

Contents lists available at ScienceDirect

# Dyes and Pigments



journal homepage: http://www.elsevier.com/locate/dyepig

# Barbituric acid-based mono/bi-heterocyclic dyes showing distinct spectral behaviors induced by solvents and pH



Xiaolei Zhao<sup>a, c</sup>, Wei Zheng<sup>c</sup>, Xuepei Miao<sup>a</sup>, Wei Huang<sup>b, c, \*</sup>

<sup>a</sup> Research Center of Resources and Environment, School of Chemical Engineering and Materials, Changzhou Institute of Technology, Changzhou, Jiangsu Province, 213032. PR China

<sup>b</sup> Shenzhen Research Institute of Nanjing University, Shenzhen, Guangdong Province, 518057, PR China

<sup>c</sup> State Key Laboratory of Coordination Chemistry, School of Chemistry and Chemical Engineering, Nanjing University, Nanjing, Jiangsu Province, 210093, PR China

### ARTICLE INFO

Keywords: Mono/bi-heterocyclic dyes Barbituric acid Hydrazone form Deprotonated azo anion Solvatochromism TD-DFT calculation

# ABSTRACT

A series of barbituric acid-based heterocyclic dyes were prepared and fully characterized by ESI-MS, NMR and UV–Vis absorption spectroscopy. UV–Vis spectral comparisons reveal that in contrast to mono-heterocyclic dyes the absorption maxima of barbituric acid-based bi-heterocyclic dyes display significantly bathochromic shifts in wavelength due to the increasing  $\pi$ -conjugated system within the whole molecules. The effects of varying solvent media on the absorption spectra of this group of dyes were investigated, in which bi-heterocyclic dyes are liable to be affected by nature of solvents and present distinct solvatochromism in four kinds of organic solvents. Our results demonstrate that though the equilibrium between the hydrazone and deprotonated azo anion can be driven by pH values for this group of barbituric acid-based heterocyclic dyes, the acid-base effect on their absorption spectra behave differently. In order to further elucidate their different structural and spectral behavior, time-dependent density functional theory (TD-DFT) calculations with the implicit solvent model (SMD) were performed.

#### 1. Introduction

Azo dyes containing heterocyclic moieties have been the focus of research due to their modified dying power and optical properties compared with their benzenoid counterparts. The influence of heteroatoms on the low aromaticity and hyperpolarizibility together with the dependence of energy levels on substituents are the most important characteristics for heterocyclic dyes to achieve various photophysical properties [1]. In recent decades, the usage of various heterocyclic diazo and coupling components such as thiophene [2], thiazole [3], benzoquinoline [4] as well as pyridine [5] has become popular in synthesizing of hetarylazo dyes because they exhibit high tinctorial strength and brightness relative to analogues aromatic dyes.

Since it was first reported by Adolf von Baeyer in 1864, barbituric acid (BA) and its derivatives are widely used in therapic areas ranging from simple sedation to cancer treatment [6–8]. Azobarbituric acid derivatives, which are synthesized using barbituric acids as coupling components, could show various tautomeric structures under acidic or alkaline conditions [9,10]. These compounds are distinguished by great hiding power, high tinctorial strength and light fastness which all indebt

to their tautomeric structures. In this regard, they are used as pigments in distempers, printing inks or emulsion paints. Although, many patents and papers describe the synthesis and properties of BA based mono-heterocyclic dyes [9,11–14] developing new bi-heterocyclic dyes with distinctive photo-physical properties derived from BA are needed in the field of industrial and scientific applications. In contrast to the benzene-containing partial heterocyclic dyes, bi-heterocyclic dyes not only present significant bathochromic shifts on account of their increasing  $\pi$ -conjugated system, but also are susceptible to solvent nature, substituents, pH and others, thus showing abundant photo-physical performance [15–18].

