Synthesis, Spectroscopic, and Dyeing Properties of New Azo and Bisazo Dyes Derived from 5-Pyrazolones

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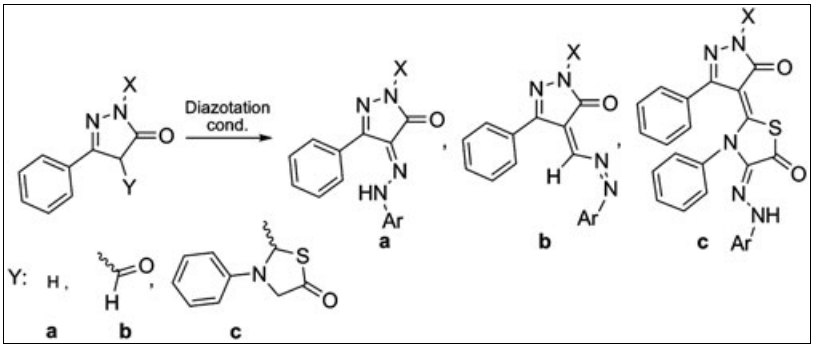

This study is in continuation of our work related to 5-pyrazolones aimed at synthesizing new heterocycles with dyeing and anticipated biological properties. Compounds **1** and **2**; 1-methyl- or 1-(2,4-dimethylphenyl)-3-phenyl-1*H*-pyrazol-5(4*H*)-one, **3**; 1-methyl-5-oxo-3-phenyl-4,5-dihydro-1*H*-pyrazole-4-carbaldehyde and **4**; 2-(1-methyl-5-oxo-3-phenyl-1*H*-pyrazol-4(5*H*)-ylidene)-3-phenylthiazolidin-5-one were prepared and subjected to diazotation with aromatic amines and diamines. New azo (**1a–c**, **2a, b**, **3a**, **b**, **4a**, **c**) and bisazo dyes (**2c**, **d**, **4b**) were obtained, and their structures were confirmed by spectroscopic and analytical methods. In addition, UV–vis measurements, dyeing performance, and fastness tests were carried out for all compounds.

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INTRODUCTION

The azo colors consist a large group of synthetic organic coloring material and are versatile color-producing molecules for industrial use [1, 2]. Pyrazolones linked to azo compounds are extensively used in the dye industry. Nowadays, the synthesis of new dyes with nontoxic effects, for fabric material coloring, is especially important. In this regard, pyrazolone derivatives are an important class of organic molecules with diverse biological properties and prospective nontoxic coloring features. They are widely used in pharmaceutical industry to alleviate inflammation, fever, pain, infections, and also used as insecticides and herbicides [3–6].

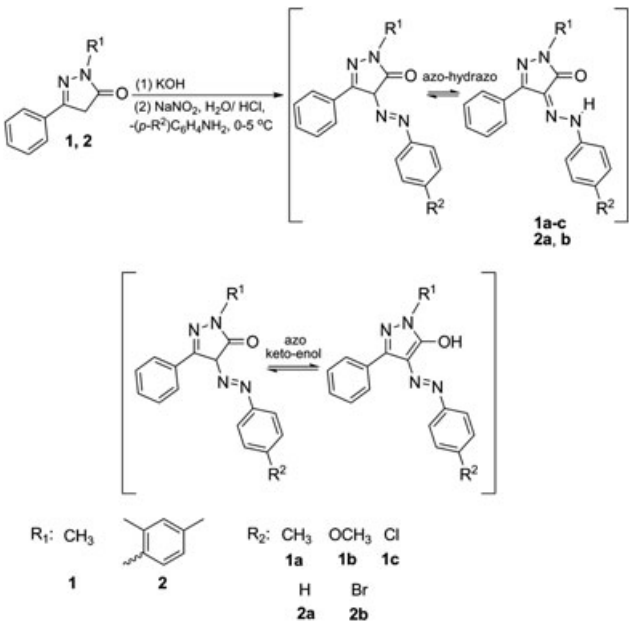
Metwally et al. have reported the importance of some pyrazolone rings containing azo disperse dyes with good to excellent dyeing characteristics [7]. Although many researchers have discussed the synthesis and dyeing features of compounds, few investigations have been made with respect to the relations between dyeing properties and the general structure of the compounds. In our previous work, we have reported the synthesis of some pyrazolone derivatives [8]. Because of the importance of these compounds and our interest in them, we decided to extend our study to the coloring and spectroscopic features of new pyrazolone derivatives with potential biological activity. Therefore, we chose as starting materials (5-methyl-2-phenyl-2,4-dihydro-3*H*-pyrazol-3-ones, **1–3**), as edaravone analogs, a strong free radical scavenger for treatment of cardiovascular diseases [9, 10].

Accordingly, we synthesized various 4-aryl azo- (**1a–c**, **2a**, **b**), 4,4′-aryl-bisazo pyrazol-5-ones (**2c**, **d**), the hydrazone and hydrazide (**3a**, **b**) derived from pyrazolone-4-carbaldehyde (**3**), and 4-arylazo(thiazolidin-5-one-ylidene)pyrazol-5-ones (**4a–c**). The synthetic pathways and the structures of novel pyrazolones have been established. UV–vis investigations in $CHCl_3$, acidic, and basic solutions in MeOH of these dyes are discussed. Moreover, dyeing and fastness determinations of the azo, bisazo dyes under study, were carried out and the results are rationalized.

Synthesis of the compounds. In the first phase of our work, 5-pyrazolones **1** and **2** were prepared. As **2** is a new compound, its structure was mainly confirmed by ^{1}H-NMR spectroscopy. **1** and **2** were directly used to synthesize compounds **1a–c** and **2a**, **b** through azo-coupling by a known procedure [11]. The resulted azo dyes can exist in two possible tautomeric forms, namely the azo-hydrazo and the azo keto-enol forms. Reactions were carried out in the presence of KOH due to the active methylene protons of 5-pyrazolones, and the products were purified either by chromatography or rinsing the crystalline material with an appropriate solvent (Scheme 1).

The structures of compounds **1a–c** and **2a**, **b** were confirmed by their FTIR, ^{1}H- and ^{13}C-NMR, and MS data. The infrared spectra of these groups of dyes did not show NH absorption bands, although the NH group in the ^{1}H-NMR spectra exhibited broad singlets between 13.80 and 14.04 ppm. This phenomenon is suggestive of the fact that these dyes do not exist as hydrazo forms in the solid state. The absorption peaks at around 1646–1657 and 1585–1591 cm^{-1} were attributed to the C O and C N stretch vibrations, respectively. The presence of the C O groups in the FTIR spectra, and no peaks for OH protons in the ^{1}H-NMR spectra indicate that the compounds do not prefer the azo-enol tautomeric form neither in the solid nor in the liquid states. The ^{1}H-NMR spectra of **1a–c** and **2a** and **b** showed the disappearance of the characteristic methylene single peaks of the 5-pyrazolone ring in **1** and **2** at 4.10 and 5.88 ppm, respectively. The spectra of **1a–c** and **2a** and **b** revealed signals for methyl protons (3.53 ppm for NMe in **1**; 2.09 and 2.30 ppm for 2,4-$(CH_3)_2$Ph in **2**), and aromatic H-atoms at expected chemical shifts. In addition, the ^{13}C-NMR data and elemental analyses, which were in agreement with the proposed structures, the mass spectra of all new compounds showed the expected molecular ion peaks.

