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SHORT COMMUNICATION

# Synthesis, characterization, and antimicrobial activity of heterocyclic azo dye derivatives

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**ABSTRACT**

The novel mordent and disperse heterocyclic dyes were prepared by coupling of various diazo solution of aromatic amines with *N*-{4-[2-{3,5-bis(4-methoxyphenyl)-4,5-dihydro-pyrazol-1-yl}-2-oxoethoxy]phenyl}-1-(phenyldiazenyl)methanimine The resultant mordent and disperse heterocyclic dyes were characterized by elemental analyses, IR and NMR spectral studies. The UV-visible spectral data have also been discussed in terms of structural property relationship. All the disperse azo dyes were applied on polyester textile fibers. The percentage dye bath exhaustion and fixation on the polyester fibers have been found to be very good. Moderate to very good light fastness and washing fastness properties were indicated by the dyed fabrics. Structures of synthesized compounds were confirmed by physical and spectral analysis. The compounds are evaluated for their antimicrobial activities.

***Keywords*:** Schiff bases, heterocyclic dyes, UV absorber, antimicrobial-screening

## 1. INTRODUCTION

Azo dyes are the most widely used class of coloring materials because of their massive applications in various fields of science and technology [1–3]. The azo dyes are synthesized by

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diazotization of aromatic amines and coupling reagent, which include one or more azo groups (–N=N–) attached to one or more aromatic moieties (Karci et al)[4]. These compounds represent the single largest chemical class industrial colorants[5]. Azo compounds are the oldest and largest class of industrial synthesized organic dyes due to their versatile application in various field, such as dyeing textile fiber, biomedical studies, advanced application in organic synthesis and high technology areas such as laser, liquid crystalline displays, electro-optical devise and ink-jet printers[6-8]. The range of shades that could be obtained from azo dyes includes yellows, reds, oranges, violets, navy blues and blacks but green shades are limited. Azo compounds have reasonably good technical properties, including light and weather fastness and resistance to solvents and water. The biological importance of azo compounds is well known due to their use as inflammatory,[9,10] anticancer,[11,12] antibacterial,[13-15,25,26] and antifungal.[16-21,27,28]

Azo dye compounds have many applications in industry including photosensitive, photodynamic therapy, electro photographic and photographic system applications and are predominant organic photo-conductive materials.[22,23] Heterocyclic coupling components produce heterocyclic azo disperse dyes with color ranging from yellow to red. The synthesis and application of azo dyes derived from quinoline and quinoline quinazoline systems have been reported.[24]

## 2. MATERIALS AND METHODS

### 2. 1. Experimental

Melting points were taken in open capillary tube and were uncorrected. IR spectra were recorded on I.R. Spectrophotometer of Buck scientific Model No. 500 and instrument used for NMR Spectroscopy was Bruker Advance II 400 and DMSO used as internal standard. Solvent used were $CDCl_3$ and DMSO. Purity of the compounds were checked by TLC on silica- G plates. All the compounds were tested for their antibacterial and antifungal activities by broth dilution method

## 3. MATERIALS AND METHODS

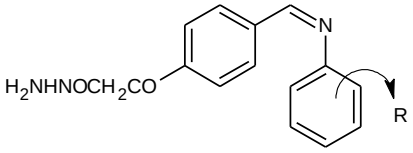
### 3. 1. Preparation of *N*-[{4-[2-{3,5-bis(4-methoxyphenyl)-4,5-dihydro-pyrazol-1-y-oxoethoxy] phenyl} methylene]substituted aniline (1a-j)

A mixture of 2-(4-{[subsitutedphenyl)imino]methyl}phenoxy)acetohydrazide (0.1M), ethanol (25 ml) and 1,3-bis(4-methoxyphenyl)prop-2-en-1-one (0.1M) with piperidine (1 ml) was refluxed for 16 hours. The resulting mixture was concentrated, cooled and poured into cold water containing 6 to 8 drops of HCl, when orange colored product separated. It was filtered, washed with water and crystallized from methanol-petroleum ether mixture.

