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pri SMEITS-u



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Apstrakti prihvaćenih radova objavljeni su u štampanom dvojezičnom zborniku zajedno sa programom Procesinga '20.

Jedan broj radova je izabran za objavljivanje u drugom broju časopisa „Procesna tehnika“ (M53) koji izlazi krajem 2020 godine.

Programski koncept Kongresa o procesnoj industriji – Procesinga obuhvata bazne oblasti procesne tehnike:

Procesne tehnologije (naftna, hemijska i petrohemijska industrija, crna i obojena metalurgija, industrija nemetalnih minerala, industrija plastičnih materijala, industrija građevinskih materijala, industrija vatrostalnih i termoizolacionih materijala, industrija papira i celuloze, farmaceutska industrija, prehrambena industrija, proizvodnja alkoholnih i bezalkoholnih pića, proizvodnja stočne hrane, proizvodnja veštačkih đubriva i agrohemijska, duvanska industrija, tekstilna industrija, gumarska industrija);

Projektovanje, izgradnja, eksploatacija i održavanje procesnih postrojenja (projektovanje procesnih postrojenja, izgradnja procesnih postrojenja, puštanje u rad, eksploatacija i održavanje procesnih postrojenja, ispitivanje funkcionalnosti i bezbednosti, sistemi automatskog upravljanja i kontrole procesa, informacione tehnologije u projektovanju i upravljanju procesnim postrojenjima);

Osnovne i pomoćne operacije, aparati i mašine u procesnoj industriji (toplotne, difuzione, mehaničke, hidromehaničke, biohemijske i hemijske operacije, pomoćne operacije i opremu, cevovodi i armature);

Merenja i upravljanje u procesnoj industriji (osnovne merne veličine u procesnoj industriji; zakonska regulativa i standardizacija iz oblasti merenja i ispitivanja, merenja u cilju kontrole, vođenja i automatskog upravljanja procesom, merni sistemi, organizacija složenih sistema merenja sa akvizicijom podataka).

Razvoj novih tehnologija kao i potrebe povećanja energetske efikasnosti, uštede energije, korišćenja obnovljivih izvora energije, tretmana svih vrsta otpadnih materija, uvođenja koncepta cirkularne ekonomije i zaštite životne sredine u procesnoj industriji, nametnulo je da su ove teme poslednjih godina sve više uključene i u program Procesinga.

Program Procesinga '20 obuhvatio je 11 tematskih oblasti: 1. Procesne tehnologije; 2. Projektovanje, izgradnja, eksploatacija i održavanje procesnih postrojenja; 3. Osnovne i pomoćne operacije, aparati i mašine u procesnoj industriji; 4. Energetska efikasnost u industriji; 5. Inženjerstvo životne sredine i održivi razvoj u procesnoj industriji; 6. Procesi i postrojenja u pripremi i prečišćavanju vode u procesnoj industriji; 7. Sušenje i sušare; 8. Gasna tehnika; 9. Modelovanje i optimizacija procesnih i termoenergetskih postrojenja; 10. Merenja i upravljanje u procesnoj industriji; 11. Tehnička regulativa, standardizacija i sistem kvaliteta.

Procesing '20 organizovalo je Društvo za procesnu tehniku pri SMEITS-u, a u Naučno-stručnom i Organizacionom odboru prisutni su predstavnici mašinskih i tehnoloških fakulteta iz Srbije. Međunarodni karakter kongresa karakteriše učešće u Naučno-stručnom odboru predstavnika drugih zemalja, kao i jedan broj prijavljenih radova iz inostranstva.

U Beogradu
oktobra 2020.

