STUDIA UBB CHEMIA, LXXI, 1, 2026 (p. 19-30)
(RECOMMENDED CITATION)
DOI:10.24193/subbchem.2026.1.02

SYNTHESIS, CHARACTERIZATION AND *CIEL*a*b** COLOR SPACE STUDY OF TWO ECO-FRIENDLY DIRECT STILBENE AZOIC DYES

Maria Elena RADULESCU-GRAD[a], **Simona POPA**[b,*], **Sorina BORAN**[b], **Giannin MOSOARCA**[b]

ABSTRACT. The article presents the synthesis of two disazo-stilbene dyes with symmetrical structure. A non-carcinogen, non-mutagen/teratogen intermediate, 4,4'-diaminostilben-2,2'-disulfonic acid was used as central component and the 8-amino-1-naphtol-3,6-disulphonic acid and the 6-hydroxynaphthalene-2-sulphonic acid as coupling components respectively. To evaluate the characterization of the dyes, well known and applied methods were used TLC, UV-VIS and FT/IR spectroscopy. Color variations (ΔE^*ab and Δh^*) were determined relative to a single standard, (C.I.77891 P.W.6). The results highlight a metamerism effect and good coloring properties of the studied dyes.

Keywords: *azo-stilbene dyes, CIEL*a*b* color space*

INTRODUCTION

As is known, azo dyes are synthetic dyes that contain one or more nitrogen-nitrogen double bonds called azo groups [1]. Because of their diverse colors and chemical stability, they are usually used in multiple industries to color textiles, paper, plastics, etc [2-5] and consider their photophysical properties and anti-bacterial activity, in medicine as well [6,7].

---

[a] *"Coriolan Dragulescu" Institute of Chemistry, Romanian Academy, Mihai Viteazu Bd. No. 24, 300223, Timisoara, Romania.*
[b] *Faculty of Chemical Engineering, Biotechnologies and Environmental Protection, Politehnica University Timisoara, V. Parvan Bd. No. 6, 300223 Timisoara, Romania.*
[*] *Corresponding author: simona.popa@upt.ro*

Due to the instability of the azo bonds existing in their structure, the degradation of the dyes can take place by photo-oxidation, photolysis, biodegradation, and chemical degradation [8,9]. Literature underlines that toxic amines can result from these degradation processes both for the dye molecules and for the intermediates used in their synthesis and, at consequence, their use may be restricted [10,11].

The researchers' efforts are now to find alternative dyes that use instead of benzidine, a diamine toxic intermediate having a carcinogen, mutagen/teratogen character, dyes with properties like the benzidine ones. The replacement for benzidine dyes represents a notable challenge, results in this area show that the 4,4'-diaminostilben-2,2'-disulfonic acid may offer a viable alternative as an intermediate in the synthesis of azo dyes. However, a limited number of studies are known in recent years regarding the synthesis of new dyes with azo-stilbene structure [12-15].

The basis of all color measurement systems is the one CIE proposed, *CIEL*a*b** space being a three-dimensional color model that represents all colors visible to the human eye, in cartesian and/or cylindrical coordinates. Therefore, any specific single color may be represented as a point in the three-dimensional color space, which is powerful and versatile at the same time, qualities that make it useful for a wide range of applications. The color difference equations may be developed and are generally based on the principle of calculating the distance in three-dimensional color space between two colors, for example between a sample and a standard [16-19].