Scheme 1

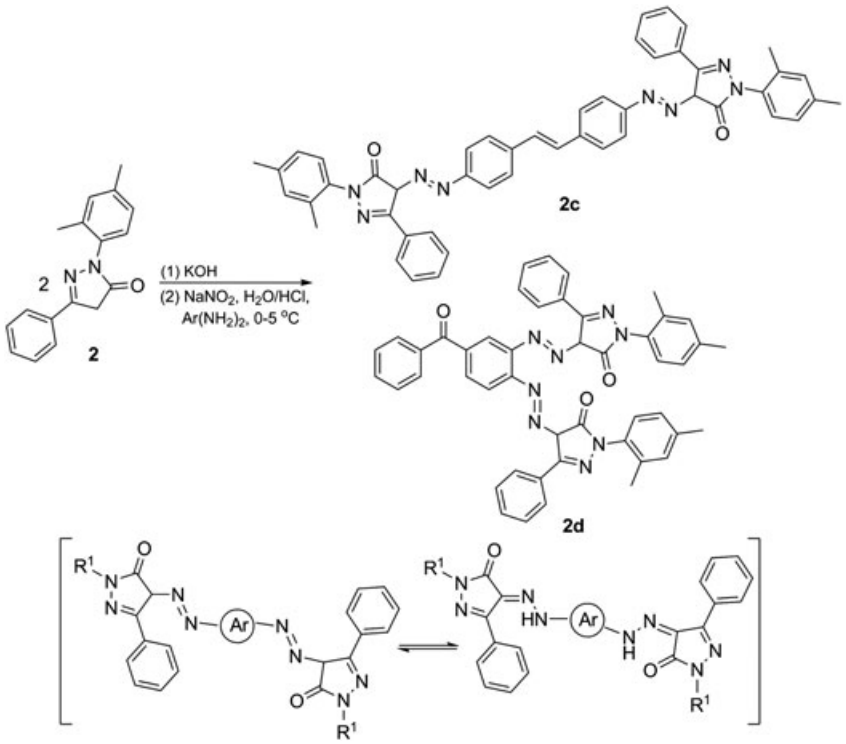


New bisazo dyes **2c** and **d** were prepared by diazotation 4,4′-diaminostilben and 3,4-diaminobenzophenone and subsequent coupling to compound **2** (Scheme 2).

The structures of **2c** and **d** have been confirmed by FTIR, ^{1}H-NMR, ^{13}C-NMR, and ESI MS data. In the FTIR spectra, they exist in the azo-form, but **2c** is in its hydrazo-form (NH at 14.01 ppm), **2d** is in the enol-form (OH at 5.96 ppm) as revealed from their respective ^{1}H-NMR spectra. The ESI-MS spectra of **2c** and **d** showed the characteristic molecular ion peaks.

It is noteworthy that the 5-pyrazolones as well as the hydrazonomethyl derivatives of 5-pyrazolones could possess diverse biological and medicinal activities in addition to their

Scheme 2



dyeing properties as synthetic dyes [12, 13]. In the second part of our work, new hydrazonomethyl-5-pyrazolones (**3a**, **b**) were prepared by condensation reaction of 5-pyrazolone-4-carbaldehyde (**3**) with (2,4-dimethylphenyl)hydrazine, **3a**, and (4-hydroxyphenyl)benzhydrazide, **3b**. The new molecules can exist in different tautomeric forms, namely as the keto imine/hydrazo-methylene/azo, the imine/hydrazo keto-enol, or the enol imine/hydrazo-methylene/azo (Scheme 3).

FTIR spectra of the new molecules showed the absence of the aldehyde C O band at 1609 cm^{-1} indicating that the reaction was complete. In addition, in the ^{1}H-NMR spectra, an increase of the integral for the aromatic protons with the expected chemical shifts at 7.04–7.11; 7.42–7.49; 7.62 and 6.74–6.84; 7.10–7.41; 7.62 ppm for **3a** and **b**, respectively, were noted, confirming the addition of aromatic hydrazine and hydrazide to the aldehyde **3**. According to the aforementioned spectra, NH absorption bands in the FTIR spectra showed the stability of the keto imine/hydrazo tautomeric structure in the solid state, and the absence of a signal for NH in the ^{1}H-NMR spectra indicated the existence and the preference of the keto methylene/azo tautomeric structure in solution.

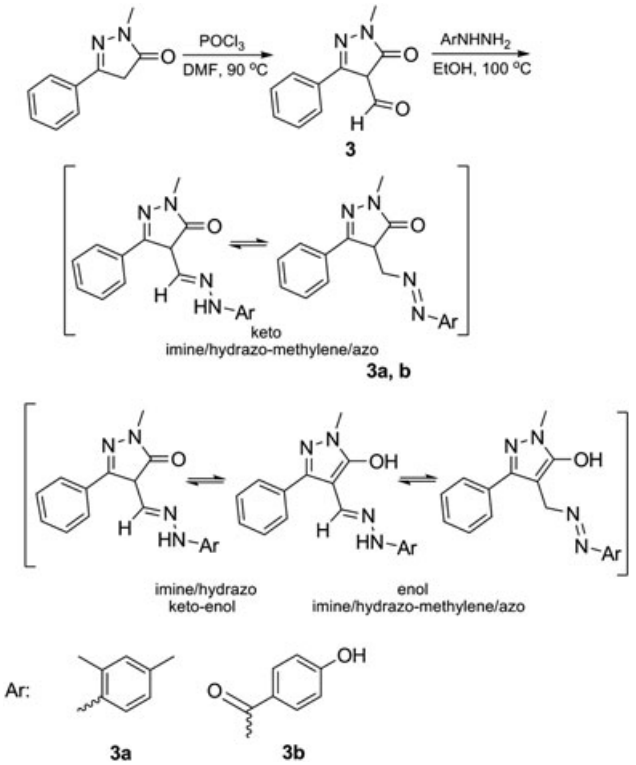
In the last part of our work, we extended the study to get new disperse dyes with enchanced potential biological activity [8]. Toward that end, new aryl azo-thiazolidin-5-one-ylidene-pyrazol-5-ones were synthesized. The starting material **4** was treated with the diazo salts of two different aromatic amines namely; aniline and *o*-hydroxyaniline to give **4a–c**, respectively. The azotation with aniline diazo salt, gave two azo-products, **4a** and **4b**, in the presence of sodium acetate, which were separated chromatographically, (R_f: 0.65 and 0.85, respectively, in EtOAc/*n*-hexane 2 : 1 v/v). For the dye **4a**, the molecular ion peak was seen at 453 that is the exact molecular weight of the compound. The FTIR spectra revealed NH bands at 3360 cm^{-1}, unlike azo-pyrazol-5-ones indicating the stability of the hydrazo tautomeric structure in the solid state. In addition, ^{1}H-NMR spectra showed NH signals at 9.45 ppm as a proof for the presence of a hydrazo group in the solution as well, which explains that the tautomeric equilibrium is not in favor of the azo group neither in the solid state nor in $CHCl_3$ for this group of dyes (Scheme 4).