As the photo-physical performance of the heterocyclic dyes is strongly related to their tautomeric equilibria and structures, the study on tautomeric phenomenon of heterocyclic dyes is one of the most interesting fields in dye chemistry. In our previous work, a series of mono- and bi-heterocyclic dyes based on pyrazolone and pyridone derivatives have been studied and their corresponding hydrazone-azo tautomerism driven by pH were investigated via UV–Vis and NMR spectroscopy [19–22]. However, the precise elucidation and assignments of the spectroscopic signs of azo or hydrazone form in various

https://doi.org/10.1016/j.dyepig.2020.109087

Received 12 November 2020; Received in revised form 10 December 2020; Accepted 10 December 2020 Available online 25 December 2020 0143-7208/© 2020 Elsevier Ltd. All rights reserved.

<sup>\*</sup> Corresponding author. Shenzhen Research Institute of Nanjing University, Shenzhen, Guangdong Province, 518057, PR China. *E-mail address:* whuang@nju.edu.cn (W. Huang).

environments for heterocyclic dyes are still incomplete. For example, though barbituric acid-based heterocyclic dyes showcase distinct solvatochromic shifts of the absorption maxima induced by different solvents, their spectral behavior have not been analyzed from theoretical viewpoints in order to obtain a deeper insight into spectral and structural properties.

With this in mind, we report a family of BA based mono/biheterocyclic dyes and present their photophysical properties. The main concerns behind our investigation are as follows: one is comprehensive spectral comparisons on mono- and bi-heterocyclic dyes with the change of  $\pi$ -conjugated molecule system. The other is to characterize effects of acidic/alkaline media and solvents on the proton transfer of the hydrazo group between the solute and the solvent. Herein, two aromatic heterocyclic amine and two aniline derivatives were used as the diazo components to respectively couple with 1,3-dimethyl-pyrimidine-2,4,6-trione to produce mono-heterocyclic dyes 1–2 and bi-heterocyclic dyes 3-5 (Scheme 1). Notably, the absorption maxima of BA based hetarylazo dyes are affected by their conjugate system. Moreover, the pH titration and solvatochromism experiments indicate that the monoand bi-heterocyclic dves exist in different structural species and therefore showcase distinguishable spectral behavior. Further theoretical calculation results manifest that the most probably preferred form of the heterocyclic dyes in solution is in agreement with the experimental data. To the best of our knowledge, no such detailed investigations of monoand bi-heterocyclic dyes based on BA derivatives were performed before, especially by using combined experimental and theoretical approach, which definitely confirm the structural state of each of the studied compounds in different media.

## 2. Results and discussion

# 2.1. Syntheses and spectral characterizations

As seen from Scheme 1, BA based mono- and bi-heterocyclic dyes 1-4 were synthesized via the diazotization and succeeding coupling reactions between 4-methoxy-2-nitroaniline/2,3-dimethylaniline/5-nitrobenzo [c] isothiazol-3-amine/2-amino-4-chloro-5-formylthiophene-3-carbonitrile and 1,3-dimethyl-pyrimidine-2,4,6-trione, respectively. The key step of the synthesis is that the coupling component 1,3-dimethyl-pyrimidine-2,4,6-trione should be dissolved in aqueous solution of sodium hydroxide to forma barbiturate enolate anion to obtain higher yields for the target compounds. In this study, distinguishable arylamines were used as the diazo components to explore the impact of molecular conjugated system on their original UV-Vis spectra, while the barbituric acid was used as the coupling component to explore the influences of different acid-base media on the change of their multiple tautomers. In general, better solubility may be more conducive to crystallizing the target compound. Thus, the methylal derivative 5 was synthesized (Scheme 1) to improve the solubility of its reaction precursor 4 in nonpolar solvent and the corresponding single crystals could be isolated for further structural characterization.



Scheme 1. Synthetic route of compounds 1-5.