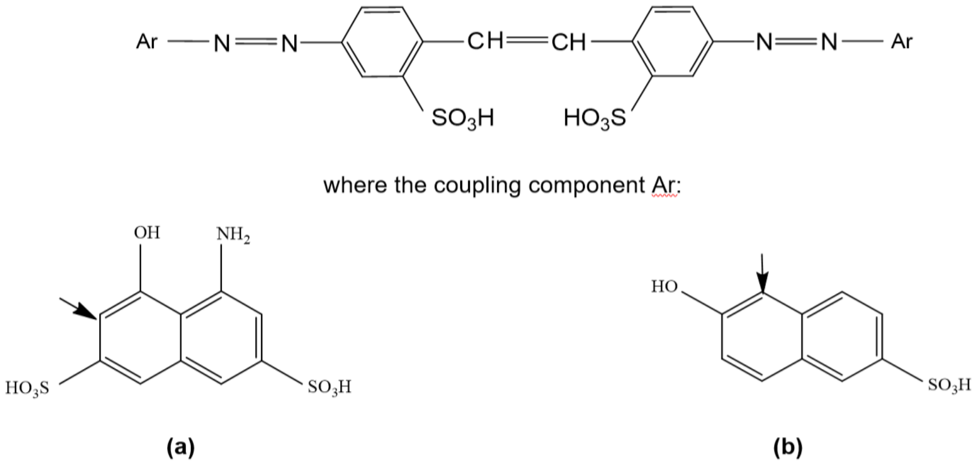
This paper presents the synthesis, the characterization, and the colorimetric study of two eco-friendly disazo direct dyes with symmetrical structure derived from 4,4'-diaminostilbene-2,2'-disulphonic acid and containing 8-amino-1-naphthol-3,6-disulphonic acid and 6-hydroxynaphthalene-2-sulphonic acid respectively as coupling components.

To the best of our knowledge, the new approach of the color analysis performed upon direct stilbene azoic dyes, such in this paper, was not yet presented.

RESULTS AND DISCUSSION

Synthesis of the dyes

The synthesis of the dye I and II with structures shown in Scheme 1 involved the bis-diazotization of 4,4'-diaminostilbene-2,2'-disulphonic acid and the coupling reactions of the resultant bis–diazonium salt with 8-amino-1-naphthol-3,6-disulphonic acid and 6-hydroxynaphthalene-2-sulphonic acid respectively as coupling components in a 1:2 molar ratio.



Scheme 1. Structures of the symmetrical azo-stilbene dyes Ar (a) - (dye I); (b) - dye **II**

In the first step (diazotization), 4,4'-diaminostilbene-2,2' disulphonic acid was treated with sodium nitrite ($NaNO_2$) in an acidic hydrochloric acid (HCl) solution (see for details) [20]. This process creates the diazonium salt, which is the key component for dye formation.

In the second step (coupling), the diazonium salt solution was directly added to an alkaline solutions containing 8-amino-1-naphthol-3,6-disulphonic acid and 6-hydroxynaphthalene-2-sulphonic acid respectively (the coupling components). The optimal versions of the coupling process for the synthesis of dye I and II were established after several experimental attempts namely, the direct addition of the acid suspension of the bis-diazonium salt of 4,4'-diaminostilbene-2,2' -disulphonic acid to the basic solutions of the coupling components (8-amino-1-naphthol-3,6-disulphonic acid and 6-hydroxynaphthalene-2-sulphonic acid respectively) and vice versa. The reaction conditions were established knowing that coupling reactions with phenols and naphtols take place in a weakly alkaline medium and at low temperature.

Consequently, the reactions maintained at around 10°C and at a pH around 8, with the caution addition of Na_2CO_3 form the desired dyes' molecules. In order, to ensure the completion of the reactions, the mixtures were kept under stirring for 3.5 h for dye I and 3 h for dye II. The purification was performed by fractioned crystallization from dioxane:pyridine 90:10 (v:v), according to the solubility difference in the mixture' s corresponding components, of the synthesized dyes I and II respectively.

Characterization of the dyes

The thin layer chromatography (TLC) and the UV-VIS, FT/IR spectroscopy were used to establish the purity and the structure of the synthesized disazo dyes I and II.