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SINTEZA I SOLVATOHROMNA SVOJSTVA NOVIH AZO-AZOMETINSKIH BOJA

SYNTHESIS AND SOLVATOCHROMIC PROPERTIES OF NOVEL AZO-AZOMETHINE DYES

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Organske sintetske boje koje u svojoj strukturi sadrže azo i imino grupu predstavljaju klasu azo-azometinskih jedinjenja. Azometinska jedinjenja, poznata kao Schiff-ove baze, imaju značajnu ulogu u biomedicinskim istraživanjima zbog potencijalne antibakterijske, antifungalne, antimalarijske, antikancerogene, antiinflamatorne i antivirusne aktivnosti. Azo-azometinske boje se mogu koristiti u industriji za bojenje tekstilnih vlakana, zatim u LCD ekranima, ink-džet i laserskim štampačima, fotonaponskim uređajima i metalnim kompleksima. U ovom radu prikazana je mikrotalasna sinteza i strukturna karakterizacija tri nove azo-azometinske boje, polazeći iz arilazo piridonske boje i različito supstituisanih anilina. Solvatohromna svojstva i tautomerija novih azo-azometinskih jedinjenja proučavani su u rastvaračima različitih svojstava.

Ključne reči: mikrotalasna sinteza; azo-hidrazon tautomerija; UV-Vis spektroskopija

Dyes bearing imino group along with azo one in the structure, present the class of azo-azomethine dyes. Azomethine compounds, known as Schiff bases, find application in biomedical research considering their potential antibacterial, antifungal, antimalaric, anticancer, antiinflammatory and antiviral activity. Furthermore, azo dyes are used in textile fiber dyeing, ink-jet and laser printers, LCDs, photovoltaic devices and metal complexes. With respects to the strong biological activity and a broad spectrum of potential application in industry, herein the microwave assisted synthesis and characterization of three new azo-azomethine dyes is presented. New azo-azomethine dyes were obtained by merging arylazo pyridone dye with different aniline cores resulting in azo-azomethine structure. In addition, tautomerism and solvatochromic properties of the dyes have been discussed.

Key words: microwave assisted synthesis; azo-hydrazone tautomerism; UV-Vis spectroscopy

1 Introduction

Azo dyes represent the largest class of industrial organic dyes. They have diverse application in different fields, such as textile fiber dyeing, lasers, LCDs, electro-optical devices, ink-jet printers, as well as, in biomedical studies [1].

Azomethine compounds, also known as *Schiff* bases are the significant class of organic compounds. They have gained importance in medicinal and pharmaceutical fields considering their broad spectrum of biological activities, such as antiinflammatory, analgesic, antimicrobial, antitubercular, anticancer, antioxidant and so forth [2,3]. Strong biological activity of *Schiff* bases can be ascribed to the nitrogen atom of azomethine (imino) group, which is involved in the formation of a hydrogen bond with cell receptors, and interferes in cell processes. Also, studies enlightened that azomethine metal complexes show remarkable biological activity [3,4].

Furthermore, dyes bearing imino along with azo group in the structure, present the class of azo-azomethine dyes. They have a broad range of antibacterial, antifungal, antitumor and antioxidant activities. Apart from biological activities, azo-azomethine dyes are also used as catalysts, dyestuffs, polymer stabilizers, and corrosion inhibitors [5,6].

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The physico-chemical properties of azo, and azo-azomethine dyes are closely related to their tautomerism. Determination of tautomeric forms in the solid state, as well as in solutions is very important from the theoretical and practical standpoints, since the tautomers differ in physical properties and dyeing performances [6].

In this work, we reported the microwave assisted synthesis and the structure characterization of three new azo-azomethine dyes, based on arylazo pyridone structure. The solvatochromic properties of novel dyes have been studied in seven solvents of different properties. In addition, the effects of solvents and different substituents, on the tautomeric equilibrium, have been discussed.

2 Experimental

2.1 Materials and methods

All chemicals were obtained from Merck, Fluka and Acros and were used without further purification. Fourier transform infrared spectroscopy (FT-IR) spectra of the dyes were recorded using a Nicolet™ iS™ 10 FT-IR Spectrometer (Thermo Fisher SCIENTIFIC), with Smart iTR™ Attenuated Total Reflectance (ATR) sampling accessories. The ATR-FTIR spectra were recorded in the 500–4000 cm^{-1} range with 20 scans per spectrum. The melting points were determined on melting point system Stuart SMP30. The ^1H NMR spectrum were taken on a Bruker Ascend 400 apparatus (400 Hz) in deuterated dimethylsulfoxide ($\text{DMSO-}d_6$) with tetramethylsilane (TMS) as an internal standard. The ultraviolet–visible (UV–Vis) absorption spectra were recorded on a Shimadzu 1700 spectrophotometer, at concentration of the solutions $2.5 \cdot 10^{-5} \text{ mol} \cdot \text{L}^{-1}$. All spectroscopic measurements were carried out at room temperature (25 °C). Microwave assisted synthesis was performed in a Anton Paar Monowave 300 reactor using a 30 mL reactor vial.

