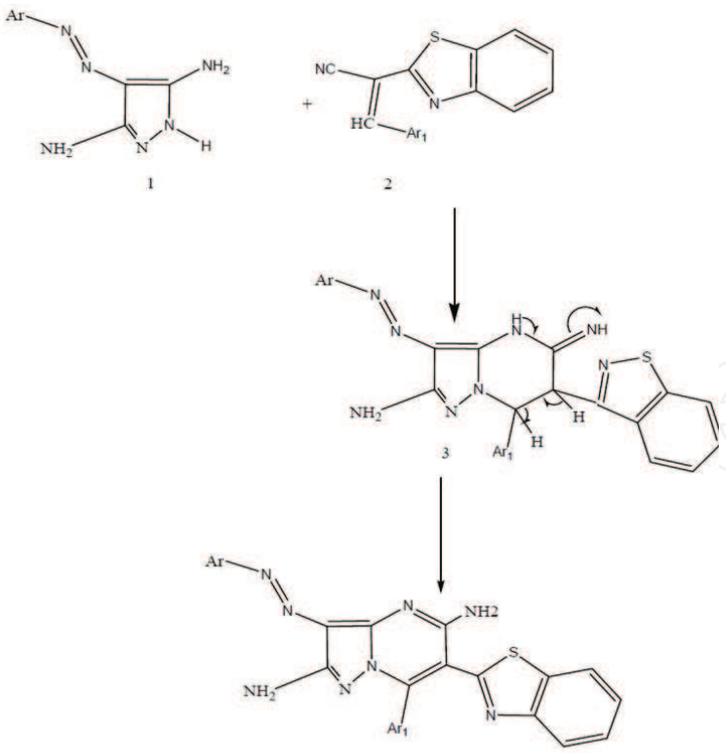
(0.01 mole) of diazotized aniline derivatives coupled with (0.01 mole) of malono nitrite in the presence of (20 ml) ethanol and (5 gm) sodium acetate at 0-5°C. The precipitated solid is filtrated and dried (0.01) mole of the dried solid is dissolved in (20 ml) ethanol then (0.01 mole) of hydrazine hydrate is added drop wise, the precipitated solid of arylazopyrazole derivatives is filtrated and re-crystallized from ethanol.

Preparation of Cyanomethylarylidine benzothiazol-2-yl

Cyanomethylarylidinebenzothiazol-2-yl is prepared by the condensation reaction of (0.01 mole) of cyanomethyl benzothiol-2yl with (0.01) mole of aromatic aldehyde derivatives in (20 ml) ethanol and drops of piperidine at room temperature. The collected precipitate is filtrated and recrystallized in ethanol

General Procedure of synthesis of arylazo-pyrazolopyrimidines dyes:

To a solution of derivatives (1) (10 mmol) in ethanol (50 mL), the (2) (10 mmol) and drops of pipridine were added. The reaction mixture was refluxed for 4 h then left to cool. The formed product was filtered off, washed with ethanol, and recrystallized from ethanol to afford the corresponding arylzaopyrazolopyrimidines 4a-e. *(Scheme I)*



Scheme 1.

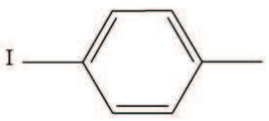
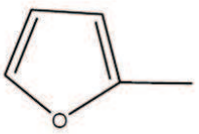
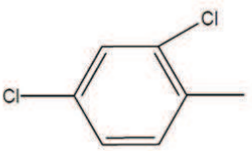
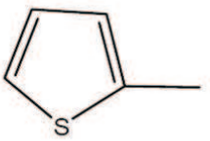
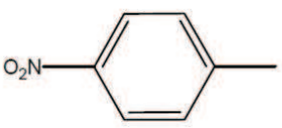
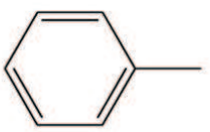
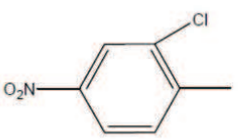
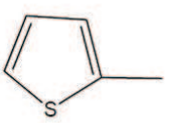
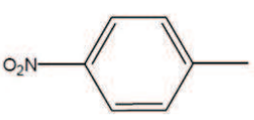
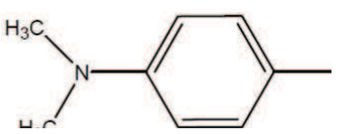
Dye number.	Ar	Ar_1
4a		
4b		
4c		
4e		
4d		

Table 1. Represents Ar and Ar1 groups

2.2. Measurements

Melting point

Melting points were measured by Electrothermal IA 9000 series digital melting point apparatus. Element analysis:

Elemental analytical data were obtained from the micro-analytical unit, National Research Center, Dokki, Giza, Cairo, Egypt.