According to the FT/IR spectra (Figure 1), the reaction products reveal two absorption bands, around 3500 cm^1 and 1380 cm^1, corresponding to the stretching and deformation vibrations respevtively of the hydroxyl group. At the same time dye I and II show an absorption band in the region of 1120-1187 cm^{-1} and absorption band in the region of 1070-1078 cm^{-1}, described by the asymmetric and symmetric stretching vibrations of the sulphonic function (-SO_3H). The medium stretching vibration band related to the olefinic bound was recorded for both studied dyes in the region 1630-1680 cm^{-1} In azo derivatives, the stretching vibration of the −N=N− bond generally appears in the IR region around: −N=N− stretching: ~1400–1500 cm^{-1} (sometimes reported up to 1600 cm^{-1}) But in symmetric azo derivatives, this band is very weak or even absent in IR, because the vibration does not produce a significant change in dipole moment. [21].

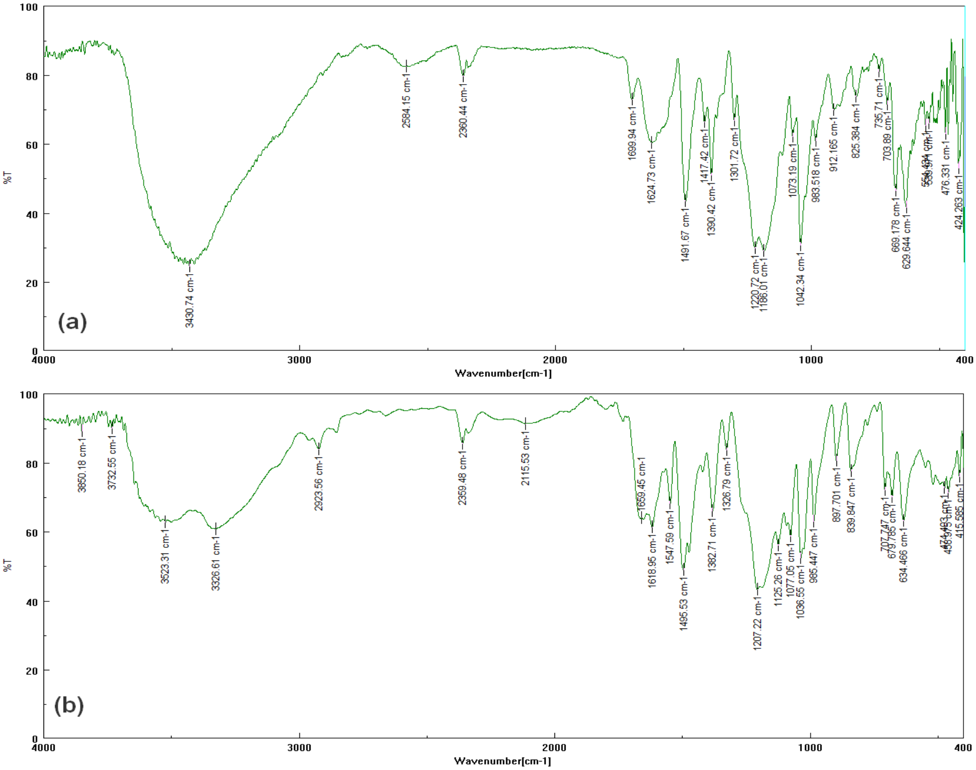


Figure 1. FTIR spectra for: (a) – dye I and (b) – dye II

The electronic spectra of the analyzed dyes exhibit in a 50% aqueous methanol (MeOH) solution an absorption namely, in the yellow region 560-590 nm for dye I and absorption in the green region 500-560nm for dye II as expected.

Colorimetric measurement of the dyes

The synthesized compounds, dye I and dye II, have extensive conjugation of the double bonds on their entire molecules. The presence of two naphthalene molecules, each containing an auxochrome hydroxyl group, in dye I in α-position and in dye II in β-position, is the reason why they have dark colors. Because dye I has also an auxochrome amino group on each naphthalene molecule, it presents a dark violet color comparative to dye II, which is dark purple.

To understand how concentration affects the dyes color, we mixed them at various concentrations with a water-based acrylic resin containing titanium dioxide (TiO_2) paste (C.I.77891 P.W.6). When the dyes concentrations increase, the material reflects less light, resulting in a darker or more intense color, an aspect presented by other authors as well. [22].