2.2 Synthesis of azo-azomethine dyes

The azo dye, 3-cyano-5-(4-formylphenylazo)-6-hydroxy-2-pyridone (**1**) was synthesized according to literature data [7]. The structure is confirmed by the following characteristics: dark orange powder; yield 85%; m.p. > 300 °C; ATR-FTIR (v/cm^{-1}): 3157 (NH), 2223 (CN), 1680, 1665 (C=O); ^1H NMR (400 MHz, $\text{DMSO-}d_6$, δ/ppm): 2.51 (3H, s, CH_3), 7.85 (2H, d, $J = 8.0$ Hz, Ar-H), 8.00 (2H, d, $J = 8.0$ Hz, Ar-H), 9.98 (1H, s, CHO), 12.10 (1H, s, NH pyridone), 14.44 (1H, s, NH hydrazone).

General synthesis of azo-azomethine dye: In the reaction vial, 3-cyano-5-(4-formylazo)-6-hydroxy-2-pyridone (0.5 mmol, 0.141 g) was dissolved in *N,N*-dimethylformamide (4 mL), and then corresponding aniline (0.5 mmol) along with 3 drops of acetic acid was added. The reaction mixture was irradiated in the microwave reactor for 5 minutes at the temperature 100 °C. After completion of reaction, the mixture was cooled to the room temperature and water (10 mL) was added in order to precipitate azo-azomethine dye. The resulting solid product was collected by filtration and then air dried. The overall synthetic pathway is presented in Fig. 1.

6-Hydroxy-4-methyl-2-oxo-5-((4-((phenylimino)methyl)phenyl)diazanyl)-1,2-dihydropyridine-3-carbonitrile (1a). Red powder; yield 55%; m.p. > 300 °C; ATR-FTIR (v/cm^{-1}): 3151 (NH), 2217 (CN), 1645, 1659 (C=O), 1620 (N=C); ^1H NMR (400 MHz, $\text{DMSO-}d_6$, δ/ppm): 2.55 (3H, s, CH_3), 7.25–7.32 (3H, m, Ar-H), 7.43 (2H, t, $J = 8.0$ Hz, Ar-H), 7.81 (2H, d, $J = 8.0$ Hz, Ar-H), 8.04 (2H, d, $J = 8.0$ Hz, Ar-H), 8.64 (1H, s, CH=N), 12.10 (1H, s, NH pyridone), 14.60 (1H, s, NH hydrazone).

6-Hydroxy-5-((4-((4-methoxyphenylimino)methyl)phenyl)diazanyl)-4-methyl-2-oxo-1,2-dihydropyridine-3-carbonitrile (2a). Dark red powder; yield 60%; m.p. > 212–215 °C; ATR-FTIR (v/cm^{-1}): 3145 (NH), 2221 (CN), 1646, 1660 (C=O), 1621 (N=C).

6-Hydroxy-4-methyl-5-((4-((4-nitrophenylimino)methyl)phenyl)diazanyl)-2-oxo-1,2-dihydropyridine-3-carbonitrile (3a). Dark orange powder; yield 57%; m.p. > 212–215 °C; ATR-FTIR (v/cm^{-1}): 3134 (NH), 2222 (CN), 1637, 1651 (C=O), 1627 (N=C).