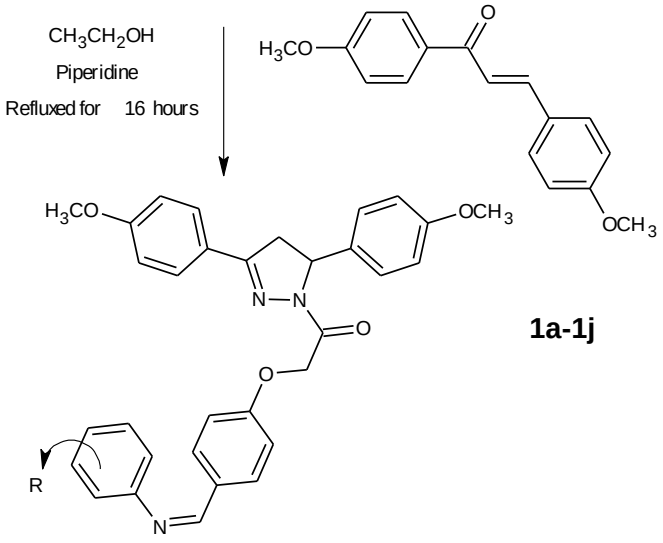
**IR; 1-c** ($cm^{-1}$): 3015 (=CH-), 2935 (-CH-), 1720 (>C=O), 1655 (C=N-), 1590 (>C=C<), 1440 ($-CH_2-$), 1385 ($-CH_3-$), 1250 (C-N) 1215 (-N-N-), 1105(-C-O-C).

**$^1$H NMR (DMSO): 1-i:** 2.5425, doudlet (2H) ($CH_2$-cyclic ), 3.7814, singlet (6H) ($-OCH_3-$), 4.6601, singlate (2H) ($-CH_2-$), 5.0071 triplet (1H) (-CH<) 8.5118, singlet (1H) (Ar-CH=N-), 6.8315-8.0939 multiplate (16H) (Ar-H)

**Reaction Scheme**

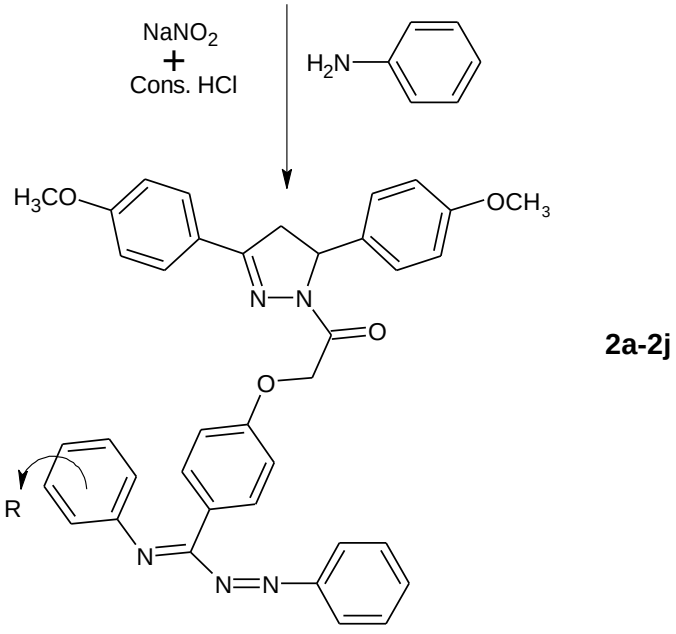



2-(4-{[(substitutedphenyl)imino]methyl}phenoxy)acetohydrazide




**1a-1j**

*N*-[{4-[2-{3,5-bis(4-methoxyphenyl)-4,5-dihydro-pyrazol-1-yl}-2-oxoethoxy]phenyl}methylene]substitutedaniline




**2a-2j**

***N*-(substitutedphenyl)-1-{4-[2-{3,5-bis(4-methoxyphenyl)-4,5-dihydro-pyrazol-1-yl}-2-oxoethoxy]phenyl}-1-(phenyldiazenyl)methanimine**

### 3. 2. Preparation of *N*-(substitutedphenyl)-1-{4-[2-{3,5-bis(4-methoxyphenyl)-4,5-dihydro-pyrazol-1-yl}-2-oxoethoxy]phenyl}-1-(phenyldiazenyl)methanimine (2a-2j)

A solution of aniline (0.01M) in glacial acetic acid (15 ml) concentrated hydrochloric acid (5 ml) was added at 0 to 5 °C. Then, a solution of saturated $NaNO_2$) (1 g in 5 ml of water) was mixed to above solution. The diazonium salt solution thus prepared was added drop by drop to a solution of compound N-[{4-[2-{3,5-bis(4-methoxyphenyl)-4,5-dihydro-pyrazol-1-yl}-2-oxoethoxy]phenyl}methylene]aniline (0.01M), in methanol (40 ml) with constant stirring at 0 °C temperature. The reaction mixture was kept at room temperature for a day and then poured into crushed ice. The solid product was washed with the water and crystallized from absolute ethanol.

