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Simple route to a novel class of pyrazolidine-3,5-dione based azo dyes

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ABSTRACT

We report an easiest synthesis strategy of a new class of synthetic dyes by coupling of functionalized pyrazolidine-3,5-dione derivatives via diazotization reaction with aromatic diamine for the azoic dyes or via dimerization reaction to synthesize the H chromophore dyes. Electron delocalization between the two coupled components has been studied using UV–vis spectroscopy, infrared, and NMR spectroscopy. In addition, the formation mechanism of such compounds has been discussed.

1. Introduction

Heterocycles are an inescapable and integral feature of numerous diverse fields of chemistry.[1] The organic dye chemistry is not an exception; heterocycles have been widely used in disperse dye chemistry. Azo dyes containing heterocyclic rings lead to brighter and deeper shades than their benzene analogues.[2] They are still very important for application in disperse dyes for different fibers.[3] Nitrogen heterocycles present a special interest because they constitute an important class of natural and non-natural products, many of them exhibit useful biological activities and unique electrical and optical properties.[4–8] For example, pyrazolidine-3,5-dione derivatives are one of these nitrogen heterocycles, which are generally well-known as a part of the five-membered nitrogen-containing heterocyclic compounds. Pyrazolidine-3,5-dione derivatives are pyrazole derivatives, which have an additional keto (C=O) group, and take an important role as substructures of numerous pharmaceuticals and compounds with biological activities.[9–11] Moreover, they are capable of prototropic tautomerism.[12] Furthermore, pyrazole derivatives have been used widely as whitening or brightening reagents for synthetic fibers.

On the other hand, 1,2,4-triazole is one of the isomeric chemical compounds, called triazoles, which have a five-membered ring of two carbon atoms and three nitrogen atoms. 1,2,4-Triazole derivatives are the principal aromatic heterocycles, which have been employed in a wide range of applications,[12] especially as antifungals.[13] The recent literature concerning 1,2,4-triazole-based dyes reports their application to hydrophobic fibers and their high dyeing properties.[14]

Due to the anticipated importance of these compounds and our interest to develop heterocycle-based chromophores, we report in this study the synthesis of some new heterocycle chromophores based on pyrazolidine-3,5-dione and 1,2,4-triazole cores, including three azo dye classes **8a–d**, **8e–h**, and **10a–d**, respectively, and H-chromophore dyes (**12a–d**) based on pyrazolidine-3,5-dione (Fig. 1). Our purpose is to develop new organic functional materials by satisfactory combination of pyrazolidine-3,5-dione groups through appropriate molecular design and synthesis.

2. Results and discussion

2.1. Synthesis of the pyrazolidine-3,5-dione based azo dyes

Pyrazolin-3,5-dione has been chosen for its capacity to form an azo bond with another pyrazolin-3,5-dione, or an aromatic amine derivative by diazotization reaction. This reactivity is due to the presence of a hydrogen atom in the alpha position of the carbonyl group (C-4) of pyrazolin-3,5-dione. A collection of four pyrazolin-3,5-dione derivatives has been prepared as building blocks for the synthesis of the new pyrazolin-3,5-dione dyes. Hydrazine derivatives **3b–d** have been obtained usually by following the procedures reported in the literature.[15–17] Hydrazinolysis of the malonyl dichloride **2** with hydrazine derivatives **3a–d** in THF affords the respective pyrazolidine-3,5-diones **4a–d** in 89–93% yields (Scheme 1).

The synthetic sequences for the new dyes **8a–h** are outlined in Scheme 2. The diazotization reaction of the 4-aminoaniline, and 1-