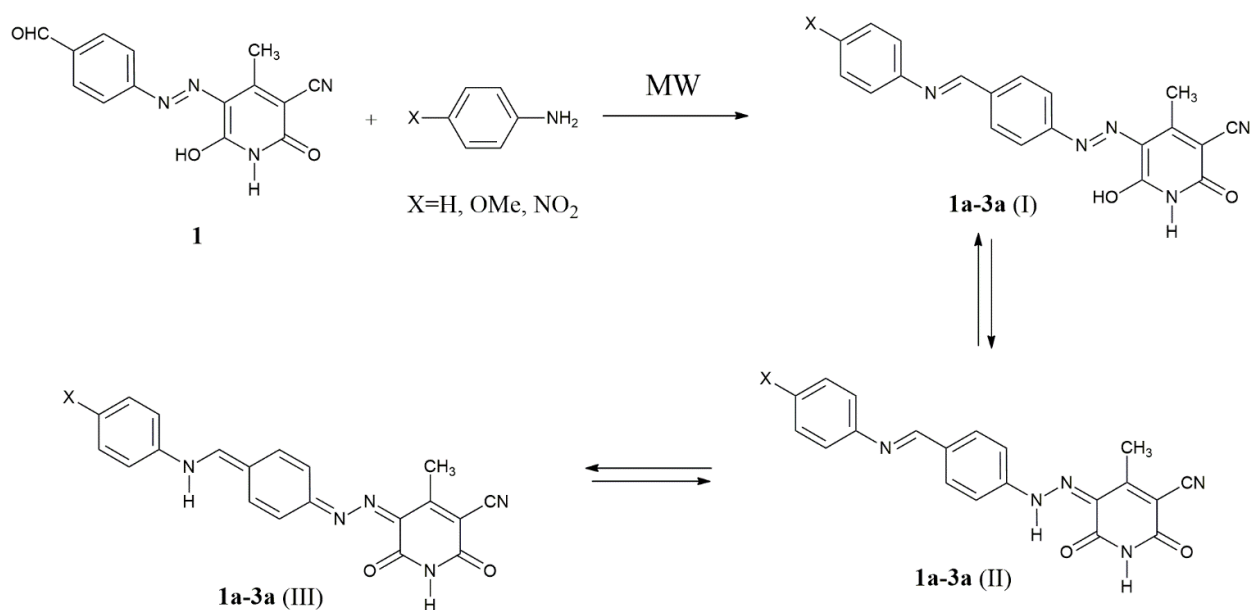


Fig. 1. Synthetic route of azo-azomethine dyes **1a-3a**. X = H (**1a**), OMe (**2a**), NO₂ (**3a**).

3 Results and discussion

3.1 ATR-FTIR and NMR results

The structure of the parent azo dye **1** was confirmed by the ATR-FTIR and NMR spectra and agrees with literature data [7]. According to previous studies, azo-azomethine dyes can exist in three different tautomeric forms (Fig. 1): imino-azo (I), imino-hydrazone (II) and amino-hydrazone (III). The ATR-FTIR and NMR data of investigated dyes have shown the existence of imino-hydrazone form in solid state, as well as in DMSO-*d*₆ solution (Fig. 1, structure II). The ATR-FTIR spectra showed characteristic vibrations of N-H hydrazone group (3134-3151 cm⁻¹), two C=O carbonyl groups (1637-1646 and 1651-1660 cm⁻¹), imino C=N group (1620-1627 cm⁻¹) and cyano -CN group (2117-2222 cm⁻¹). The signals observed at 14.60 ppm and 8.64 ppm, in the ¹H NMR spectrum of dye **1a**, were ascribed to N-H hydrazone and CH=N imino group, indicating the existence of the imino-hydrazone form.

