New Salicilic Acid-Based Azo Dyes
Synthesis, Characterization and Colour Properties

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The paper presents a study regarding colour and colouring properties of some azoic dyes derived from salicylic acid. The synthesized dyes were analyzed by thin layer chromatography and electronic spectra. Colours were measured in CIELAB system. The CIELAB (1976) colour space was used in all the colour measurements for the synthesized azo dyes under CIE recommended illuminants: D65 (natural day light), A (tungsten light), F2 (fluorescent light) and the standard 10° observer, respectively. The colour differences ΔEab and ΔECMC were calculated against one standard. The results revealed a fine colouring power of the new salicilic acid-based azo dyes. The samples are different regarding their dye concentration. The hue, luminosity and saturation are discussed as well as their colouring power.*

Keywords: azoic dyes, colouring power, CIELAB uniform colour space

The compounds under study are part of the azo pigments class. They are novel compounds. From structure standpoint, they belong to chemical derivatives of salicylic acid, known for their representation in the chemistry of azo dyes. The presented derivatives were part of a wider study, which included compounds very different as properties, from azo dyes and pigments to biologically active compounds [1-2].

Azo dyes and pigments constitute the largest class of organic dyes. Their great advantage consists in virtually unlimited possibility (of synthesis) to obtain new compounds with improved dyeing characteristics and low toxicity - it is important to take into account the legislation regarding the marketing of these products [3] and the need to be continuously tested [4]. From this point of view, one of the most important aspects is the synthesis of dyes and polymers with a minimum impact on the environment. Most of all, consequences over the public health should be known, considering their various utilizations (especially because numerous aromatic amines used as coupling components, which may have a carcinogenic potential).

There are a lot of new dyes synthesized, as presented in [5-7]. The authors which performed these researches provide their synthesis methods and characterization, including their colour properties, and for some of them even antimicrobial activity, or thermal stability.

Azo dyes and pigments may be used for colouring polymers [8]. Surface films known as paints and varnishes have some common properties: they are fluid or plastic (or can be easily transformed in one of these forms) and they can be applied mechanically (by brush or spray) as one or more layers on a surface. After application, the material is subject to drying process. In this process, the material is converted from fluid to solid state, resulting in a film firmly anchored on the surface of the object which was applied on. This film may contain different paints which ensure the desired colour of the plastic. Generally, nitrogen compounds are soluble in the polymer matrix (plasto-soluble). In addition to plastics, nitrogen compound paints synthetic fibres, rubber, food etc. In most cases, they ensure strong painting, vivid and pure colours [9].

In line with these considerations a series of salicylic acid derivatives azo dyes have been synthesized. Coupling components were N-substituted amides of salicylic acid and p-nitroaniline as diazo component. The synthesized compounds are structurally new, with shades of the yellow-orange to brown-red and belong to the pigments class [10].

Synthesis of dyes underwent two stages:
- the diazonium salt synthesis
- coupling reaction.

Colour is the way the HVS (the human visual system) measures a part of the electromagnetic spectrum, approximately between 300 and 830 nm. There are different methods to describe the characteristics of a particular colour. Visible reflectance spectroscopy is wide-spread to measure the colour of opaque objects such as textile fabrics, films and plastics for purposes such as colour matching and dye or pigment recipe prediction. This technique may be considered as complementary to the use of visible absorption spectroscopy for the measurement of transparent dye solutions [11].

The grounds of colorimetry were established by Commission Internationale d'Eclairage (CIE) based on visual experiments. In this regard, CIE L* a* b* (CIELAB) is the most uniform colour model used conventionally to describe all the colours visible to the human eye, being well known due to the properties of high importance like device-independency and perceptual linearity [12–13].

Colour properties of dyes were also an important issue for some studies [14-17].

In this work, the synthesis, the physicochemical properties and the colorimetric evaluation of three new azo direct dyes derived from 2-hydroxy-benzoic acid are presented.

Experimental part
Materials and methods

The chemicals employed in this study as p.a. commercial products were provided by S.C. Chimopar S.A., Fluka Co., Merck Co., S.C. Azur S.A. and Monicolour S.A.

The thin layer chromatography (TLC) data were established using silica gel (60F-254) plates (Merck). The solvent system employed was toluene: methanol = 10:4.