Because of poor solubility of dyes 1–4, their <sup>1</sup>H NMR spectra were recorded in DMSO-d<sub>6</sub> solution. However, the <sup>13</sup>C NMR spectra of compounds 1 and 2 could not be acquired even after several attempts due to low solubility of the dyes. In <sup>1</sup>H NMR spectra of BA based monoheterocyclic dyes 1-2, a signal of 14.61-15.27 ppm appearing at a lower field should be attributed to the proton of the N-H group, which stems from the hydrazone tautomer and can be interpreted by the strong intramolecular H-bonding between C=O and N-H groups. Regarding this, the predicted structures of dyes 1-2 in DMSO should exist in the hydrazone form. Comparably, the absence of hydrazone proton peaks in bi-heterocyclic dyes 3 and 4 implies that they exist as the deprotonated azo form. The aldehyde proton apparent in dye 4 at 9.75 ppm was replaced by the acetal CH(OMe)<sub>2</sub> proton at 5.59 ppm in 5. Furthermore, a new peak at 15.10 ppm assigned as the hydrazone proton could be observed in dye 5 in nonpolar solvent CDCl<sub>3</sub>. It is deduced that the structures of BA based bi-heterocyclic dyes can be affected by properties of organic solvents, where the hydrazone form is dominating in nonpolar solvent while the azo-form is preferential in the basicity character of DMSO solvent.

In order to uncover the effects of molecular conjugated system and solvents on their structural alterations, the solvatochromism of dyes **1–4** is studied in four organic solvents with different properties. As seen in Fig. 1 and Table 1, the prime wavelengths of four BA based heterocyclic dyes are different for the absorption maxima in MeOH. For mono-heterocyclic dye **1**, the  $\lambda_{max}$  value of 434 nm assigning to  $\pi$ – $\pi$ \* transition within the whole molecule displays a significant bathochromic shift of 36 nm relative to dye **2** ( $\lambda_{max} = 398$  nm), which can be assigned that the –NO<sub>2</sub> group in dye **1** rendering the molecule more polar and therefore experiences more solvent-solute interactions [10]. In contrast to mono-heterocyclic dyes, the prime maxima of bi-heterocyclic dyes **3** and **4** in the range of 497–539 nm indicate that the more delocalized  $\pi$ –conjugated system facilitates the  $\pi$ – $\pi$ \* transition in the whole molecule, and consequently leading a greater bathochromic shift.

Secondly, mono-heterocyclic dyes 1-2 are hardly responsive to solvatochromism, while distinguishable red shifts of the absorption maxima values can be observed in bi-heterocyclic dyes 3-4, where large red shifts of 119 and 95 nm from CHCl<sub>3</sub> to DMSO are found, respectively. Another important feature is that more than one absorption peak with different absorption strength could be noticed in dye 1. This characteristic might be due to the formation of two tautomers in dye 1, where



Fig. 1. Normalized UV–Vis absorption spectra for dyes 1 (a), 2 (b), 3 (c) and 4 (d) in four organic solvents at room temperature.

# Table 1

The  $\lambda_{max}$  values (nm) of compounds 1–4 in four organic solvents.

Compound	$\lambda_{\rm max}$ (CHCl <sub>3</sub> )	$\lambda_{\rm max}$ (CH <sub>3</sub> OH)	$\lambda_{\rm max}$ (DMF)	$\lambda_{\rm max}$ (DMSO)
1	437	434	375/432	379/439
2	403	398	395	397
3	463	539	583	582
4	421	497	514	516

the absorption band at longer wavelengths is due to the hydrazone form while the peak observed at shorter wavelength is attributed to  $\pi$ - $\pi$ \* transition of azo group (Scheme 2) [23]. The increasing ratio of azo tautomer for mono-heterocyclic dye **1** is probably due to the unstable excited state of  $\pi$ - $\pi$ \* transition of azo tautomer with increasing solvation by a polar solvent [1]. For mono-heterocyclic dye **2**, the lack of spectral changes can only mean that the hydrazone tautomer always exists even if the used solvents differ substantially. In the cases of bi-heterocyclic dyes **3**-**4**, the  $\lambda_{max}$  values appearing at 463 and 421 nm in CHCl<sub>3</sub> should be attributed to the  $\pi$ - $\pi$ \* electronic transition within the whole molecule in the hydrazone form, which has been clearly confirmed by the above-mentioned <sup>1</sup>H NMR spectra of dye **5**. Evidently, the hydrazone form in CHCl<sub>3</sub> has been converted to the azo anion form under the high basicity character of DMSO and DMF, owning to the proton migration of the hydrazone group between the solute and the solvent.