Using the reflectance spectra, the Kubelka-Munk equation (see Equation 1) one may determine a material's color strength across the visible spectrum. This equation allows us to calculate a value called "K/S" which indicates the relative intensity or strength of a material's color [23, 24].

$$\frac{K}{S} = \frac{(1-R)^2}{2R} \quad (1)$$

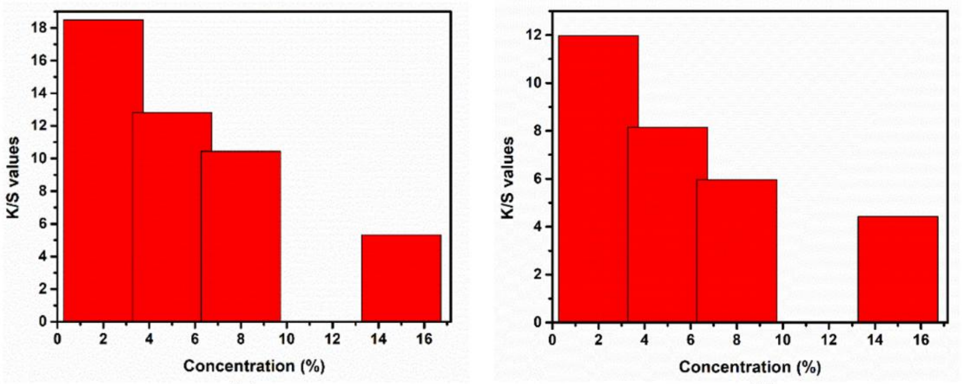
The equation considers three key factors that influence a material's color:

- Reflectance ratio (R) - which represents the proportion of light reflected by the material compared to the light that hits it. A lower reflectance ratio indicates that more light is absorbed by the material, potentially resulting in a more intense color.

- Absorbance coefficient (K) - which measures how strongly the material absorbs light at a specific wavelength. A higher absorbance coefficient means the material absorbs light more efficiently, contributing to a stronger color.

- Scattering coefficient (S) - which reflects how light gets dispersed within the material. A lower scattering coefficient allows for clearer light absorption and potentially a more vibrant color.

Figure 2 presents the results of these values for both dyes (I and II), showing that their color strength decreases with increasing their concentration in resin (2%, 5%, 8% and 15%). Similar results have been reported in other papers [23, 25-27].



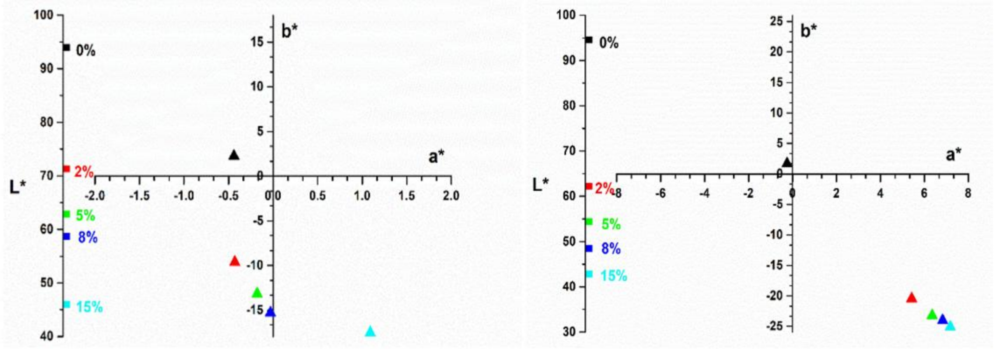
(a)

(b)

Figure 2. Color strength (K/S) at different compound concentrations (2%, 5%, 8% and 15%) in water-based acrylic resin, for dye **I** (a) and for dye **II** (b)

The colored resin samples containing dye I (Figure 3,a) show exactly what expected. As the amount of dye increases, the material becomes darker (lower *L** value). Additionally, the higher red (*a**) and yellow (*b**) values at higher dye concentrations tell us the color becomes a more intense violet.