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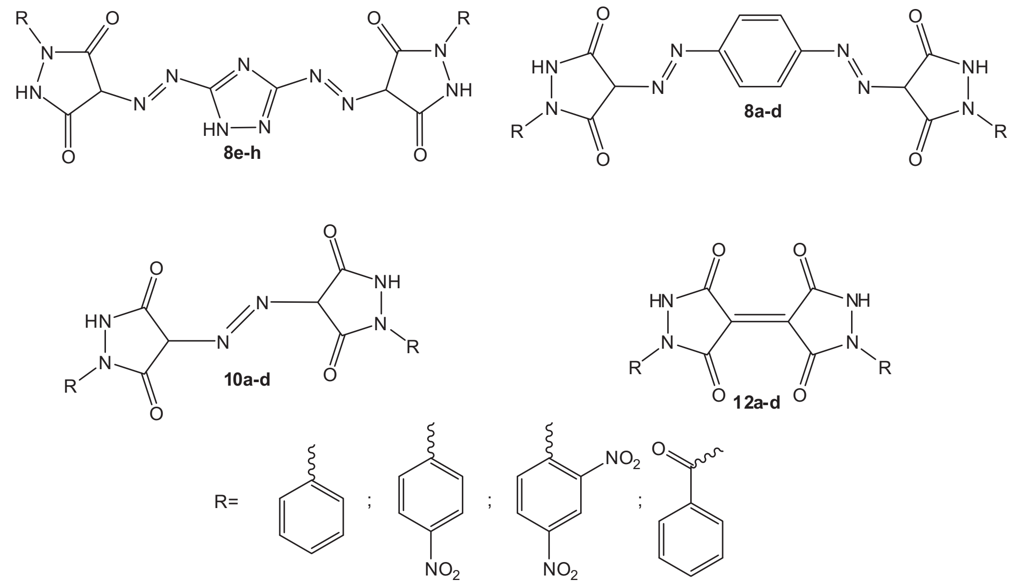
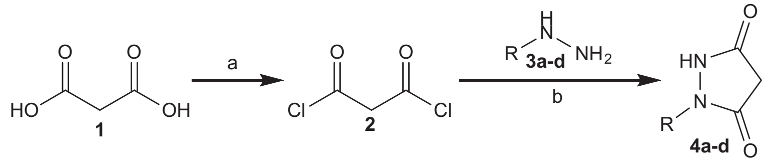
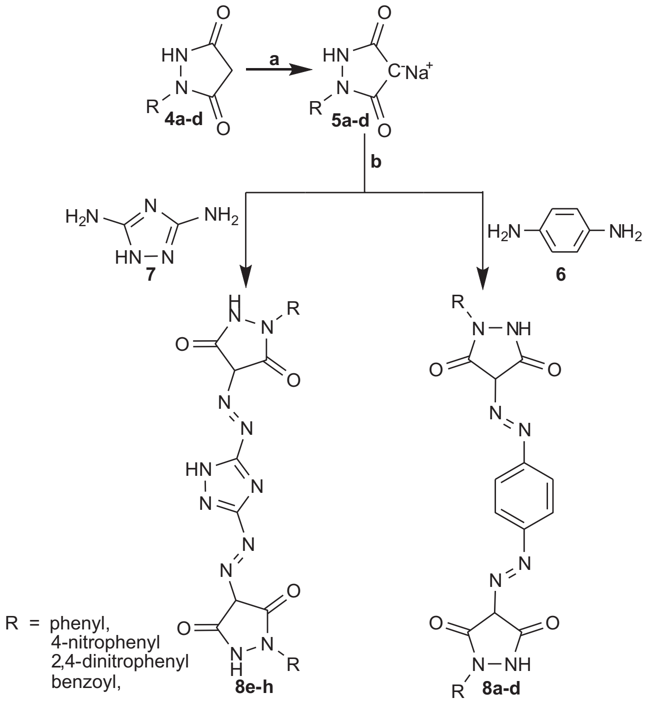


Figure 1. The molecular structures of the heterocyclic chromophores.



Scheme 1. Synthesis of the pyrazolidine-3,5-dione derivatives via coupling of malonic acid and hydrazine derivatives. Reagents and conditions: (a) $SOCl_2$, DCM, rt, 12 h; (b) THF, rt, 12 h, 89–93%.



Scheme 2. Synthetic sequences for dyes **8a**–**h**. Reagents and conditions: (a) sodium acetate, THF/H_2O; (b) $NaNO_2$, HCl 1 N, H_2O, 0 °C–rt, 12 h, 90–94%.

H-1,2,4-triazole-3,5-diamine in the presence of sodium nitrite, HCl 37% and water as solvents at 0 °C gives the corresponding bis-diazonium salts which treated with pyrazolidine-3,5-dione sodium salt **5a–d** afford the new dyes **8a–h** in 90–94% yields.