pH Titrations are powerful tools to specify the exact structural species under different pH values for heterocyclic dyes. As seen in Fig. 2a and b, the BA based mono-heterocyclic dyes 1-2 exhibited acid-base behavior. It is observed that when certain amounts of diluted hydrochloric acid were added to the dye solutions in methanol, the absorption peaks at  $\lambda_{max} = 431$  nm in dye **1** and 398 nm in dye **2** show no noticeable shifts, indicating that these compounds in methanol always exist in their hydrazone form. The shortest absorption peaks observed in the range of 250–277 nm can be assigned as  $n-\pi^*$  transitions between the phenyl rings and the middle hydrazone units. When the pH increases from 6.67 to 12.37 by addition with certain amounts of diluted NaOH solution, the main absorption maxima disappear while two new blue-shifted maxima centered at 358 and 359 nm emerge. This phenomenon clearly suggests that the hydrazone form has changed to its deprotonated azo anion in the basic solution. To ulteriorly prove our conjecture, <sup>1</sup>H NMR spectra of dye 2 in  $CD_3OD-d_4$  with and without base were provided. As can be shown in Fig. SI14, two single peaks at  $\delta = 3.38$  and 3.40 ppm can be attributed to methyl protons of barbituric ring. When certain amounts of NaOH were added to the dye solution in  $CD_3OD-d_4$ , the previous two single peaks are completely converted to one single peak at  $\delta = 3.38$  ppm in the <sup>1</sup>H NMR spectra (Fig. SI15), clearly indicating the conformation of deprotonated azo anion. In contrast, <sup>1</sup>H NMR spectra of dye **1** are not available since the solubility of dye 1 in  $CD_3OD-d_4$  is very poor. Additionally, clear isoabsorptive points at 252/300/388 and 246/264/372 nm in the spectra of dyes 1 and 2 indicate an equilibrium between hydrazone and deprotonated azo form (Fig. SI16).

It is observed that BA based bi-heterocyclic dyes **3–4** are not responsive to base while they are very sensitive to acid, as shown in Fig. 2c and d. With addition of diluted hydrochloric acid to the solution, the absorption bands at 539 nm in **3** and 497 nm in **4** weaken and two new peaks at 457 and 413 nm emerge, respectively. Moreover, the absorption bands at 539 and 497 nm disappear completely under strong acidic conditions. The most reasonable explanation is based on formation of the preponderant azo anion for bi-heterocyclic dyes **3–4** in MeOH and therefore they are unlikely to be ionized under the basic condition.



Scheme 2. Possible two tautomers of dye 1.



Fig. 2. UV–Vis absorption spectra for compounds 1 (a), 2 (b), 3 (c) and 4 (d) at different pH values in MeOH at room temperature.

This form is readily to be protonated under acidic condition, and therefore, the deprotonated azo anion might be converted into the hydrazone structure. In fact, the two new peaks at 457 and 413 nm at the high-energy band are analogous to those in CHCl<sub>3</sub>. The electronic spectra of both dyes show clear isoabsorptive points at 258, 298, 331, 390, 487 nm in **3** and 252, 284, 332, 440 nm in **4**, signifying that the hydrazone-deprotonated azo form equilibrium in BA based biheterocyclic dyes **3–4** (Fig. SI16).

# 2.2. DFT and TD-DFT calculations

To better understand the structure and spectroscopy of heterocyclic dyes 1–4, theoretical calculations were performed by using the Gaussian 16 suite of programs [24]. Firstly, two possible forms including hydrazone and deprotonated azo ion for dyes 1–4 were fully optimized by utilizing the hybrid exchange-correlation B3LYP functional [25,26] including the Grimme's DFT-D3 dispersion correction [27], and using the split-valence basis set 6-311+G (d,p) [27–29]. The optimized geometry structures of dyes 1–4 are shown in Fig. SI17. Second, the  $\lambda_{calc.}$  values for dyes 1–4 were calculated in four different solvents (CHCl<sub>3</sub>, MeOH, DMF and DMSO) by performing time-dependent DFT (TD-DFT) calculations with the SMD implicit solvent model [29] to rationalize the observed spectroscopic data.