The color parameters in the *CIEL*a*b** system for dye II are presented in Figure 3,b. It is observed that the lightness (*L**) decreases as the dye concentration increases in the water-based acrylic resin, and the (*a**) and (*b**) parameters reveal an intensification of the purple color under the same conditions mentioned above.



(a)

(b)

Figure 3. *CIEL*a*b** values of dye **I** (a) and dye **II** (b) in water-based acrylic resin at different concentrations

One can use a color measurement system to determine how different a sample's color is from a standard color. This overall difference is represented by ΔE**ab* (that is the distance between the two colors in a specific color space). Equation (2) allows us to calculate this overall difference. There are also ways to analyze specific aspects of the color difference: Saturation difference (ΔC*) calculated using equation (3), which tells us how much the colors differ in terms of their intensity or vibrancy. Equation (4) helps us determine the difference in the actual color "tone" (red, green, blue, etc.) between the sample and standard, represented by the hue difference (Δh*) [17, 22].

$$\Delta E^*_{ab} = \sqrt{(\Delta L^*)^2 + (\Delta a^*)^2 + (\Delta b^*)^2} \quad (2)$$

$$\Delta C^* = C^*_{sample} - C^*_{standard} \quad (3)$$

$$\Delta h^* = \sqrt{(\Delta E^*_{ab})^2 - (\Delta L^*)^2 - (\Delta C^*)^2} \quad (4)$$

The color differences mentioned above depend on the dye concentration as presented in Figure 4. As can be observed, their values increase with product concentration, with a tendency of higher limitation at higher concentrations, a fact also revealed in the literature [17, 27, 28].

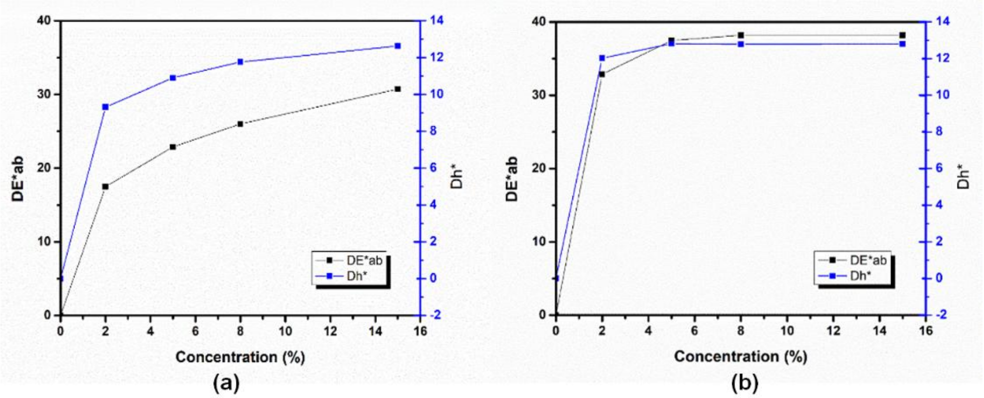


Figure 4. The total color difference (ΔE*ab) and hue difference (Δh*) of the dye **I** and dye **II** at different concentrations in water-based acrylic resin

Although the color of dye I gets more intense with increasing concentration under all three standard lighting conditions (CIE illuminants), Table 1 reveals an interesting detail. The specific shade of the dye appears different depending on the light source. This phenomenon, where materials can appear to have different colors under different lighting conditions, is called, as known, *metamerism.*

Table 1. Effect of concentration and light source (D65, A, F2) on dye I color in resin