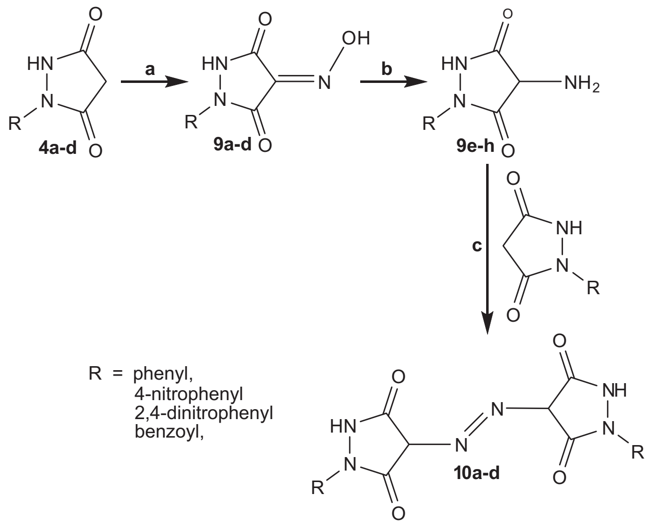
The treatment of the pyrazolidine-3-5-dione derivatives **4a–d** with sodium nitrite in aqueous solution of concentrated HCl at 0 °C affords the corresponding oxime derivatives **9a–d.** The reduction of the oxime group of compounds **9a–d** to the corresponding 4-amino pyrazolidine-3-5-dione **9e–h** is carried out in the presence of zinc dust and ammonium chloride in the methanol and under reflux for several hours.

Dyes **10a–d** are prepared in one pot from pyrazolidine-3,5-diones **4a–d** and the prepared 4-amino pyrazolidine-3-5-dione derivatives **9e–h** in high yields via diazotization reaction in the presence of sodium nitrite in a HCl solution (1 N) (Scheme 3)**.**

The dyes **8a–h** exist in different possible tautomeric forms, namely azoketo forms **A**, azo-enol form **B** and hydrazone-keto form **C** in Figure 2.

^{1}H NMR spectroscopy of the dyes **8a–d** shows only peaks of aryl protons (8.11–7.73 ppm), and a highly characteristic destabilized proton at 13.80 ppm for the hydrogen bond N–H peaks and there are no signals in the 4–6 ppm region corresponding to the proton that bears in the position C-4. These NMR data proved that the hydrazo-keto tautomers form **C** are the synthesized dyes due to their stabilization by intramolecular hydrogen bond (Table 1).

Furthermore, FTIR spectra of compounds **8a–h**, show C=O and N–H stretching vibrations at 3340 (N–H str) and at 1663 (C=O str), consistent with their existence in the keto-hydrazone tautomeric form **C** in the solid state (Table 1). We can conclude the same tautomeric form for the pyrazolidine-3-5-dione azo part in the **8e–h** dyes, where the hydrogen bears by the N=N–H bond is stabilized by the oxygen of one of both carbonyl groups present in the pyrazolidine-3-5-dione moiety (Fig. 3).



Scheme 3. Synthetic schemes for dyes **10a–d**. Reagents and conditions: (a) $NaNO_2$, HCl 1 N, H_2O, 0 °C, 10 h; (b) Zn, MeOH, NH_4Cl, reflux, 4 h; (c) $NaNO_2$, HCl 37%, H_2O, 0 °C–rt, 12 h.

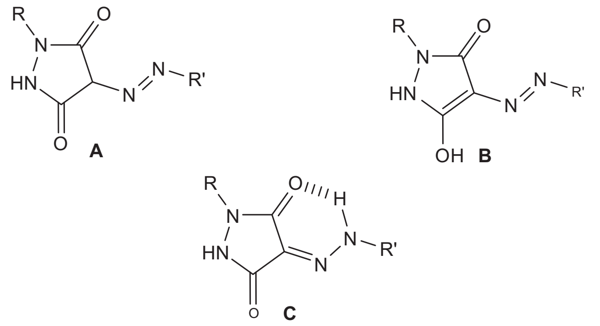


Figure 2. Tautomeric forms of azo-pyrazolidine-3-5-dione dyes.