It is obvious that the absorption spectra of dyes 1–4 at low energy, which are calculated from TD-DFT with the SMD implicit solvent model, coincide well with afore-mentioned experimental results (Table SI4). For mono-heterocyclic dye 1, the significant electronic transition in its hydrazone form results from a mixture of HOMO→LUMO and HOMO- $\rightarrow$ LUMO+1 (S2) transition and the absorption spectrum at around 373 nm (373/385/373/374 nm) is associated with this transition. Comparably, the absorption band corresponding to the deprotonated azo anion form at about 345 nm (345/355/340/341 nm) is assigned to S4 transition, respectively. Accordingly, the location of the absorption peaks and variation trend in two forms suggest that the mono-heterocyclic dye 1 exists in dominating hydrazone form in four solvents, which is also the case in mono-heterocyclic dye 2. As for bi-heterocyclic dye 3, the maximal absorption band at around 480 nm in its hydrazone form arises from the HOMO-JLUMO transition, while the lowest excited state of the deprotonated azo anion consisting of HOMO-1→LUMO and HOMO-→LUMO transitions corresponds to the calculated absorption band at around 545 nm (548/547/542/542 nm). It is evident that biheterocyclic dye **3** presents a dominating hydrazone form in  $CHCl_3$ , while the deprotonated azo anion form is preponderant because of the specific solute-solvent interactions in the other three solvents, as well as bi-heterocyclic dye **4**.

#### 2.3. Structural descriptions of compound 5

The single-crystal structure of bi-heterocyclic dye **5** has been acquired to reveal the corresponding configuration in the solid state. The molecular structure for dye **5** with atom-numbering scheme is shown in Fig. 3. Details of the data collection and structural refinements are listed in Table 2, and selected bond distances and angles are provided in Table SI1. X-ray single-crystal diffraction analyses disclose that dye **5** crystallizes in the triclinic  $p\overline{1}$  space group. The dihedral angle of 6.1 (3)° between A and B rings proves that all the non-hydrogen atoms are almost planar. The bond lengths of O4–C12 and O5–C12 are 1.399 (4) and 1.404 (5) Å, attesting to the formation of the methylal group.

Localization of the hydrogen atom H4 connected with atom N4 depends on the difference Fourier method, and large peak and hole in the final difference Fourier map cannot be observed near atoms O1 and O3, which manifest that dye **5** is in the hydrazone structure in the solide state. The formation of hydrazone form can be further supported by bond lengths of related atoms (Table SI1), i.e. double-bond character for C1–N3 and C2–O1 (1.309 (4) and 1.230 (4) Å) and single-bond character for their neighboring N3–N4 and C1–C2 (1.324 (4) and 1.462 (5) Å). In compound **5**, a dimeric packing mode is observed with a head-to-tail manner, as shown in Fig. 4, where  $\pi$ – $\pi$  accumulation actions are found between the thiophene and phenyl rings from adjacent molecules with the centroid-to-centroid separations of 3.793 and 3.712 (4) Å.

#### 3. Conclusion

In this study, a family of novel mono- and bi-heterocyclic dyes 1–5 with the common coulpling component 1,3-dimethyl-pyrimidine-2,4,6-trione have been synthesized and characterized by standard analytical methods. The UV–Vis spectral comparisons demonstrate that the  $\lambda_{max}$  values for BA based bi-heterocyclic dyes 3–4 showcase bathochromic shifts in polar solvents compared with benzene subtituted mono-heterocyclic dyes 3–4 originating from the constitution of stronger  $\pi$ -cogjugated system. Moreover, the molecular structures of dyes affected by solvent properties are essential factors for their solvatochromic behavior. Namely, strong solvatochromism can be observed for bi-heterocyclic dyes 3–4 because of the transformation



Fig. 3. ORTEP drawing of compound 5 with the atom-numbering scheme. Displacement ellipsoids are drawn at the 30% probability level and the H atoms are shown as small spheres of arbitrary radii. The dotted lines represent intramolecular hydrogen bonds (Å) and the dihedral angles between adjacent aromatic rings are given (°).

Table 2

Crystal data and structural refinements for compound 5.