Color parameter	Concentration	D65		A		F2	
		Color	Value	Color	Value	Color	Value
L*	2%	■	71.33	■	70.56	■	70.39
a*			-0.43		-1.62		-0.1
b*			-9.63		-10.68		-11.65
L*	5%	■	62.84	■	61.79	■	61.64
a*			-0.18		-2.28		0.1
b*			-13.16		-14.47		-15.74
L*	8%	■	58.68	■	57.46	■	57.34
a*			-0.03		-2.85		0.26
b*			-15.31		-16.77		-18.25
L*	15%	■	46.05	■	44.3	■	44.69
a*			1.09		-3.22		1.1
b*			-17.53		-19.13		-20.68

A similar approach may be underlined for dye II, that can be seen in Table 2, the color changes under different illuminants. Based on these observations it was concluded that dye II exhibits a *metamerism* effect as well.

Table 2. Effect of concentration and light source (D65, A, F2) on dye II color in resin

Color parameter	Concentration	D65		A		F2	
		Color	Value	Color	Value	Color	Value
L*	2%	■	62.19	■	61.19	■	60.57
a*			5.42		2.18		3.98
b*			-20.46		-21.16		-24.12
L*	5%	■	54.42	■	53.23	■	52.63
a*			6.35		2.11		4.6
b*			-23.21		-24		-27.27
L*	8%	■	48.48	■	47.35	■	46.77
a*			6.83		2.4		4.9
b*			-23.01		-23.65		-26.95
L*	15%	■	42.78	■	41.82	■	41.36
a*			6.48		2.24		4.54
b*			-23.99		-20.99		-23.99

CONCLUSIONS

Considering that 4,4'-diaminostilben-2,2'-disulfonic acid may be a favorable alternative for benzidine, as intermediate, assignable to its low toxicity, as well as the possibility of extending the conjugation on the whole molecule was successfully employed to synthesize two eco-friendly symmetrical disazo-stilbene direct dyes. The used coupling components were 8-amino-1-naphtol-3,6-disulphonic acid and 6-hydroxynaphthalene-2-sulphonic acid respectively. The thin layer chromatography (TLC) was used to establish the purity of the dyes (I, II) and the UV-VIS, FT/IR spectroscopy data were useful for the confirmation of their structures. The new approach of the color analysis performed upon these direct dyes with azo-stilbene structure, using the *CIEL*a*b** color system, emphasizes the color properties of dyes, showing their dark color, one dark purple and the other dark violet, highlighting their good coloring properties and that metamerism effect is present for both dyes, as well. Attempts to use symmetric-structure azo-stilbene dyes in obtaining film-forming materials have led to encouraging results [29].

EXPERIMENTAL SECTION

Synthesis of the dyes

The protocol used to obtain the disazo direct stilbene dyes is also mentioned in the previously published papers [15].

The diazotization step:

A suspension of 1.95 g of 4,4′-diaminostilbene-2,2′-disulfonic acid (95%, 0.005 mol) was prepared in 25 mL of distilled water. To this mixture, 1.1 mL of 30% aqueous NaOH (0.01 mol) was added gradually, and the resulting solution was cooled to 5 °C. The sodium salt formed in situ was then acidified with 3 mL of 32% HCl (0.03 mol). Bis-diazotization of the resulting suspension was carried out by adding 0.71 g of solid $NaNO_2$ (98%, 0.0101 mol) at 5 °C while maintaining the pH at approximately 1. After the addition of $NaNO_2$, the reaction mixture was stirred for 1,5 hours to ensure complete diazotization. Excess nitrous acid was subsequently destroyed by treatment with urea.

The coupling step:

In an aqueous 10% NaOH solution were dissolved 3.54 g of 8-amino-1-naphtol-3,6-disulphonic acid and 2.48 g of 6-hydroxynaphthalene-2-sulphonic acid (98%, 0.011 mol), respectively. Further the diazonium salt solution was directly added to an alkaline solutions containing 8-amino-1-naphthol-3,6-disulphonic acid and 6-hydroxynaphthalene-2-sulphonic acid respectively. By periodically adding a 10% aqueous Na_2CO_3 solution, the pH of the reaction mixture was maintained at approximately 8–8.5, and the temperature at about 8–10 °C**.** The progress of reaction was monitored by drop reaction (with an alkaline solution of 8-amino-1-naphtol-3,6-disulphonic acid respectively with the diazonium salt of 4-nitroaniline) and by TLC. In order, to ensure completion of the reactions, the mixtures were kept under stirring for 3.5 h for dye **I** and 3 h for dye **II**. The separation of the crude dyes was carried out by filtration. The purification of the dyes was carried out by recrystallization from a 90:10 (v:v) dioxane:pyridine mixture to obtain the pure products with yields of 80–82%.