Fourier-Transition Infrared Spectroscopy (FTIR):

Fourier- transition infrared spectroscopy (FTIR) was performed using a Pye-Unicam spectra-1000 machine to determine the functional groups on the surface of the linen samples. Potassium bromide (KBr) disc was used.

^1H – NMR spectra:

The NMR spectra were recorded on a Varian Mercury VX-300 NMR spectrometer. ^1H spectra were run at 300 MHz in deuterated dimethylsulphoxide(DMSO-d_6).

3.5 Mass spectra:

Mass spectra were measured on a Varian MAT CH-5 spectrometer (70 eV). 3.6 Spectrophotometric measurements:

The absorbance of the dyes were measured in the ultraviolet -visible region at wave length between 300-700 nm. by a UNICAM UV spectrophotometer using a 1cm. quartz cell . The dyes were dissolved in absolute ethanol at a concentration of 10^{-4} mole/l.

2.3. Antibacterial activity measurements

The newly synthesized pyrazolopyrimidines were assessed for their *in vitro* antibacterial activity in the Micro Analytical Centre of Cairo University using Kirby-bauer disc diffusion method [9].

3. Results and discussion

The formation of 2,5-di-amino-3-arylazopyrazolopyrimidine ring system (4a-e) from compounds 1 and 2 under basic condition is assumed to proceed via addition of the most basic N atom in compound 1 to the unsaturated double bond in compound 2 to give the intermediate 3 this Michel adducts is followed by neuclophilic addition of NH_2 group to CN group. The reaction was established and confirmed by studying their element analysis, and (IR –^{1}H-NMR – Mass) spectra. The following results were obtained

2,5-di-amino-3-(4-iodo)-arylazo-6-benzothiazol-2-yl-7-fur-2-yl-pyrazolopyrimidines (4a)

brown crystals, m.p. ≥300° C; yield: (85%)., IR (KBr), 3377-3328 (NH_2), cm^{-1}. , ^{1}H NMR (300 MHz, DMSO-d_6): δ 6.6-7.7. (m, 4H, Ar-H), 8.3 (s, D_2O exchangeable, 2H, NH_2).,MS (70 eV): *m/z* = 577 (M^+, 576)., Element analysis for $C_{23}H_{15}N_8SI$ molecular weight (576), Calc.: C, 47.83 ; H, 2.59; N,27.72 ; O, 10.77 ; S, 5.54. ; I, 22.01, Found: C, 47.73 ; H, 2.49 ; N, 27.62 ; O, 10.67 ; S, 5.44 ; I, 22.0 2,5-di-amino-3-(2,4-dichloro)-arylazo-6-benzothiazol-2-yl-7-thiophen-2-yl–pyrazolopyrimidine (4b)

Red crystals, m.p. ≥300°C; yield: (90%), IR (KBr), 3377-3328 (NH_2), cm^{-1}, ^{1}H NMR (300 MHz, DMSO-d_6): δ 6.6-7.7. (m, 4H, Ar-H), 8.6 (s, D_2O exchangeable, 2H, NH_2), MS (70 eV): *m/z* = 537 (M^+, 535),Element analysis for $C_{23}H_{14}N_8S_2Cl_2$ molecular weight (537), Calc.: C, 51.39 ; H, 2.60 ; N, 20.83 ; S, 11.91; Cl, 13.22., Found: C, 51.29 ; H, 2.50 ; N, 20.73 ; S, 11.81; Cl, 13.21 2,5-di-amino-3-(4-nitro)-arylazo-6-(benzothiazol-2-yl)-7-phenylpyrazolopyrimidine (4c)

yellow crystals, m.p. ≥300°C; yield: (85%), IR (KBr), 3377-3328 ($2NH_2$), cm^{-1}, ^{1} H NMR (300 MHz, DMSO-d_6): δ 6.6-7.7. (m, 4H, Ar-H), 8.3 (s, D_2O exchangeable, 2H, NH_2), MS (70 eV): *m/z* = 505 (M^+, 504), Element analysis for$C_{25}H_{17}N_9SO_2$ molecular weight (505), Calc.: C, 59.40; H, 3.36 ; N, 24.25 ; S, 6.33; O, 6.33, Found: C, 59.30 ; H, 3.26 ; N, 24.15 ; S, 6.23; O, 6.23.