UV–vis studies. The absorption spectra of the examined dyes were recorded within the wavelength range 200–600 nm in $CHCl_3$ and MeOH at room temperature.

5-Pyrazolones and their azo and bisazo derivatives can show different tautomeric structures as has been shown by many researchers [4, 14]. To understand the tautomeric equilibrium in the acidic and basic medium, MeOH + 0.01 *M* HCl and MeOH + 0.01 *M* KOH, respectively, were also used (Table 1). The absorption spectra of the dyes in $CHCl_3$ are shown in Figure 1.

UV–vis absorption spectra were evaluated for all the new molecules. The absorption bands approximately between at

Scheme 3



Scheme 4

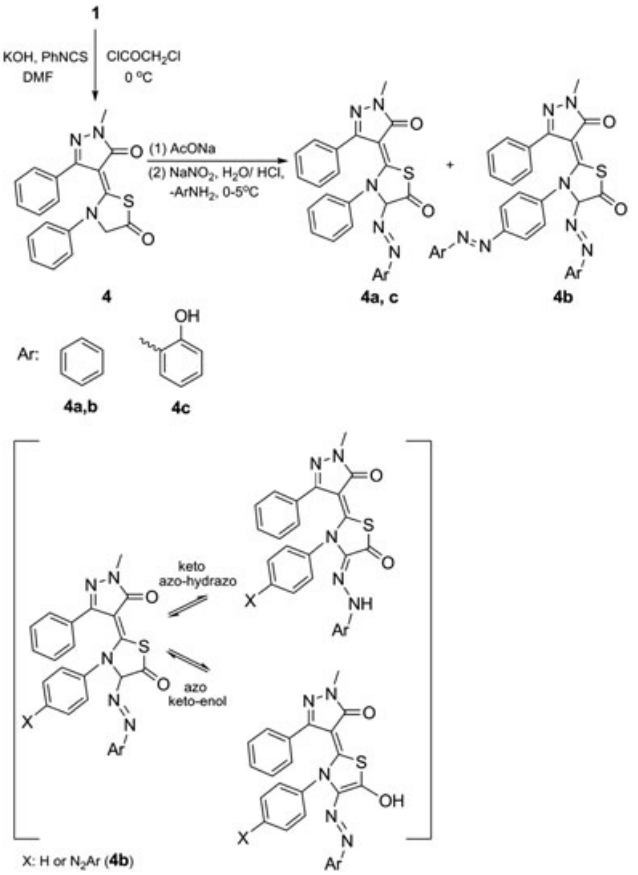


Table 1

Absorption maxima of the dyes in acidic[a] and basic[b] solutions of methanol.

Dye No.	UV–visible λ_{max} (nm)				
	Color	Chloroform	Methanol	Methanol + HCl[a]	Methanol + KOH[b]
1a	Orange	243,410	408,573	409,581	406,573
1b	Yellow	245,427	206,243,423	204,243,425	243,422
1c	Orange	245,412	208,244,400	209,244,400	203,244,400
2a d.[c]	Orange	260,405	402,573	403,581	400,581
2b	Yellow	249,407	405,581	406,581	405,581
2c	Red	254,491	441	438	464
2d	Cream	260	255	256	255
3a l.[c]	Orange	242,340	283,359	282,362	282,339
3b	Yellow	ns[d]	209,255	210,259	211,294,357
4a	Yellow	243,312,465	327,482	317,487	352,535
4b	Yellow	244,401	389	395	388
4c	Orange	313,504	322,497	309,494	325,536

[a]HCl (0.01*M*).
[b]KOH (0.01*M*).
[c]d: dark, l: light.
[d]ns: not soluble.

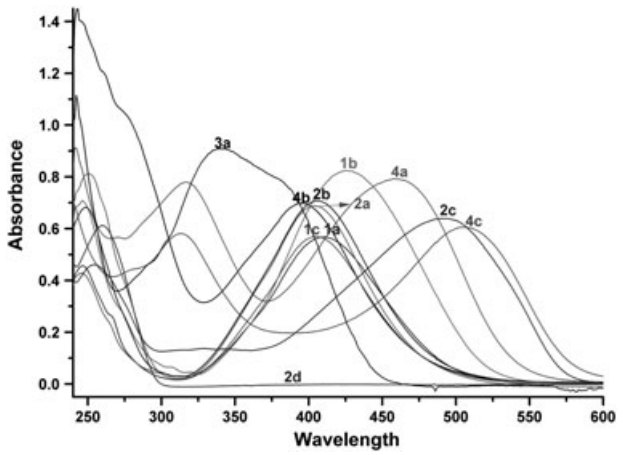
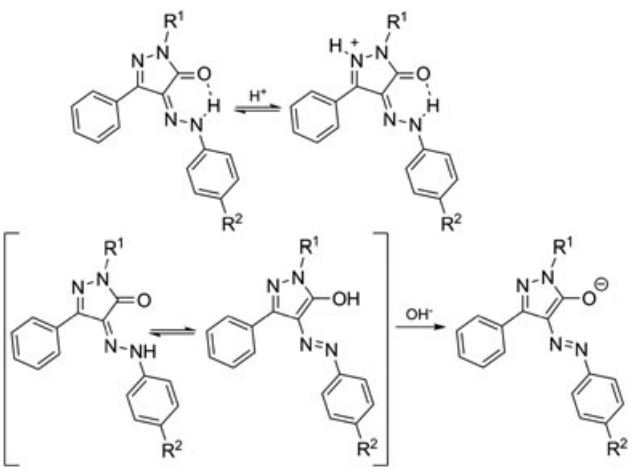


Figure 1. Absorption spectra of the dyes in $CHCl_3$.

the λ_{max} 312 and 498 nm were assigned to n→π* and π→π* transitions of diazo groups in the dyes [15].

Compounds derived from **1** and **2** all showed one absorption maximum in $CHCl_3$ at the upper wavelength of 300 nm. It can be suggested that they are predominantly in the single tautomeric form in $CHCl_3$. One absorption band was observed for **1b**, **c**, **2c** and two absorption bands for **1a**, **2a**, **b** in MeOH. Two absorption maxima indicate that they can be a mixture of tautomeric forms. Dyes **1b**, **c**, **2c** showed one absorption band in $CHCl_3$ and MeOH, MeOH + HCl, and MeOH + KOH that could reveal the existence of only one tautomeric structure (the hydrazo form) in a polar solvent-like MeOH. It was also observed that the absorption spectrum of dye **1b** bathochromically shifted in $CHCl_3$ ($\delta\lambda$ = 15 nm) relative to dyes **1a** and **1c**, this may be due to the property of the methoxy group in **1b** as the strongest electron donor among the azo dyes derived from **1**. Dyes **1a** and **2a** showed 8 nm bathochromic shifts with the addition of 0.01 *M* HCl to methanol, **2a** showed the same shift with the addition of 0.01 *M* KOH. Dye **2c** showed large bathochromic shift ($\delta\lambda$ = 23 nm) by the addition of 0.01 *M* KOH. The absorption spectra of **1b–d** and **2b** did not significantly change after the addition of HCl or KOH. These results indicate that dyes **1a**, **2a** may be a mixture of tautomeric forms (Scheme 1) or a cationic form in acidic solutions and **2c** may be in dianionic form in basic solutions. The positive charge is probably located on the nitrogen rather than oxygen because of the probable hydrogen bonding between the carbonyl of pyrazolone ring and NH of hydrazo groups (Scheme 5).