Characterization of the dyes

The UV/VIS spectroscopy measurements were performed using a CECIL CE 7200 spectrophotometer in the 300–800 nm range, while the FT/IR (KBr) spectroscopy data were carried out on a JASCO FT/IR-4200 spectrometer in the 4000–400 cm^{-1} range.

For I: TLC (silicagel plates 60F−254:methyl−ethyl ketone:ammonia 25%:MeOH=2:3:2 (v:v:v)) (R_f: 0.77); VIS (50% aqueous MeOH) (λ_{max}/nm; lgε: 591; 4.40); IR (KBr) (ν/cm^{-1}: 3430 (OH), 1185, 1073 (SO_3H), 1681(C=C)).

For dye II: TLC (silicagel plates 60F−254:methyl−ethyl ketone: ammonia 25%:MeOH=4:4:1.5 (v:v:v)) (R_f: 0.81); VIS (50% aqueous MeOH) (λ_{max}/nm; lgε : 542; 4.42); IR (KBr) (ν/cm^{-1}: 3523 (OH), 1125, 1077 (SO_3H), 1640 (C=C)).

Colorimetric measurement of the dyes

Experimental details of the color analysis of the above-mentioned dyes may be found in previous published studies [15, 29]. The dyes were mixed in different concentrations (2%, 5%, 8% and 15%) with a water-based acrylic resin containing titanium dioxide (TiO_2) paste (C.I.77891 P.W.6) – the standard for all color analysis (0%). The mixtures were then applied on a white cellulosic support, and their color properties (L* - lightness; a* - the transition from green to red and b* - the transition from blue to yellow, as well as the Reflectance) were recorded using a MINOLTA CM 3220d spectrophotometer with the CIE D65 as the illuminant (natural day light) and the standard 10° observer function, and for thee metamerism effect determination, two other illuminants were used, namely A – warm light and F2 – cold light.