3.2 UV-Vis analysis

UV-Vis spectra of the investigated azo **1** and azo-azomethine **1a-3a** dyes in methanol are presented in Fig. 2. The absorption band of dye **1**, with maximum at 430 nm, corresponds to hydrazone tautomeric form. The UV-Vis absorption maxima of azo-azomethine dyes **1a-3a**, which appear in the range of 432-454 nm, are ascribed to imino-hydrazone tautomeric form. It can be clearly seen that aniline modified azo-azomethine dyes **1a-3a** exhibit bathochromic shifts in comparison with their common parent azo dye **1**. The presence of strong electron-donating methoxy group in dye **2a** gives the largest shift of 22 nm, unsubstituted dye **1a** makes smaller shift of 15 nm and electron-withdrawing nitro group in dye **3a** result in negligible shift of 2 nm. However, observed bathochromic shifts from **1** to **1a-3a** reflect the increase of π -conjugated system in azo-azomethine molecules. Furthermore, comparing azo-azomethine dyes **2a** and **3a** to the unsubstituted dye **1a**, it can be concluded that electron-donating methoxy group causes bathochromic shift, while electron-withdrawing nitro group induces the hypsochromic shift of UV-Vis absorption maxima. This behavior is the consequence of different substituent effects, where electron donating groups stabilize dye molecule, since they enhance intramolecular charge transfer, and contrary, electron accepting groups destabilize dye structure, due to the negative resonance effect [8, 9].

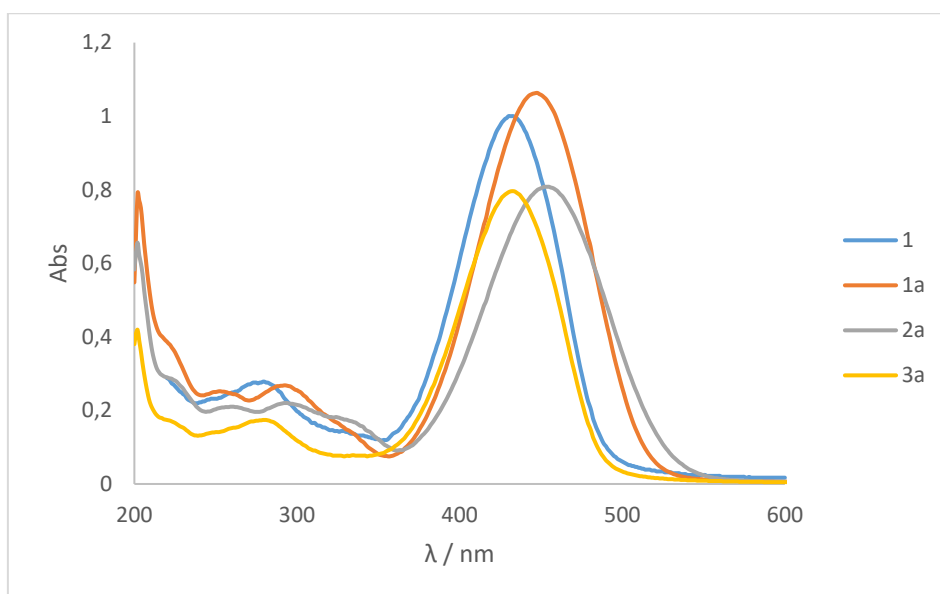


Fig. 2. UV-Vis spectra in methanol.

Solvatochromic properties of investigated azo-azomethine dyes have been studied in seven solvents of different properties. Resulting UV-Vis absorption maxima (λ_{max}) and molar extinction coefficients (ϵ) are presented in Table 1.

Table 1. UV-Vis properties of investigated dyes **1a-3a**

Dye		2-Butanone	Acetonitrile	DMF	DMSO	Diethyl ether	Chloroform	Methanol
1a	λ_{max} / nm	446	445	449	453	442	456	447
	ϵ / dm ³ mol ⁻¹ cm ⁻¹	4.73	4.65	4.65	4.59	3.70	4.57	4.63
2a	λ_{max} / nm	455	450	451	461	451	464	454
	ϵ / dm ³ mol ⁻¹ cm ⁻¹	4.59	4.57	4.53	4.37	3.60	4.44	4.50
3a	λ_{max} / nm	431	431	445	440	428	437	432
	ϵ / dm ³ mol ⁻¹ cm ⁻¹	4.74	4.27	4.44	4.74	3.84	4.34	4.50

It can be concluded from data given in Table 1, that all azo-azomethine dyes have one absorption maximum in all solvents, ascribed to the imino-hydrazone form. The UV-Vis absorption maxima of all investigated compounds exhibit bathochromic shifts in DMSO and chloroform, while in non-polar solvents, such as diethyl ether, hypsochromic shifts are observed.