Scheme 5



Dye **3a** has two absorption maxima in $CHCl_3$ while showing only one maximum in MeOH and in acidic and basic solutions of MeOH indicating the possibility of two tautomeric forms in $CHCl_3$ and one tautomeric form in MeOH at the upper wavelength of 280 nm. It reacted differently from the others when 0.01 *M* KOH was added by shifting to blue, $\delta\lambda = 20$ nm (Fig. 2). This shows the existence of the enol methylene/azo tautomeric structure's anionic form in the basic solution (Scheme 6).

The aryl azo-thiazolidin-5-one-ylidene-pyrazol-5-ones **4a** and **c** have two bands in $CHCl_3$, MeOH, MeOH + 0.01 *M* HCl, and MeOH + 0.01 *M* KOH while **4b** has only one absorption maxima in these solutions. These results can be explained in terms of the existence of two tautomeric forms, namely the keto azo-hydrazo and the azo keto-enol (Scheme 4), for **4a**, **c** and the presence of one tautomeric structure for **4b** in the aforementioned solutions. Dyes **4a** and **c** showed bathochromic shifts ($\delta\lambda = 70$; 39) with the addition of basic methanol solutions that caused color change from yellow to violet (Fig. 3). These large shifts indicated the existence of the anionic forms for the dyes in basic medium (Scheme 7).

Dyeing and fastness properties. In this chapter, we describe the application of the synthesized compounds as new disperse dyes for dyeing acetate, cotton, nylon, polyester, acrylic, and wool fabrics where a range of color shades have been obtained, as the visual color shades varied from yellow, orange, to red. Three color fastness tests were applied to all compounds; fastness to washing, fastness to perspiration (acidic and basic), and

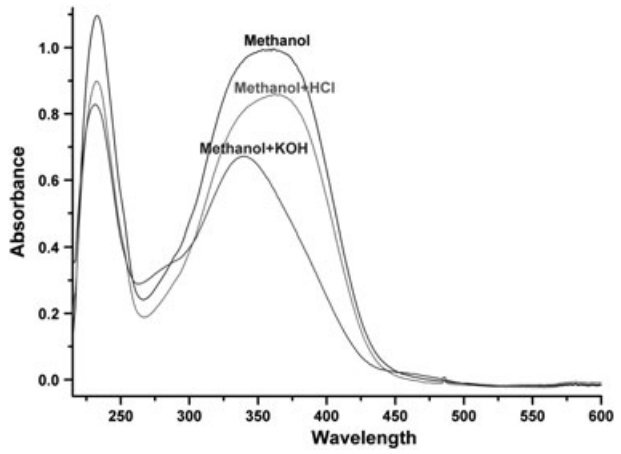
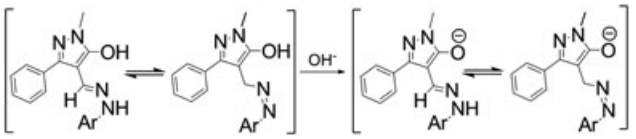


Figure 2. Absorption spectra of dye **3a** in acidic and basic solutions.

Scheme 6



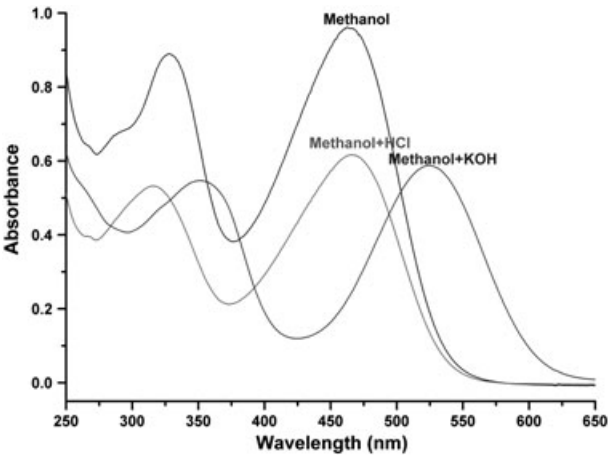
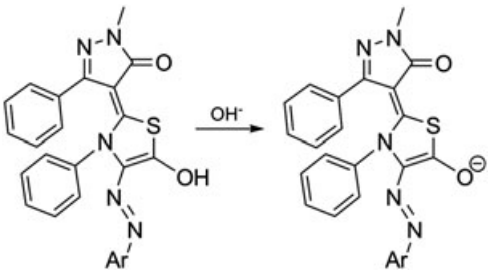


Figure 3. Absorption spectra of dye **4a** in acidic and basic solutions.

Scheme 7



fastness to light tests were carried out according to TS EN ISO that is an international standard. The stanning on the white adjacent fabrics was assessed according to the international gray scale.

The performance of the new compounds in the tests is good to excellent except for **2c** and **d** and **4c**. Color fastness tests of these dyes were poor for all kinds of fabrics, probably due to the solubility problem during the dyeing procedure.

These compounds are classified into four structurally different groups and the fastness tests results show that the substituents such as CH_3, Cl, and Br have a lightening effect on the dyes. The different substitution on the 4-position of pyrazol-5-one ring (CH_3 for **1** and 2,4-$(CH_3)_2$Ph for **2**) resulted with no remarkable difference in the colors. The dyes (**3a**, **b**) derived from the condensation of aromatic hydrazines with 5-pyrazolone-4-carbaldehyde (**3**) had yellowish colors. Dyes **3a** and **b** with longer carbon chains on the azo group showed the lightening effect and compound **4** derivatives with a thiazolidin-5-one ring attached to 5-pyrazolone from 4-position do not have a remarkable color difference.

The colors of all compounds were evaluated using a spectrophotometer and as a representative example the Spectral Graphic (upper left), the Line Graph Object (upper right), the xy Chromaticity Diagram (left lower part), and the 3D Graph (right lower part) of **1b** is shown in Figure 4.

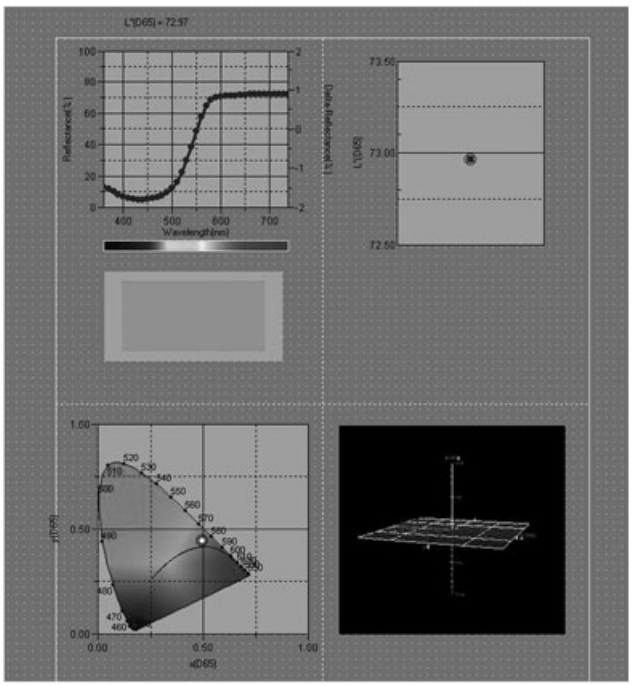


Figure 4. Spectrophotometric evaluation of **1b**.