REFERENCES

1. H. Zollinger; *Color Chemistry: Syntheses, Properties and Applications of Organic Dyes and Pigments*, 3rd ed.; Wiley-VCH: Weinheim, Germany, **2003**.
2. A. Z. Omar; M. G. Mohamed; E. A. Homed; M. A. El-Atavy; *J. Saudi Chem.*, **2023**, *27(1)*, 101594.
3. A. Matei; C. Constantinescu; B. Mitu; M. Filipescu; V. Ion; I. Ionita; S. Brajnicov; A. P. Alloncle; P. Delaporte; A. Emandi; M. Dinescu; *Appl. Surf. Sci.*, **2015**, *336*, 200-205.
4. K. Yamjala; M. S Naiar; N. R. Ramisetti; *Food Chem.*, **2016**, *192*, 813–824.
5. S. Benkhaya; S. M'rabet; A. El-Harfi; *Heliyon*, **2020**, *6(1)*, e03271.
6. E. U. Mughal; Q. A. Raja; A. Y. A. Alzahrani; N. Naeem; A. Sadiq; E. Bozkurt; *Dyes Pigm.*, **2023**, *220*, 111762.
7. F. Eltaboni; N. Bader; R. El-Kailany; N. Elsharif; A. Ahhmida; *J. Chem. Rev.*, **2022**, *4(4)*, 313-330.
8. P. D. Josephy; E. Allen-Vercoe; *Food Chem Toxicol.*, **2023**, *178*, 113932.
9. T. Platzek; *Toxicol. Lett.*, **2013**, *221*, S53.
10. Bundesgesetzblatt; *Zweite Verordnung zur Änderung der Atomrechtlichen Verfahrensordnung*, nr. 82; Bonn, Germany, **1994**.
11. Bundesgesetzblatt; Vierte Verordnung zur Änderung der Bedarfsgegenständeverordnung, nr. 8; Bonn, Germany, **1995**.
12. Y. C. Chao; S. S. Yang; *Dyes Pigm.*, **1995**, *29(2)*, 131-138.
13. M. E. Grad; V. Rădiţoiu; L. Wagner; A. Rădiţoiu; A. X. Lupea; *Rev. Chim. (Bucharest)*, **2007**, *58(8)*, 786-790.
14. M. E. Grad; G. M. Simu; S. G. Muntean; G. Ilia; *J. Iran Chem Soc.*, **2013**, *10(4)*, 807-814.
15. M. E. Rădulescu-Grad; A. Visa; M. S. Milea; R. I. Lazău; S. Popa; S. Funar-Timofei; *J. Mol. Struct.*, **2020**, *1217*, 128380.
16. J. A. Paulo, D. I. Santos, *Ind. Crop. Prod.*, **2023**, *205*, 117513.
17. R. M. Christie; *Colour Chemistry*, 2nd ed.; The Royal Society of Chemistry: Cambridge, UK, **2013**.
18. S. Yufa; F. A. M. Al-Zahrani; L. Lin; *Dyes Pigm.*, **2023**, *208*, 110854.
19. J. Biswas; S. Yana; S. Gosh; *J. Non-Cryst. Solids.*, **2024**, *630*, 122890.
20. H. Sanielevici; F. Urseanu; *Sinteze de Coloranţi Azoici*, vol. 2; Ed. Tehnică: Bucureşti, Romania, **1987**.
21. A. E. Balaban; M. Banciu; I. Pogany; *Aplicatii ale metodelor fizice in chimia organica*; Ed. Didactică şi Pedagogică: Bucureşti, Romania, **1980**.
22. A. Raditoiu; V. Raditoiu; C. A. Nicolae; M. F. Raduly; V. Amariutei; L. E. Wagner; *Dyes Pigm.*, **2016**, *134*, 69-76.
23. R. Mia; M. Minhajul Islam; T. Ahmed, M. Azhar Waquar; N. Jahan Khanam; S. Sultana; M. Sajjadul Karim Bhuiyan; M. Nizam Uddin; *Clean. Eng. Technol.*, **2022**, *8*, 100471.

24. P. M. Bhate; R. V. Devi; R. Dugane; P. R. Hande; L. Shaikh; S. Vaidya; S. Masand; *Dyes Pigm.*, **2017**, *145*, 208-215.
25. D. R. Patel; B. M. Patel; N. B. Patel; K. C. Patel; *J. Saudi Chem. Soc.*, **2024**, *18(3)*, 245-254.
26. M. Filgueiras Rebelo de Matos; P. Quênia Muniz Bezerra; L. Conceição Argôlo Correia, V. Denise Nunes; A. de Oliveira Rios; J. Izabel Druzian; I. L. Nunes; *Food Chem.*, **2021**, *365*, 130446.
27. A. T. M. Gulam Moula; Md. Dulal Hosen; Md. Abu Bakar Siddiquee; Md. Abdul Momin; Z. Kaisar; Md. Abdullah Al Mamun; Md. Azharul Islam; *Heliyon*, **2022**, *8*, e11246.
28. M. Tousirot; W. Nowik, E. Hnawia, N. Lebouvier, A.E. Hay; A. de la Sayette; M.G. Dijoux-Franca; D. Cardon; M. Nour; *Dyes Pigm.*, **2014**, *102*, 278-284.
29. S. Popa; M.E. Radulescu-Grad; A. Perdivara; G. Mosoarca; *Sci. Rep.*, **2021**, *11*, 5889.