2,5-di-amino - 3-(2-chloro - 4 - nitro) - arylazo - 6 - benzothiazol - 2 - yl) - 7 - (thiophen-2yl) pyrazoloPyri midine (4d)

brown crystals, m.p. ≥300°C; yield: (85%), IR (KBr), 3377-3328 ($2NH_2$) , cm^{-1}, ^{1} H NMR (300 MHz, DMSO-d_6): δ 6.6-7.7. (m, 4H, Ar-H), 8.1 (s, D_2O exchangeable, 2H, NH_2),MS (70 eV): *m/z* = 547 (M^+, 546), Element analysis for $C_{23}H_{14}N_9S_2O_2Cl$ molecular weight (547), Calc. : C, 50.45 ; H, 2.55 ; N, 23.03 ; S,11.70. ; O, 5.85; Cl, 6.39, Found : C, 50.3 ; H, 2.45 ; N, 23.0 ; S,11.60 ; O, 5.75 ; Cl, 6.29.

2,5-di-amino-3-(4-nitro)-arylazo-6-(benzothiazol-2-yl)-7-(4-(dimethylamino)phenyl)Pyrazolo pyrimidine (4e)

orange crystals, m.p. ≥300°C; yield: (85%), IR (KBr), 3377-3328 (NH_2), cm^{-1}, ^1H NMR (300 MHz, DMSO-d_6): δ 6.6 -7.7. (m, 4H, Ar-H), 8.00 (s, D_2O exchangeable, 2H, NH_2), 4.00 (s, D_2O exchangeable, 2H, NH_2) ppm., MS (70 eV): m/z = 577 (M^+, 499), Element analysis for $C_{27}H_{22}N_{16}SO_2$ molecular weight (577), Calc.: C, 58.99 ; H, 4.00 ; N, 25.45 ; S, 5.81.; O, 5.81.

Found: C, 58.89 ; H, 4.00 ; N, 25.35 ; S, 5.71. ; O, 5.71.

3.1. Electronic Effects and Ultraviolet-visible spectra

The electronic absorption spectra of arylazopyr- azolopyrimidine dyes 4a-e have been studied, their UV spectrum was found to be ranging between 360-440 nm.

Arylazopyrazolopyrimidine dyes have different resonating structures; the groups attached to rings play an important role in the resonance of the dyes.

It is well known that, the stabilization of these dyes are effected by the substituents originates from the charge separation through the conjugated system between different substituents. However, stabilization of different resonating structures depends on the introduction of an electron – withdrawing group in the aromatic ring and electron donating group of the other aromatic ring. deep bathchromicshifts by the presence of (N,N-dimethyl) as an electron donating group or as a rule the longer conjugation in the molecule; the deeper will be the color this is due to increase of the number of electron in the oscillation which facilities polarizations , this phenomena is clear from the bathochromic shift of dye no. 4d ƛ max=430

3.2. Antibacterial activity of the synthesized dyes

It is clear from the results, in table (III) that all of the newly synthesized dyes (4a- e) with different color shades possess excellent inhibition of the bacteria growth against the tested gm positive and gm negative bacteria and the inhibition zone diameters obtained are in the range of (17-21) mm which is quite good compared to the control value of 0. It appears also that dyes (4b) and (4d) possessed relatively higher inhibition zone diameter value than the other dyes and this may be attributed to its chemical structure and to the presence of Cl and NO_2 groups in its structure [10].

Dye	Inhibition zone diameter (mm)			
Sample	Bacillus Subtilis (G+)	Esherichia Coli (G-)	Staphylococcus Aureus (G+)	Pseudomonea Aeuruginous (G-)
Tetracycline	30	30	30	30
Control	0.0	0.0	0.0	0.0
4a	19	20	19	19
4b	21	21	20	21
4c	17	20	19	19
4d	19	21	21	20
4e	17	18	17	19

Table 2. Inhibition zone diameter of dyes (4a-e) against Gram positive and Gram negative bacteria

Different novel functionalized 2, 5-di-amino-3-arylazopyrazolopyrimidines derivatives (4a-e) are prepared in good yield as well as good antibacterial properties.

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