CONCLUSIONS

In conclusion, new azo dyes were synthesized derived from four structurally related but different molecules, namely 1-CH_3- or 2,4-$(CH_3)_2$Ph-substituted 5-pyrazolones, hydrazono-methyl derivatives of 5-pyrazolones, and 4-aryl azo-(thiazolidin-5-one-ylidene)pyrazol-5-ones. All compounds were characterized and investigated for their dyeing characteristics and tautomeric equilibrium. The results show that dyes may exist as mixtures of several tautomeric forms in acidic, basic medium or in the solid, liquid states. It has been known that some azo compounds are used as acid–base indicators due to the different colors of their acid and salt forms. Dyes **4a** and **4c** may be used for this purpose as well. Almost all dyes exhibit very good to excellent washing, perspiration, and light fastness properties. In addition, all new synthesized molecules may be valuable for their potential biological activity and that will be investigated in a future study.

EXPERIMENTAL

General. The chemicals used for the synthesis of the compounds were obtained from either Aldrich or Merck and were used without further purification. All solvents were of reagent grade. Column chromatography (CC): silica gel 60 (Merck). Thin-layer chromatography (TLC): silica gel precoated (0.2 mm layer) aluminum sheets (Merck). m.p: Gallenkamp-melting-point apparatus; uncorrected. IR Spectra: Perkin-Elmer FTIR spectrometer; ATR; in , cm^{-1}. NMR Spectra: Bruker Digital-FT-NMR-Avance 400 (MHz) and Varian-Inova (500 MHz) $CDCl_3$ or CD_3OD solutions.; δ in ppm relative to $SiMe_4$ as internal standard, *J* in Hz. MS (Negative-ion ESI mass spectra): Agilent 6460-A; LC-Triple Quadrupole MS/MS system (Jet Stream Electro Spray Ionization source) and Varian Saturn 2100T/GC3900 GC-MS spectrometers; in *m/z* (%). Ultraviolet/visible (UV–vis) absorption spectra: Agilent 8453 spectrophotometer at wavelength of maximum absorption (λ_{max}, nm). Elemental analyses (C, H, N, S) were conducted using the Elemental Analyser Thermo Flash-EA-1112, their results were found to be in good agreement (±0.2%) with the calculated values. Color determinations: Konica Minolta Spectrophotometer/cm-3600d.

Dyeing and fastness determinations. International standard of TS EN ISO; Standard for fastness to washing: TS EN ISO 105-C06/November 2001 (A1S, 40°C); Gray scale for assessing stainine: ISO 105-A03; Gray scale for assessing change in color: ISO 105-A02. Standard for fastness to light: TS 1008 EN ISO 105 B02/April 2001. Gray scale for assessing change in color: ISO 105-A02. Standard for fastness to perspiration: TS EN ISO 105 E04/April 2006; Gray scale for assessing stainine: ISO 105-A03; Gray scale for assessing change in color: ISO 105-A02.

General procedure for the synthesis of pyrazol-5-ones. The hydrazine [3 mmol; methylhydrazine for **1**; (2,4-dimethylphenyl) hydrazine for **2**] and ethyl benzoyl acetate (3 mmol) was dissolved in dioxane (for **1**; 10 mL) or EtOH (for **2**; 10 mL) and the mixture stirred overnight at room temperature. The resulting solid was filtered off and washed with cold Et_2O twice.

1-Methyl-3-phenyl-1H-pyrazol-5(4H)-one (1). White solid in 87% yield. mp: 208–210°C (Ref. 16; 210–211°C).

1-(2,4-Dimethylphenyl)-3-phenyl-1H-pyrazol-5(4H)-one (2). CC (AcOEt/*n*-hexane, 2 : 1), cream solid (65%), mp: 95–98°C; ^{1}H-NMR (400 MHz, $CDCl_3$): δ = 2.09 (s, 3H, CH_3), 2.30 (s, 3H, CH_3), 5.88 (s, 2H, CH_2), 7.00–7.05 (m, 2H, ar), 7.16-7.24 (m, 3H, ar), 7.29–7.33 (m, 1H, ar), 7.75–7.77 (m, 2H, ar) ppm; ^{13}C-NMR (100 MHz, $CDCl_3$): δ = 18.33 (CH_3), 21.13 (CH_3), 34.06 (CH_2), 126.20, 126.41, 127.13, 127.29, 129.68, 130.81, 131.91, 133.45, 135.39, 140.27, 150.18 (C N), 173.01 (C O) ppm; IR (ATR): = 3053, 3032 (ar, CH), 1712 (C O), 1585 (C N) cm^{-1}; UV–vis (Chloroform, $c = 1.26.10^{-4}$ mol L^{-1}): λ_{max} = 260 (2579.36) nm ($mol^{-1}Lcm^{-1}$); $ESI^{(-)}$-MS: *m/z* (%) = 284 ($[(M+(Na-H)]^-$, 20.19), 250 $[(M-CH_3)^-$, 7.60]. Anal. Calc. for $C_{17}H_{16}N_2O$: C, 77.25; H, 6.10; N, 10.60. Found: C, 77.22; H, 6.17; N, 10.57.

General procedure for preparation of azo and bisazo compounds. To a cold solution of compounds **1**, **2**, or **4** (5 mmol, 10 mmol for bisazo compounds) in EtOH (10 mL), (for **2** and **4**; DMF for **1**) containing KOH [40 mmol; for **1** and **2**; NaOAc (35 mmol) for **4**] were added a diazonium chloride solution (5 mmol), which was prepared by adding concentrated HCl (1 mL) to aryl amine (5 mmol) at 0–5°C and then treating the resulting salt with a cold solution of $NaNO_2$ (7.5 mmol) in H_2O (5 mL) with stirring at 0–5°C. The mixture was then stirred in ice for 5 h. EtOH was evaporated under reduced pressure. In the case of the reaction in DMF, the product was poured into ice-water.