**IR; 2-g** ($cm^{-1}$): 3010 (=CH-), 2920 (-CH-stretch), 1710 (>C=O),1654 (C=N-str), 1600 (N=N), 1610 (>C=C<) aromatic, 440 (-$CH_2$-bend), 1380 (-$CH_3$-bend), 1240 (C-N) 1220 (-N-N-), 1120 (-C-O-C), 615 (C-Cl).

**$^1$H NMR (DMSO); 2-i:** 2.5247, doudlet (2H) ($CH_2$-cyclic), 3.8379 singlet (6H) ($OCH_3$-), 4.8062, singlate (2H) (-$CH_2$-), 4.9351 triplet (1H) (-CH<) 6.8194-8.2087multiplate (21H) (Ar-H)

**Table 1.** *N*-(substitutedphenyl)-1-{4-[2-{3,5-bis(4-methoxyphenyl)-4,5-dihydro-pyrazol-1-yl}-2-oxoethoxy]phenyl}-1-(phenyldiazenyl)methanimine

| Sr. No. | Sample No. | R | Molecular Formula | Molecular Weight | Melting Point C | Yield | % C | | % H | | % N | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | | | | | | | Found | Required | Found | Required | Found | Required |
| **1** | **2a** | 1-Phenyl | $C_{38}H_{33}N_5O_4$ | 623.70 | 135 | 65 | 73.15 | 73.18 | 5.3 | 5.33 | 11.21 | 11.23 |
| **2** | **2b** | 1-Amino | $C_{42}H_{35}N_5O_4$ | 673.76 | 119 | 71 | 74.85 | 74.87 | 5.21 | 5.24 | 10.35 | 10.39 |
| **3** | **2c** | 4-$CH_3$ | $C_{39}H_{35}N_5O_4$ | 637.73 | 105 | 68 | 73.41 | 73.45 | 5.5 | 5.53 | 10.96 | 10.98 |
| **4** | **2d** | 3-$CH_3$ | $C_{39}H_{35}N_5O_4$ | 637.73 | 123 | 73 | 73.42 | 73.45 | 5.49 | 5.53 | 10.95 | 10.98 |
| **5** | **2e** | 2-$NO_2$ | $C_{38}H_{32}N_6O_6$ | 668.70 | 120 | 70 | 68.21 | 68.25 | 4.8 | 4.82 | 12.55 | 12.57 |
| **6** | **2f** | 3-$NO_2$ | $C_{38}H_{32}N_6O_6$ | 668.70 | 138 | 66 | 68.2 | 68.25 | 4.79 | 4.82 | 12.54 | 12.57 |
| **7** | **2g** | 4-$NO_2$ | $C_{38}H_{32}N_6O_6$ | 668.70 | 110 | 68 | 68.22 | 68.25 | 4.78 | 4.82 | 12.53 | 12.57 |
| **8** | **2h** | 2-Cl | $C_{38}H_{32}ClN_5O_4$ | 658.14 | 127 | 72 | 69.31 | 69.35 | 4.88 | 4.9 | 10.6 | 10.64 |
| **9** | **2i** | 3-Cl | $C_{38}H_{32}ClN_5O_4$ | 658.14 | 125 | 69 | 69.32 | 69.35 | 4.86 | 4.9 | 10.61 | 10.64 |
| **10** | **2j** | 4-Cl | $C_{38}H_{32}ClN_5O_4$ | 658.14 | 116 | 64 | 69.3 | 69.35 | 4.87 | 4.9 | 10.62 | 10.64 |