2.2. Synthesis of the H-chromophore dyes pyrazolidine-3-5-dione based

The majority of dyes belong to the chromophoric class known as the donor–acceptor system, the essential structure of such systems being the presence of one or more electron donating groups conjugated to one or more electron withdrawing groups via an unsaturated bridge. Visible light absorption is then associated with the displacement of the electron density from the donor region of the molecule to the acceptor region. Moreover, the H-chromophores named **12a–d** in Scheme 4 are a special type of donor–acceptor system, where the cross conjugated chromophore described as basic color-producing system consists of a C═C double bond substituted by two opposing donor and acceptor groups. The inherent cross conjugation of the molecule has been recognized as responsible of the high batochromicity of these systems.[18] These donor–acceptor systems are called 'H-chromophore' due to its structural geometry[19], which can be easily synthesized by dimerization of the pyrazolidine-3-5-dione units. The bis-pyrazolin-3,5-dione dyes have been easily synthesized by dimerization of the pyrazolidine-3-5-dione derivatives. The deprotonation of C-4 of the pyrazolidinedione derivatives **4a–d** under basic conditions, using 2 equiv of sodium hydride as a base, affords the corresponding bi-carbanion **11a–d** as an electron donor. On the other hand, the di-bromination of the same pyrazolidine-3-5-dione **4a–d** with Br_2 under acidic conditions yields the 4,4′-dibromo-pyrazolidine-3-5-dione derivatives **11a–d** as an electron acceptor. The new H-chromophore dyes **12a–d** have been synthesized by the coupling step of the bis-carbanions **11e–h** with the 4,4-dibrominated pyrazolidinedione derivatives **11a–d** (Scheme 4).

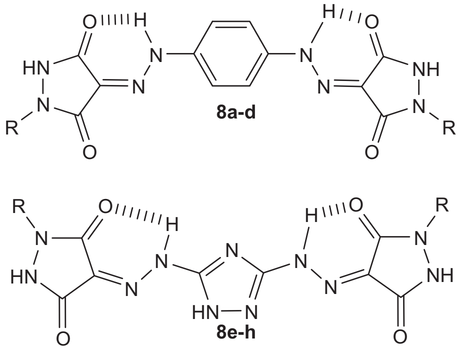


Figure 3. Stable tautomer form of the **8a–h**.

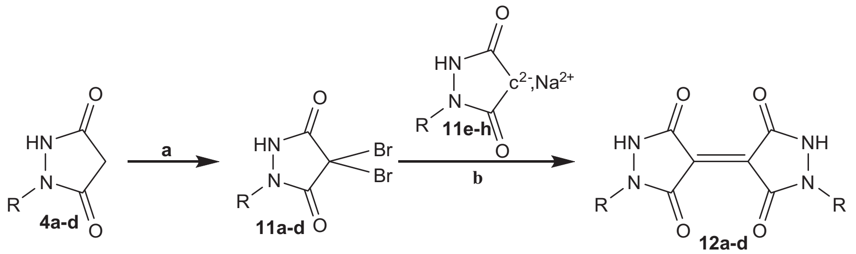
2.3. UV-vis study

The general structures of the target molecules are showed in Figure 1. These molecules consist of a typical D-π-A-π-D structure, where the substituted phenyl pyrazolidine-3-5-dione, phenyl or triazole, and azo groups are employed as donor (D), p-conjugated center (p), and acceptor (A) moieties, respectively. Moreover, such a structural modification could be expected to result in notable changes in the π-conjugated length and red shifts in the absorption spectra. UV–vis absorption spectra of these molecules in diluted DMSO solutions (2×10^{-5} M) are given in Table 2. It can be noticed from Table 2 that the compounds comprise two bands in the wavelength range from 250 to 590 nm, while no linear absorption is observed beyond 600 nm. The bands at short wavelength (250–280 nm) correspond to the localized π–π^* transition of the phenyl or substituted phenyl moieties, while the long wavelength bands