1-Methyl-3-phenyl-4-(p-tolyldiazenyl)-1H-pyrazol-5(4H)-one (1a) [17]. CC (AcOEt/*n*-hexane, 1 : 2), orange crystals (53%), mp: 156-157 °C; ^{1}H-NMR (400 MHz, $CDCl_3$): δ = 2.37 (s, 3H, CH_3), 3.53 (s, 3H, NCH_3), 7.22 (d, *J* = 8.8 Hz, 2H, ar), 7.34 (d, *J* = 8.8 Hz, 2H, ar), 7.41-7.49 (m, 3H, ar), 8.11 (dd, *J* = 1.9; 6.8 Hz, 2H, ar), 13.93 (br.s., 1H, NH) ppm; ^{13}C-NMR (100 MHz, $CDCl_3$): δ = 20.23 (CH_3); 30.37 (NCH_3); 114.73; 126.59; 127.32; 128.85; 129.47; 129.00; 130.01; 134.20; 138.00; 144.59 (C N); 157.92 (C O); IR (ATR); = 3025 (ar, CH), 1646 (C O), 1589 (C C and

C N) cm^{-1}; UV–vis (Chloroform, $c = 2.28.\times 10^{-4}$ mol L^{-1}): λ_{max} = 248 (1988.68), 410 (2488.95) nm (mol^{-1} L cm^{-1}); $ESI^{(-)}$-MS: *m/z* (%) = 292 (M^-, 62.75), 291 [$(M-H)^-$, 13.35]. Anal. Cal. for $C_{17}H_{16}N_4O$: C, 69.85; H, 5.52; N, 19.17. Found: C, 69.79; H, 5.48; N, 19.26.

4-[(4-Methoxyphenyl)diazenyl]-1-methyl-3-phenyl-1H-pyrazol-5(4H)-one (1b). Compound **1b** was isolated from water-DMF with extraction of EtOAc twice (15 mL), dried ($MgSO_4$), filtered, and evaporated. CC (AcOEt/*n*-hexane, 2 : 1), red crystals (68%), mp: 218–219°C; ^{1}H-NMR (400 MHz, $CDCl_3$): δ = 3.53 (s, 3H, NCH_3), 3.84 (s, 3H, OCH_3), 6.97 (d, *J* = 8.8 Hz, 2H, ar), 7. 40–7.48 (m, 5H, ar), 8.11 (d, *J* = 7.8 Hz, 2H, ar), 14.04 (br.s., 1H, NH) ppm; ^{13}C-NMR (100 MHz, $CDCl_3$): δ = 30.40 (NCH_3), 54.84 (OCH_3), 114.18, 116.21, 116.64, 126.74, 127.62, 128.80, 129.43, 129.86, 144.55 (C N), 152.85, 157.82 (C O) ppm; IR (ATR): = 3068 (ar, CH), 1657 (C O), 1592 (C N) cm^{-1}; UV–vis (Chloroform, $c = 2.16.\times 10^{-4}$ mol L^{-1}): λ_{max} = 246 (3277.67), 423 (3804.94), 430 (3805.97) nm (mol^{-1} L cm^{-1}); $ESI^{(-)}$-MS: *m/z* (%) = 308 (M^-, 4.42), 307 [$(M-H)^-$, 58.20]. Anal. Cal. for $C_{17}H_{16}N_4O_2$: C, 66.22; H, 5.23; N, 18.17. Found: C, 66.30; H, 5.11; N, 18.23.

4-[(4-Chlorophenyl)diazenyl]-1-methyl-3-phenyl-1H-pyrazol-5(4H)-one (1c). The solid product was filtered and washed (ice-water), dried at room temperature, orange crystals (52%), mp: 177–178°C; ^{1}H-NMR (400 MHz, $CDCl_3$): δ = 3.52 (s, 3H, NCH_3), 7.35–7.48 (m, 7H, ar), 8.08 (d, *J* = 8.8 Hz, 2H, ar), 13.86 (br.s., 1H, NH) ppm; ^{13}C-NMR (125 MHz, $CDCl_3$): δ = 30.38 (NCH_3), 116.00, 126.06, 126.63, 127.56, 128.52, 128.80, 129.42, 129.91, 138.87, 144.52 (C N), 157.81 (C O) ppm; IR (ATR): = 3060, 3022 (ar, CH), 1648 (C O), 1586 (C N) cm^{-1}; UV–vis (Chloroform, $c = 1.06.10^{-4}$ mol L^{-1}): λ_{max} = 245 (4030.16), 412 (5251.52) nm (mol^{-1} L cm^{-1}); $ESI^{(-)}$-MS: *m/z* (%) = 312 (M^-, 6.67), 311 [$(M-H)^-$, 36.23]. Anal. Cal. for $C_{16}H_{13}ClN_4O$: C, 61.41; H, 4.19; N, 17.91. Found: C, 61.31; H, 4.11; N, 18.12.

1-(2,4-Dimethylphenyl)-3-phenyl-4-(phenyldiazenyl)-1H-pyrazol-5(4H)-one (2a). CC (AcOEt/*n*-hexane, 1 : 3), dark orange crystals (58%), mp: 130–131°C; ^{1}H-NMR (400 MHz, $CDCl_3$): δ = 2.25 (s, 3H, CH_3), 2.32 (s, 3H, CH_3), 7.03–7.12 (m, 3H, ar), 7.15-7.25 (m, 3H, ar), 7.34–7.46 (m, 5H, ar), 8.16 (d, *J* = 6.2 Hz, 2H, ar), 13.95 (br.s., 1H, NH) ppm; ^{13}C-NMR (100 MHz, $CDCl_3$): δ = 18.35 (CH_3), 21.15 (CH_3), 117.41, 118.70, 126.61, 127.28, 127.31, 127.39, 128.57, 129.70, 130.37, 131.85, 132.77, 132.87, 134.92, 138.76, 140.32, 146.35 (C N), 158.36 (C O) ppm; IR (ATR): = 3012 (ar, CH), 1651 (C O), 1591 (C N) cm^{-1}; UV–vis (Choloroform, $c = 9.04.10^{-5}$ mol L^{-1}): λ_{max} = 250 (8978.40), 405 (7603.49) nm ($mol^{-1}Lcm^{-1}$); $ESI^{(-)}$-MS: *m/z* (%) = 368 (M^-, 10.77), 367 [$(M-H)^-$, 41.48]. Anal. Cal. for $C_{23}H_{20}N_4O$: C, 74.98; H, 5.47; N, 15.21. Found: C, 74.85; H, 5.43; N, 15.39.

4-[(4-Bromophenyl)diazenyl]-1-(2,4-dimethylphenyl)-3-phenyl-1H-pyrazol-5(4H)-one (2b). It was washed (cold EtOH) twice and dried at room temperature, light orange solid (73%), mp: 293–294° C; ^{1}H-NMR (400 MHz, $CDCl_3$): δ = (s, 3H, CH_3), 2.38 (s, 3H, CH_3), 7.10–7.15 (m, 1H, ar), 7.26–7.29 (m, 2H, ar), 7.34 (d, *J* = 9.4 Hz, 2H, ar), 7.45–7.51 (m, 3H, ar), 7.55 (d, *J* = 8.6 Hz, 2H, ar), 8.17 (dd, *J* = 1.6; 7.8 Hz, 2H, ar), 13.98 (br.s., 1H, NH) ppm; ^{13}C-NMR (100 MHz, $CDCl_3$): δ = 18.33 (CH_3), 21.46 (CH_3), 113.70, 121.12, 127.16, 127.40, 126.70, 127.29, 129.68, 130.31, 131.13, 131.80, 132.68, 132.81, 134.97, 137.00, 140.13, 146.58 (C N), 157.98 (C O) ppm; IR (ATR): = 3063, 3002 (ar, CH), 1652 (C O), 1585 (C N) cm^{-1}; UV–vis (Chloroform, $c = 1.49.10^{-4}$ mol L^{-1}): λ_{max} = 249 (4476), 407 (4615.95) nm (mol^{-1} L cm^{-1}); $ESI^{(-)}$-MS: *m/z* (%) = 447 (M^-, 100), 445 [$(M-2H)^-$, 96]. Anal. Cal. for $C_{23}H_{19}BrN_4O$: C, 61.75; H, 4.28; N, 12.52. Found: C, 61.62; H, 4.32; N, 12.58.