3.3 UV-Vis analysis in DMF

Previous studies of arylazo pyridone dyes established that in polar aprotic solvents, such as DMF, the equilibrium between hydrazone form and common anion exist [8]. The relative position of the UV-Vis absorption maxima of the hydrazone and anion form of azo pyridone dyes depends on the substituents at the phenyl moiety [10]. Equilibrium between imino-hydrazone (I) and common anion (IV) is also observed in DMF for investigated **1a-3a** (Fig. 3).

Since hydrazone form is dominant at lower pH values, acetic acid was added dropwise into DMF dye solutions, in order to determine its position (Fig. 4). It is observed that imino-hydrazone form of all investigated azo-azomethine dyes exist at a lower wavelength, than the common anion, regardless of the electronic effects of the substituents.

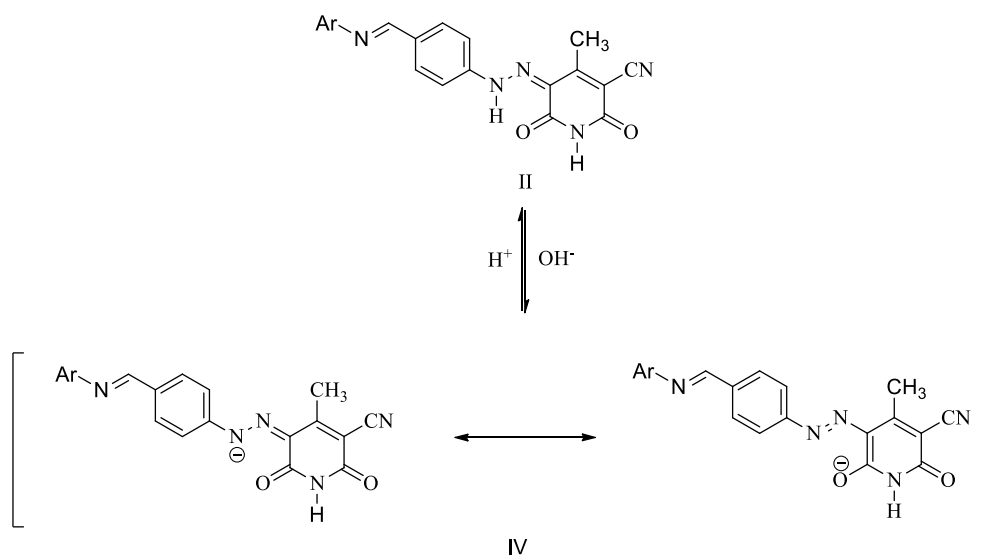


Fig. 3. Acid-base equilibrium of the investigated dyes in DMF.

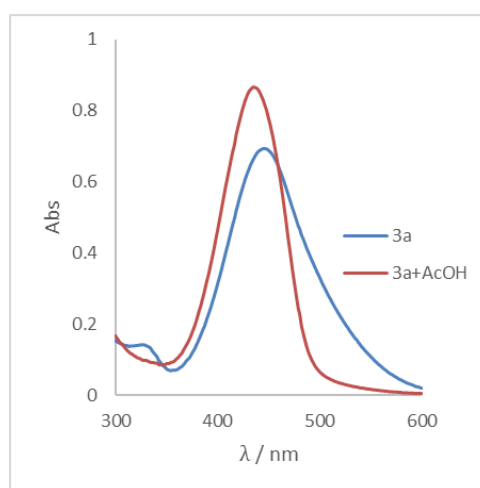


Fig. 4. UV-Vis spectrum of dye 3a in DMF and DMF with addition of the acetic acid.