Compound	5	
Empirical formula	C14H14ClN5O5S	
Formula weight	399.82	
Temperature/K	291 (2)	
Wavelength/Å	0.71073	
Crystal Size (mm)	$0.10\times0.10\times0.12$	
Crystal system	Triclinic	
Space group	$P\overline{1}$	
a/Å	7.420 (5)	
b/Å	10.169 (6)	
c/Å	12.018 (7)	
$\alpha/^{\circ}$	84.278 (7)	
$\beta/^{\circ}$	82.050 (8)	
$\gamma /^{\circ}$	73.457 (8)	
V/Å <sup>3</sup>	859.1 (9)	
$Z/D_{\text{calcd}}$ (g/cm <sup>3</sup> )	2/1.546	
F (000)	412	
$\mu/\text{mm}^{-1}$	0.382	
$h_{\min}/h_{\max}$	-5/9	
$k_{\min}/k_{\max}$	-12/13	
l <sub>min</sub> /l <sub>max</sub>	-15/15	
Data/parameters	3771/243	
Final R indices $[I > 2\dot{o}(I)]$	$R_1 = 0.0622 \text{ w} R_2 = 0.1693$	
R indices (all data)	$R_1 = 0.0913 \text{ w} R_2 = 0.2114$	
S	1.061	
Max./min. $\hat{o}\rho/e\cdot \hat{A}^{-3}$	0.80/-0.53	

 $R_1 = \Sigma ||Fo| - |Fc|| / \Sigma |Fo|, wR_2 = [\Sigma [w(Fo^2 - Fc^2)^2] / \Sigma w(Fo^2)^2]^{1/2}.$ 



**Fig. 4.** Drawing of  $\pi$ - $\pi$  stacking interactions (Å) in compound **5**.

from hydrazone to deprotonated azo form induced by the specific solutesolvent interaction, which is not the case in mono-heterocyclic dyes 1-2because of their consistent hydrazone structures. In addition, theoretical computation results also support the spectroscopic and structural characterizations of heterocyclic dyes 1-4.

Interestingly, it is found that this family of heterocyclic dyes exhibit distinct structural information in pH-titration experiments. In the case of mono-heterocyclic dyes 1–2, they exist in dominating hydrazone form and can be transformed into the deprotonated azo anion with increasing pH values in MeOH. Comparably, the azo anions of bi-heterocyclic dyes 3–4, which can be converted to the protonated hydrazone ones in the acidic condition, are predominating in their original solutions. As an extensive study, we believe that the theoretical calculations and experimental results of BA based mono/bi-heterocyclic dyes in this work give a better insight into the influence of solvent-solute interaction on contribution of the molecular structures, which is also applicable to other heterocyclic dye systems [16,22].

#### CRediT authorship contribution statement

Xiaolei Zhao: Investigation, Data curation, Formal analysis, Writing - original draft. Wei Zheng: Writing - review & editing. Xuepei Miao: Data curation, Formal analysis. Wei Huang: Conceptualization, Funding acquisition, Methodology, Supervision, Writing - review & editing.

#### Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

The authors declare the following financial interests/personal relationships which may be considered as potential competing interests.

#### Acknowledgements

This work was supported by Natural Science Foundation of the Jiangsu Higher Education Institutions of China (No. 19KJB150022), Changzhou Science and Technology Bureau (No. CJ20200036), National Natural Science Foundation of China (No. 21871133 and 21601060), and Science, Technology and Innovation Commission of Shenzhen Municipality (No. JCYJ20180307153251975).

# Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi. org/10.1016/j.dvepig.2020.109087.