Table 1
Spectroscopic data of dyes **8a–h**

Dyes	^{1}H NMR[a]		FTIR		
	N–H signals	Aroms–H	ν_{N-H}	ν_{Arom-H}	$\nu_{C=O}$
8a	13.4	7.65–7.33 (m, 8H), 6.91–6.89 (m, 2H), 6.31–6.22 (m, 4H)	3340	3049	1663
8b	13.4	8.16–8.21 (m, 4H), 7.15–7.11 (m, 4H), 6.31–6.21 (m, 4H)	3342	3050	1660
8c	13.3	8.74–7.53 (m, 6H), 6.33–6.21 (m, 4H)	3341	3052	1661
8d	13.4	8.06–7.96 (m, 4H), 7.88–7.77 (m, 6H), 6.32–6.21 (m, 4H)	3340	3050	1659
8e	13.3	7.66–7.33 (m, 8H), 6.92–6.87 (m, 2H)	3341, 3339	3049	1660
8f	13.4	8.26–8.21 (m, 4H), 7.15–7.10 (m, 4H)	3340, 3336	3051	1655
8g	13.4	8.74–7.54 (m, 6H)	3341, 3337	3049	1657
8h	13.4	8.07–7.95 (m, 4H), 7.88–7.77 (m, 6 H)	3330, 3333	3051	1659

[a] The ^{1}H NMR spectrums are carried out in $CDCl_3$ as the solvent.



Scheme 4. Synthetic sequences for the H-chromophore dyes **12a–d**. Reagents and conditions: (a) AcOH, Br_2, 0 °C–rt, 12 h (b) NaH, THF, rt, 12 h.

Table 2
Spectral properties of the pyrazolidine-3-5-dione dyes in different solvents

Dyes	Dimethyl sulfoxide		Acetonitrile		Chloroform	
	λ_{max} (nm)	ε (M^{-1} cm^{-1})	λ_{max} (nm)	ε (M^{-1} cm^{-1})	λ_{max} (nm)	ε (M^{-1} cm^{-1})
8a	369	27165	361	26563	365	27675
8b	414	29574	406	28444	408	28923
8c	438	30473	428	28175	433	27895
8d	404	28562	399	27482	401	27057
8e	377	38756	366	35278	371	34156
8f	429	40973	411	37785	417	38359
8g	443	43883	432	41674	439	42383
8h	418	39563	401	37438	411	37643
10a	377	28342	369	27894	372	26735
10b	421	30174	411	29016	419	28563
10c	451	33564	435	31734	441	32153
10d	417	29749	405	28093	412	27538
12a	521	31467	511	30728	525	29649
12b	547	33583	523	31629	537	32555
12c	573	34538	559	32853	566	33945
12d	522	32376	513	31004	518	29624

with λ_{max} ranging from 369 to 573 nm can be assigned to the intramolecular charge-transfer transitions, which involve the whole electronic system of the compounds with a considerable charge-transfer character, which originate mainly from the substituted phenyl moiety and pointing toward the azo group. The position of this band is strongly influenced by the structure of the compounds, for example, the type of substitution pattern in the donor and the acceptor moieties. Communication between the electron donating and accepting termini can be evaluated by comparing the λ_{max} values. The influence of the strength of the acceptor group is demonstrated by comparing the absorption maximum of compounds **8a, 8b**, and **8c** as the longest wavelength transition is shifted from 369 nm in **8a** (Table 2, dye **8a**), 414 nm for **8b (**Table 2, dye **8b)** to 438 nm for **8c** (Table 2, dye **8c**). This difference might be attributed to the stronger electron-withdrawing effect of the nitro group.

The effect of the solvent polarity on the optical properties of the dyes synthesized in this study has been investigated, because many azo dyes depend on the solvent polarity, and their optical characteristics change (Table 2). All of the synthesized dyes exhibited some small blue shifts along with a decreased solvent polarity and optical characteristic of the pyrazolidine-3,5-dione dyes exhibited similar trends but these dyes don't show regular variations with the polarity of solvents (solvent polarity: DMSO > acetonitrile > chloroform).

3. Conclusions

In summary, we have achieved the first synthesis of a series of azo and *H*-chromophore dyes pyrazolidine-3-5-dione-based **8a–h**, **10a–b**, and **12a–d**, and have measured their UV–vis absorptions. By comparing the derivatives synthesized, it can be noticed that the withdrawing group on the phenyl-azo moiety and the type of substituent on the nitrogen atom of the pyrazolidine-3-5-dione ring have significant influence on the UV–vis absorption properties.

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Supplementary data

Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.tetlet.2010.08.002.

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