4 Conclusion

In this work, three novel azo-azomethine dyes have been synthesized using microwave technique, and their structures have been confirmed by ATR-FTIR, NMR and UV-Vis spectroscopies. According to ATR-FTIR and NMR spectral data, investigated dyes exist in the imino-hydrazone form, in solid state as well as in DMSO- d_6 solution. UV-Vis analysis in methanol have shown the bathochromic shifts of absorption maxima of azo-azomethine dyes, comparing to parent azo dye. It is observed that electron-donating methoxy group causes bathochromic shift, while electron-withdrawing nitro group induces the hypsochromic shift of UV-Vis absorption maxima, comparing to unsubstituted azo-azomethine dye. Solvatochromic properties of novel dyes have been examined in seven solvents. In all solvents one absorption band exists and it is ascribed to the imino-hydrazone form. The UV-Vis absorption maxima of all investigated compounds have exhibited bathochromic shifts in DMSO and chloroform, while in non-polar solvents, such as diethyl ether, the absorption maxima have been shifted to the lower wavelengths. The acid-base equilibrium between imino-hydrazone and common anion in DMF has been studied. It is concluded that imino-hydrazone form of the investigated azo-azomethine dyes exist at a lower wavelength than common anion.

Acknowledgement

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5 References

- [1] **Hunger K.** Industrial dyes chemistry, properties, applications. Weinheim: Wiley-VCH; 2003.
- [2] **Yahyazadeh A, Azimi V.** Synthesis of Some Unsymmetrical New Schiff. *Eur Chem Bull* 2013;2:453–5. <https://doi.org/10.17628/ECB.2013.2.453>.
- [3] **Tobriya SK.** Biological applications of Schiff Base and its metal complexes-A Review. *Int J Sci Res* 2012;3:1254–6.
- [4] **Al Zoubi W, Ko YG.** Schiff base complexes and their versatile applications as catalysts in oxidation of organic compounds: part I. *Appl Organomet Chem* 2017;31:1–12. <https://doi.org/10.1002/aoc.3574>.
- [5] **Khanmohammadi H, Rezaeian K.** Thermally stable water insoluble azo-azomethine dyes: Synthesis, characterization and solvatochromic properties. *Spectrochim Acta - Part A Mol Biomol Spectrosc* 2012;97:652–8. <https://doi.org/10.1016/j.saa.2012.07.013>.
- [6] **Ghasemian M, Kakanejadifard A, Azarbani F, Zabardasti A, Kakanejadifard S.** Spectroscopy and solvatochromism studies along with antioxidant and antibacterial activities investigation of azo-azomethine compounds 2-(2-hydroxyphenylimino)methyl-4-phenyldiazenyl)phenol. *Spectrochim Acta - Part A Mol Biomol Spectrosc* 2014;124:153–8. <https://doi.org/10.1016/j.saa.2014.01.005>.
- [7] **Porobić SJ, Krstić AD, Jovanović DJ, Ladarević JM, Katnić ĐB, Mijin DŽ, et al.** Synthesis and thermal properties of arylazo pyridone dyes. *Dye Pigment* 2019;170:107602. <https://doi.org/https://doi.org/10.1016/j.dyepig.2019.107602>.
- [8] **Mirković J, Božić B, Vitnik V, Vitnik Ž, Rogan J, Poleti D, et al.** Structural, spectroscopic and computational study of 5-(substituted phenylazo)-3-cyano-1-ethyl-6-hydroxy-4-methyl-2-pyridones. *Color Technol* 2018;134:33–43. <https://doi.org/10.1111/cote.12321>.
- [9] **Ladarević J, Božić B, Matović L, Nedeljković BB, Mijin D.** Role of the bifurcated intramolecular hydrogen bond on the physico-chemical profile of the novel azo pyridone dyes. *Dye Pigment* 2019;162:562–72. <https://doi.org/https://doi.org/10.1016/j.dyepig.2018.10.058>.
- [10] **Peng Q, Li M, Gao K, Cheng L.** Hydrazone-azo tautomerism of pyridone azo dyes: Part II: Relationship between structure and pH values. *Dye Pigment* 1991;15:263–74. [https://doi.org/https://doi.org/10.1016/0143-7208\(91\)80011-W](https://doi.org/https://doi.org/10.1016/0143-7208(91)80011-W).