#### References

- [1] Zamanloo MR, Shamkhali A, Alizadeh M, Mansoori Y, Imanzadeh G. A novel barbituric acid-based azo dye and its derived polyamides: synthesis, spectroscopic investigation and computational calculations. Dyes Pigments 2012;95:587-99. [2] Qian HF, Zhao XL, Dai Y, Huang W. Visualized fabric discoloration of bi-
- heterocyclic hydrazone dyes. Dyes Pigments 2017;143:223-31. [3] Kasture PP, Sonawane YA, Rajule RN, Shankarling GS. Synthesis and
- characterisation of benzothiazole-based solid-state fluorescent azo dyes. Color Technol 2010;126:342-8.
- Parekh NM, Sahoo SK, Maheria KC. Quantum chemical studies and dyeing [4] performance of some novel benzoquinoline based heterocyclic monoazo dyes on polyester fiber. Dyes Pigments 2012;95:142–8.
- [5] Mirkovic J, Rogan J, Poleti D, Vitnik V, Vitnik Z, Uscumlic G, Mijin D. On the structures of 5-(4-, 3- and 2-methoxyphenylazo)-3-cyano-1-ethyl-6-hydroxy- 4methyl-2-pyridone: an experimental and theoretical study. Dyes Pigments 2014; 104:160-8.
- [6] Pelova R. Spassowska N. Maneva L. Taxirov S. Antibacterial and antitumor activity of platinum complexes of hydrazinopyrimidines and amidrazones. Pharmazie 1987:42:251-2.
- [7] Simon TM, Kunishima DH, Vibert GJ, Lorber A. Screening trial with the coordinated gold compound auranofin using mouse lymphocytic leukemia. Canc Res 1981:41:94-7.
- [8] Izatt RM, Christensen JJ, Rytting JH. Sites and thermodynamic quantities associated with proton and metal ion interaction with ribonucleic acid, deoxyribonucleic acid, and their constituent bases, nucleosides, and nucleotides. Chem Rev 1971:71:439-81.
- [9] Mahmudov KT, Kopylovich MN, Maharramov AM, Kurbanova MM, Gurbanov AV, Pombeiro AJL. Barbituric acids as a useful tool for the construction of coordination and supramolecular compounds. Coord Chem Rev 2014;265:1-37.
- [10] Debnath D, Purkayastha A, Choudhury R, Misra TK. Conversion of 1,3-dimethyl-5-(arylazo)-6-amino-uracils to 1,3-dimethyl-5-(arylazo)-barbituric acids: spectroscopic characterization, photophysical property and determination of pKa of the products. J Chin Chem Soc 2016;63:580-9.
- [11] Viswanathan A, Sala A, Yli-Harja O, Kandhavelu M. Antimicrobial activity and molecular analysis of azoderivatives of β-diketones. Eur J Pharmaceut Sci 2015;66: 83\_9