4,4′-[4,4′-(Ethene-1,2-diyl)bis(4,1-phenylene)]bis(diazene-2,1-diyl)bis[1-(2,4-dimethyl phenyl)-3-phenyl-1H-pyrazol-5(4H)-one] (2c). Compound **2c** was washed twice (cold Et_2O), bright red solid (69%), dp: 254–255°C; ^{1}H-NMR (500 MHz, $CDCl_3$): δ = 2.32 (*s*, 6H,CH_3), 2.37 (s, 6H, CH_3), 7.11–7.16 (m, 4H, ar and 2H, CH), 7.25–7.30 (m, 6H, ar), 7.47–7.49 (m, 8H, ar), 7.60 (d, *J* = 8.5 Hz, 2H, ar), 8.20–8.22 (d, *J* = 7.2 Hz, 4H, ar); 14.01 (s, 2H, NH) ppm; ^{13}C-NMR (125 MHz, $CDCl_3$): δ = 17.36 (CH_3), 20.14 (CH_3), 114.87, 115.41, 125.67, 126.02, 126.66, 126.32, 126.79, 126.91, 127.55, 128.59, 128.62, 130.83, 133.97, 134.11, 137.68, 145.30, 150.41 (C N), 171.75 (C O) ppm; IR (ATR): = 3028 (ar, CH), 1656 (C O), 1548 (C N) cm^{-1}; UV–vis (Chloroform, $c = 8.76.10^{-5}$ mol L^{-1}): λ_{max} = 254 (4750.17), 491 (7292.47) nm (mol^{-1} L cm^{-1}); $ESI^{(-)}$-MS: *m/z* (%) = 760 (M^-,16), 759 [$(M-H)^-$, 30]. Anal. Cal. For $C_{48}H_{40}N_8O_2$: C, 75.77; H, 5.30; N, 14.73. Found: C, 75.62; H, 5.41; N, 14.77.

4,4′-(4-Benzoyl-1,2-phenylene)bis(diazene-2,1-diyl)bis[1-(2,4-dimethylphenyl)-3-phenyl-1H-pyrazol-5(4H)-one] (2d). CC (AcOEt/*n*-hexane, 1 : 1), orange solid (58%), mp: 96–97°C; ^{1}H-NMR (500 MHz, $CDCl_3$): δ = 2.17 (s, 6H, CH_3), 2.37 (s, 6H, CH_3), 5.96 (br.s., 2H, OH), 7.08–7.12 (m, 4H, ar), 7.23–7.26 (m, 8H, ar), 7.28–7.31 (m, 4H, ar), 7.37–7.40 (m, 4H, ar), 7.83 (d, *J* = 7.9 Hz, 4H, ar) ppm; ^{13}C-NMR (125 MHz, $CDCl_3$): δ = 18.32 (CH_3), 21.16 (CH_3), 68.30, 121.24, 122.19, 124.98, 126.17, 126.63, 127.26, 127.47, 127.83, 129.16, 129.58, 130.77, 131.12, 131.79, 131.89, 133.61, 135.78, 136.91, 140.32, 143.76, 147.16, 151.33 (C N), 170.98 (C O), 194.16 (C O) ppm; IR (ATR): 3058, 3023 (ar, CH), 1584 (C O), 1511 (C N) cm^{-1}; UV–vis (Chloroform, $c = 8.73.\times 10^{-5}$ mol L^{-1}): λ_{max} = 260 (7011.23) nm (mol^{-1} L cm^{-1}); GC-MS: *m/z* (%) = 291 ($C_{17}H_{15}N_4O^{\cdot}$, 16.36), 263 ($C_{17}H_{15}N_2O$, 41), 180 [$\cdot C_6H_4(C\,O)C_6H_4^{\cdot}$, 8], 105 [$(\cdot C_6H_3(CH_3)_2)$, 19], 77 ($C_6H_5$, 25). Anal. Cal. For $C_{47}H_{38}N_8O_3$: C, 74.00; H, 5.02; N, 14.69. Found: C, 73.96; H, 5.12; N, 14.62.

1-Methyl-5-oxo-3-phenyl-4,5-dihydro-1H-pyrazole-4-carbaldehyde (3). Yellow solid in 91% yield. mp: 159–161°C (Ref. 18; 160°C).

General procedure for preparation of pyrazolone-4-carbaldehyde-hydrazone or -hydrazide. Compound **3** (10 mmol) and (2,4-dimethylphenyl)hydrazine or (4-hydroxyphenyl) benzhydrazide (10 mmol) were dissolved in EtOH (10 mL), a small amount of hot K_2CO_3 was added. The reaction was left to reflux for 4 h. Resulting solution was filtered, and the solvent was removed *in vacuo*.

4-[(2,4-Dimethylphenyl)diazenyl)methylene]-1-methyl-3-phenyl-1H-pyrazol-5(4H)-one (3a). CC (AcOEt/*n*-Hexane, 1 : 2), light orange oil (48%); ^{1}H-NMR (500 MHz, $CDCl_3$): δ = 2.32 (s, 3H, CH_3), 2.43 (s, 3H, CH_3), 3.58 (s, 3H, NCH_3), 7.04–7.11 (m, 3H, ar), 7.42–7.49 (m, 3H, ar), 7.62 (dd, *J* = 1.6; 8.3 Hz, 2H, ar), 8.14 (s, 1H, CH); ^{13}C-NMR (125 MHz): δ = 19.21 (CH_3), 21.18 (CH_3), 30.41 (NCH_3), 115.00, 116.09, 123.81, 124.01, 126.48, 127.03, 127.52, 127.83, 128.92, 129.13, 129.55, 129.67, 145.16 (C N), 158.01 (C O) ppm; IR (ATR): = 3241 (NH), 3053 (ar, CH), 1645 (C O), 1579 (C N) cm^{-1}; UV–vis (Chloroform, $c = 1.04.10^{-4}$ mol L^{-1}): λ_{max} = 242 (10727.59), 340 (8735.38) nm (mol^{-1} L cm^{-1}); GC-MS: *m/z* (%) = 305 (M^+-$CH_3^{\cdot}$, 100), 290 (M^+-2$CH_3^{\cdot}$, 9), 185 ([M^+-$NHNHPh(CH_3)_2^{\cdot}$], 28), 174 ([M^+-C $NNHPh(CH_3)_2^{\cdot}$], 2), <i. e., 77 ($C_6H_5^{\cdot}$, 7),>. Anal. Cal. For $C_{19}H_{20}N_4O$: C, 71.23; H, 6.29; N, 17.49. Found: C, 71.29; H, 6.17; N, 17.53.