**Table 2.** Antimicrobial activity of *N*-(substitutedphenyl)-1-{4-[2-{3,5-bis(4-methoxyphenyl)-4,5-dihydro-pyrazol-1-yl}-2-oxoethoxy]phenyl}-1-(phenyldiazenyl)methanimine

| SR. NO. | COMP. NO. | R | ANTIBACTERIAL ACTIVITY Minimal Inhibition Concentration (µg/ml) | | | | ANTIFUNGAL ACTIVITY Minimal Inhibition Concentration (µg/ml) | | |
|---|---|---|---|---|---|---|---|---|---|
| | | | Gram negative bacteria | | Gram positive bacteria | | Fungus | | |
| | | | *E. coli* | *P. aeruginosa* | *S. aureus* | *S. pyogenus* | *C. albicans* | *A. niger* | *A. clavatus* |
| | | | MTCC 443 | MTCC 1688 | MTCC 96 | MTCC 442 | MTCC 227 | MTCC 282 | MTCC 1323 |
| 1 | 2a | 1-Phenyl | 175 | 175 | 100 | 200 | 600 | 800 | 800 |
| 2 | 2b | 1-Napthyl | 100 | 150 | 125 | 150 | 500 | 500 | 700 |
| 3 | 2c | 4-$CH_3$ | 250 | 200 | 250 | 200 | >1000 | 250 | 500 |
| 4 | 2d | 3-$CH_3$ | 150 | 150 | 150 | 125 | 800 | 600 | >1000 |
| 5 | 2e | 2-$NO_2$ | 200 | 200 | 200 | 150 | >1000 | 900 | 600 |
| 6 | 2f | 3-$NO_2$ | 100 | 200 | 225 | 175 | 800 | 800 | 500 |
| 7 | 2g | 4-$NO_2$ | 200 | 150 | 125 | 200 | 900 | 700 | 600 |
| 8 | 2h | 2-Cl | 150 | 100 | 250 | 150 | 600 | >1000 | 700 |
| 9 | 2i | 3-Cl | 250 | 125 | 200 | 125 | 500 | 900 | >1000 |
| 10 | 2j | 4-Cl | 175 | 100 | 200 | 150 | 700 | 800 | 800 |

## 4. RESULTS AND DISCUSSION

### *Antimicrobial activity*

The MICs of synthesized compounds were carried out by broth micro dilution method as described by Ratan (2000). The invitro antimicrobial activity of test compounds were assessed against 24 hr cultures of several selected bacteria and fungi. The bacteria used were *E. coli*, *S. aureus*, *P. aeruginosa*, and *S. pyogenus*; the fungi used were *C. albicans*, *A. niger*, and *A. clavatus*. The antimicrobial activity was performed by broth dilution method in DMSO. Gentamycin, Ampicilin, Chloramphenicol, Ciprofloxacin, Norfloxacin, Nystatin and Greseofulvin were used as standard for the evaluation of antibacterial and antifungal activities respectively. The activity was reported by Minimal Inhibition Concentration. The results are summarized in Table 2. Biological screening result of N-(substitutedphenyl)-1-{4-[2-{3,5-bis(4-methoxyphenyl)-4,5-dihydro-pyrazol-1-yl}-2-oxoethoxy]phenyl}-1-(phenyldiazenyl) methanimine based derivatives shows that compound (**2b, 2f**) have shown better activity against *E. coli*, *S. aureus*, while rest of all compound possessed good activity against *S. aureus* in the range of 125-250 µg/ml. Compounds with substitution 4-chloro (**2d** and **2g)**, shown good antibacterial activity against *S. pyogenus*, while rest of all derivatives possessed

good activity against *S. pyogenus* in the range of 100-250 μg/ml. Compound (**2c)** and (**2e)** is found to be significant antifungal activist against *C. albicans*, while rest of all derivatives are poor against *A. niger*, and *A. clavatus*

## 5. CONCLUSION

The Main focus of this research work was to synthesize, characterize and evaluate antimicrobial activities of the newly synthesized Chalcone derivatives, structures of synthesized compounds were confirmed and characterized with the help of analytical data's such as IR and 1H-NMR. In summary, we have described the synthesis and antimicrobial activity of novel N-(substitutedphenyl)-1-{4-[2-{3,5-bis(4-methoxyphenyl)-4,5-dihydro-pyrazol-1-yl}-2-oxoethoxy]phenyl}-1-(phenyldiazenyl)methanimine MIC values revealed that amongst newly synthesized compound having 4-chlorophenyl type linkage has shown good activity against the bacterial strains. Rest of all compounds exhibit moderate improvement in activity against some of the pathogenic strains.

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