- Dyes and Pigments 187 (2021) 109087
- [12] Palmucci J, Mahmudov KT, Guedes da Silva MFC, Marchetti F, Pettinari C, Petrelli D, Vitali LA, Quassinti L, Bramucci M, Lupidi G, Pombeiro AJL. DNA and BSA binding, anticancer and antimicrobial properties of Co(II), Co(II/III), Cu(II) and Ag(I) complexes of arylhydrazones of barbituric acid. RSC Adv 2016;6: 4237-49.
- [13] Palmucci J, Mahmudov KT, Guedes da Silva MFC, Martins LMDRS, Marchetti F, Pettinari C, Pombeiro AJL. Arylhydrazones of barbituric acid: synthesis, coordination ability and catalytic activity of their Co<sup>II</sup>, Co<sup>II</sup>/<sup>III</sup> and Cu<sup>II</sup> complexes toward peroxidative oxidation of alkanes. RCS Adv 2015;5:84142-52.
- [14] Mahmudov KT, Guedes da Silva MFC, Glucini M, Renzi M, Gabriel KCP Kopylovich MN, Sutradhar M, Marchetti F, Pettinari C, Zamponi S, Pombeiro AJL. Water-soluble heterometallic copper(II)-sodium complex comprising arylhydrazone of barbituric acid as a ligand. Inorg Chem Commun 2012;22:187–9.
- [15] Raposo MMM, Ferreira AMFP, Amaro M, Belsley M, Moura JCVP. The synthesis and characterization of heterocyclic azo dyes derived from 5-N, N-dialkylamino-2,2'-bithiophene couplers. Dyes Pigments 2009;83:59-65.
- [16] Geng J, Xu D, Chang FF, Tao T, Huang W. From heterocyclic hydrazone to hydrazone-azomethine dyes: solvent and pH induced hydrazone and azo-keto transformation for a family of pyrazolone-based heterocyclic dyes. Dyes Pigments 2017:137:101-10.
- [17] Qian HF, Zhao XL, Dai Y, Huang W. Visualized fabric discoloration of biheterocyclic hydrazone dyes. Dyes Pigments 2017;143:223-31.
- Habibi MH, Hassanzadeh A, Zeini-Isfahani A. Effect of dye aggregation and azo-[18] hydrazone tautomerism on the photocatalytic degradation of Solophenyl red 3BL azo dye using aqueous TiO<sub>2</sub> suspension. Dyes Pigments 2006;69:111-7.
- [19] Zhao XL, Qian HF, Huang W. Construction of benzothiazole/pyridone based biheterocyclic dyes and their Ni<sup>II</sup> and Cu<sup>II</sup> complexes. Dyes Pigments 2018;149: 796-803.
- [20] Tao T, Zhao XL, Wang YY, Qian HF, Huang W. 5-Hydroxy-1-phenyl-1H-pyrazole-3carboxylic acid based heterocyclic dyes. Dyes Pigments 2019;166:226-32.
- [21] Chen XC, Tao T, Wang YG, Peng YX, Huang W, Qian HF. Azo-hydrazone tautomerism observed from UV-vis spectra by pH control and metal-ion complexation for two heterocyclic disperse yellow dyes. Dalton Trans 2012;41: 11107–15.
- [22] Qiana HF, Geng J, Xu D, Huang W. Hydrazone to deprotonated azo/azo-enol transformation for isomeric pyrazolone based heterocyclic dyes via metal-ion complexation. Dyes Pigments 2019;160:853-62.
- [23] Gilani AG, Taghvaei V, Rufchahi EM, Mirzaei M. Tautomerism, solvatochromism, preferential solvation, and density functional study of some heteroarylazo dyes. J Mol Lig 2019;273:392–407.
- [24] Frisch MJ, Trucks GW, Schlegel HB, Scuseria GE, Robb MA, Cheeseman JR, Scalmani G, Barone V, Mennucci B, Petersson GA, Nakatsuji H, Caricato M, Li X, Hratchian HP, Izmaylov AF, Bloino J, Zheng G, Sonnenberg JL, Hada M, Ehara M, Toyota K, Fukuda R, Hasegawa J, Ishida M, Nakajima T, Honda Y, Kitao O, Nakai H, Vreven T, Montgomery Jr JA, Peralta JE, Ogliaro F, Bearpark M, Heyd JJ, Brothers E, Kudin KN, Staroverov VN, Keith T, Kobayashi R, Normand J, Raghavachari K, Rendell A, Burant JC, Iyengar SS, Tomasi J, Cossi M, Rega N, Millam JM, Klene M, Knox JE, Cross JB, Bakken V, Adamo C, Jaramillo J, Gomperts R, Stratmann RE, Yazyev O, Austin AJ, Cammi R, Pomelli C, Ochterski JW, Martin RL, Morokuma K, Zakrzewski VG, Voth GA, Salvador P, Dannenberg JJ, Dapprich S, Daniels AD, Farkas O, Foresman JB, Ortiz JV, Cioslowski J, Fox DJ. Gaussian 09, revision D.01. Wallingford CT: Gaussian, Inc.; 2013
- [25] Jean-Louis C. In: Parr RG, Yang W, editors. Density-functional theory of atoms and molecules, New York, Oxford: Oxford University Press: 1989, IX+333 pp., Int J Ouantum C 1993:47:101.
- [26] Burke K. Perspective on density functional theory. J Chem Phys 2012;136:150901. [27]
- Grimmea S, Antony J, Ehrlich S, Krieg H. A consistent and accurate ab initio parametrization of density functional dispersion correction (DFT-D) for the 94 elements H-Pu. J Chem Phys 2010;132:154104.
- [28] Hariharan PC, Pople JA. Accuracy of AH<sub>n</sub> equilibrium geometries by single determinant molecular orbital theory. Mol Phys 1974;27:209-14.
- [29] Marenich AV, Cramer CJ, Truhlar DG. Universal solvation model based on solute electron density and a continuum model of the solvent defined by the bulk dielectric constant and atomic surface tensions. J Phys Chem B 2009;113:6378-96.