4-[((4-Hydroxyphenyl)diazenyl)methylene]-1-methyl-3-phenyl-1H-pyrazol-5(4H)-one (3b). CC (AcOEt/EtOH, 5 : 1), yellow solid (41%), dp: 181–183°C; ^{1}H-NMR (500 MHz, CD_3OD): δ = 3.48 (s, 3H, NCH_3), 4.47 (br.s., 1H, OH), 6.74–6.84 (m, 2H, ar and 1H, CH), 7.10–7.41 (m, 5H, ar), 7.62 (d, *J* = 7.8 Hz, 2H, ar) ppm; ^{13}C-NMR (125 MHz, CD_3OD): δ = 30.47 (NCH_3), 116.01, 117.22, 121.87, 123.77, 124.15, 126.76, 127.61, 128.69, 129.51, 144.84 (C N), 154.25, 165.07 (C O), 158.11 (C O); IR (ATR): = 3270 (NH), 3196 (OH), 2926 (ar, CH), 1607 (NC O), 1588 (N N C O), 1538 (C N) cm^{-1}; UV–vis (Methanol, *c* = 1.99.10^{-4} mol L^{-1}): λ_{max} = 209 (3768.30), 255 (6671.90) nm (mol^{-1} L cm^{-1}); GC-MS: *m/z* (%) = 334 (M^+, 24), 256 ([(M^+-1)-Ph], 20), <i.e,. 172 [(M^+-$C_8H_6N_2O_2$··), 27],> 121 ([(C O(C_6H_4) OH)·], 32), 77 (C_6H_5, 67). Anal. Cal. for $C_{18}H_{14}N_4O_3$: C, 64.66; H, 4.22; N, 16.76. Found: C, 64.70; H, 4.11; N, 16.81.

2-(1-Methyl-5-oxo-3-phenyl-1H-pyrazol-4(5H)-ylidene)-3-phenylthiazolidin-5-one (4). Yellow solid in 63% yield. mp: 179–181°C (Ref. 8; 179–181°C).

2-(1-Methyl-5-oxo-3-phenyl-1H-pyrazol-4(5H)-ylidene)-3-phenyl-4-(phenyldiazenyl)thiazolidin-5-one (4a). CC (AcOEt/*n*-hexane, 2 : 1), yellow solid (45%), dp: 163–164°C; ^{1}H-NMR (400 MHz, $CDCl_3$): δ = (s, 3H, NCH_3), 6.91–7.15 (m, 10H, ar), 7.29–7.57 (m, 5H, ar), 8.42 (br.s., 1H, NH); ^{13}C-NMR (100 MHz): δ = 32.16 (NCH_3), 101.47, 103.92, 112.56, 119.42, 126.64, 127.45, 128.00; 128.36, 128.86, 132.67, 134.13, 134.25, 138.71, 138.94, 147.93 (C N), 148.26, 167.23 (NC O), 196.02 (SC O) ppm; IR (ATR): = 3174 (NH), 3112, 3059 (ar, CH), 1734 (SC O), 1635 (NC O), 1584 (C N) cm^{-1}, UV–vis (Chloroform, *c* = 7.35.× 10^{-5} mol L^{-1}): λ_{max} = 312 (10453.46), 465 (10711.42) nm (mol^{-1} L cm^{-1}); ESI$^{(-)}$-MS: *m/z* (%) = 453 (M^-, 12.61), [452 (M-H)$^-$, 43.82]. Anal. Cal. for $C_{25}H_{19}N_5O_2S$: C, 66.21; H, 4.22; N, 15.44; S, 7.07. Found: C, 66.17; H, 3.98; N, 15.64; S, 7.16.

2-(1-Methyl-5-oxo-3-phenyl-1H-pyrazol-4(5H)-ylidene)-4-(phenyldiazenyl)-3-[4-((phenyldiazenyl)phenyl)]thiazolidin-5-one (4b). CC (AcOEt/*n*-hexane, 5 : 2), yellow solid (39%), dp: 150°C; ^{1}H-NMR (400 MHz, $CDCl_3$): δ = 3.32 (s, 3H, NCH_3), 6.74 (d, *J* = 7.8 Hz, 2H, ar), 6.82 (d, *J* = 7.8 Hz, 2H, ar), 6.87–7.10 (m, 9H, ar), 7.24–7.30 (m, 6H, ar), 9.45 (br.s., 1H, NH) ppm; ^{13}C-NMR (100 MHz): δ = 32.91 (NCH_3), 101.87, 103.15, 112.42, 113.16, 118.21, 118.98, 125.97, 126.93, 127.81, 128.12, 128.44, 129.01, 132.41, 133.95, 134.16, 138.48, 138.91, 142.65, 148.12, 148.78 (C N), 168.36 (NC O), 195.95 (SC O) ppm; IR (ATR): = 3360 (NH), 3034 (ar, CH), 1731 (SC O), 1682 (NC O), 1601 (C N) cm^{-1}; UV–vis (Chloroform, *c* = 1.19.10^{-4} mol L^{-1}): λ_{max} = 244 (11811.59), 401 (5778.23) nm (mol^{-1} L cm^{-1}); ESI$^{(-)}$-MS: *m/z* (%) = 578 [(M+Na-2H)$^-$, 6.17], 277 [(M/2-1)$^{-2}$, 32.78] Anal. Cal. For $C_{31}H_{23}N_7O_2S$: C, 66.77; H, 4.16; N, 17.58; S, 5.75. Found: C, 66.81; H, 4.20; N, 17.64; S, 5.61.

4-[(2-Hydroxyphenyl)diazenyl]-2-(1-methyl-5-oxo-3-phenyl-1H-pyrazol-4(5H)-ylidene)-3-phenylthiazolidin-5-one (4c). CC (AcOEt/*n*-hexane, 1 : 3), dark yellow solid (61%), dp: 150°C; ^{1}H-NMR (400 MHz, $CDCl_3$): δ = 3.76 (s, 3H, NCH_3), 7.21–7.26 (m, 5H, ar), 7.31–7.33 (m, 4H, ar), 7.52–7.56 (m, 3H, ar), 7.62–7.63 (m, 2H, ar), 8.56 (br.s., 1H, NH), 12.86 (s, 1H, OH) ppm; ^{13}C-NMR (100 MHz): δ = 32.28 (NCH_3), 101.54, 105.51, 106.31, 110.24, 112.45, 118.57, 126.64, 127.69, 128.57, 129.13, 129.25, 134.46, 134.87, 136.71, 138.91, 139.13, 148.16 (C N), 148.67, 168.12 (NC O), 196.14 (SC O) ppm; IR (ATR): = 3342 (NH), 3170 (OH), 3059 (ar, CH), 1733 (SC O), 1687 (NC O), 1592 (C N) cm^{-1}; UV–vis (Chloroform, *c* = 1.41.× 10^{-4} mol L^{-1}): λ_{max} = 313 (4121.63), 504 (4295.10) nm (mol^{-1} L cm^{-1}); GC-MS: *m/z* (%) = 469 (M^+, 28), 452 [(M^+-OH·), 25], 122 ($C_6H_6N_2O$··, 32). Anal. Cal. For $C_{25}H_{19}N_5O_3S$: C, 63.95; H, 4.08; N, 14.92; S, 6.83. Found: C, 64.03; H, 3.96; N, 14.83; S, 6.95.

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