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Table 1
CHARACTERIZATION OF AZO DYES

No.	*Azo dye name*	*Yield, %*	*UV-VIS spectra (λ, nm)*	*R_f value*	*Colour*
1.	I	88	310 406 419 487	0.36	light-brown
2.	II	86	297 385 492	0.38	brown
3.	III	83	292 411 492	0.44	light-brown

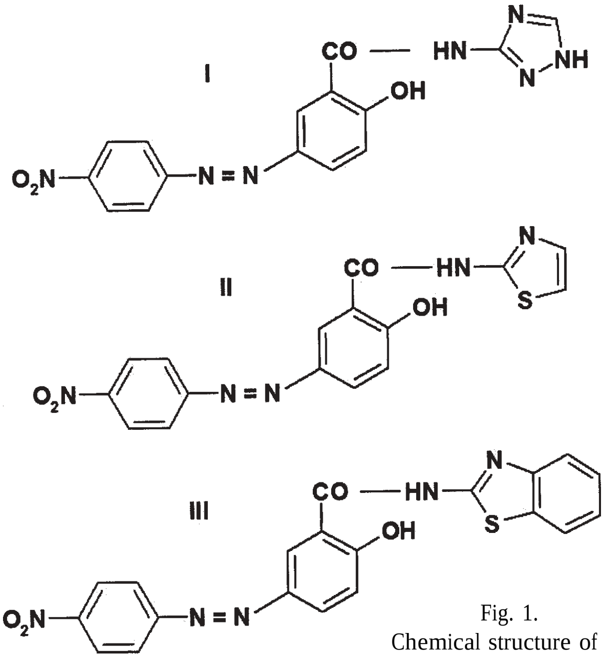

Fig. 1. Chemical structure of dyes I, II and III

All the components contained in the mobile phase were of analytical grade purity.

Electronic absorption spectra (VIS) of dyes in MeOH solution (c = 1.09 10-5mole/dm^3) were performed on a CECIL CE 7200 spectrophotometer in the range 300–800 nm.

The FT/IR (KBr) spectra were recorded on a JASCO FT/IR-4200 spectrometer in the range 400–4.000 cm^{-1}.

The colorimetric analysis of the synthesized dyes was performed for the D65/108, A/108, and F2/108 illuminant/observer CIE conditions using a MINOLTA 3220d spectrophotometer. The results were processed using the corobQUALITY 1.5 computer program.Equation style bases on Normal style. However, single space is recommendable.

The synthesis of dyes comprises of two stages: synthesis of diazonium salt and coupling reaction.

The synthesis of diazonium salt used the direct method: p-nitroaniline (0.004 mol) was dissolved in hot hydrochloric acid solution 30% (0.012 moles). The resulting solution was poured over a water-ice mixture to precipitate the amine hydrochloride. Sodium nitrite solution (0.005 mol) was added in drops while stirring over suspension amine hydrochloride. System *p*H should be maintained net acidic (1.5 to 2.0). During the reaction, the system must keep a permanent nitrite excess verifiable with iodine-starch paper. In the end, the nitrite excess is destroyed by the addition of urea. Due to instability of diazonium salt temperature must be maintained between -2 to 2 °C.

For the coupling reaction, the salicylic acid amide (coupling component) was suspended in a minimum volume of ethanol 96% with NaOH 20% added for solubilization (*p*H ~ 11).

Coupling reaction occurs at a temperature of -2 to 2 °C (ice bath), working at a molar ratio of diazonium salt: amide of 1:1. Diazonium salt was added slowly while stirring the salicylic acid amide solution. *p*H was maintained at 8.5 to 9. In the reaction system must be maintained a permanent excess of coupling component. Reaction progress was monitored by TLC (solvent system toluene: methanol = 10:4).

Preparation of reaction is for 24 h at room temperature. The obtained azo dyes were separated by adjusting the *p*H to 6.5 to 7 and diluting the mixture. The precipitate was filtered and dried at 80 ± 0.5 °C. The compounds structures are shown in figure 1. They look like dark brown powder.

Purification was achieved by re-crystallization from hot distilled water and treatment with activated charcoal. A second purification involved a re-crystallization from hot dimethylsulfoxide (DMSO). Dyes were characterized by UV-VIS and FT/IR spectra and CSS (table 1).

The FT/IR spectra(KBr) (ν/cm^{-1}): I: 3444, 1395 (OH), 1666, 1532, 1222 (CONH), 1390, 832(NO2); II: 3338, 1342 (OH), 1667, 1544, 1248 (CONH), 1514, 855 (NO2); III: 3435, 1318 (OH), 1665, 1558, 1258 (CONH), 1518, 847 (NO2).

The paper deals with the analysis of colour properties (such as hue, brightness, luminosity and colouring power). The samples to analyze are azoic dyes, derived of salicylic acid.

Figure 1 shows the chemical formulae of dyes I, II and III. Dyes are layers spread over a cellulosic substrate (natural wood). Measurements were conducted under colour CIELAB system. Each compound was compared with the standard natural wood. Samples differ by the concentration of the dye. The colour of the new three azo dyes was evaluated in terms of CIELAB parameters: lightness (L*), redness (a*), yellowness (b*), chroma or saturation (C*) and hue angle (h*) for the CIE D65 (natural day light), A (tungsten light), F2 (fluorescent light) and the standard observer function of 10°, respectively. Further details on the general procedure may be found in reference [18]. The colour differences DEab* and DECMC were calculated against the above-mentioned titanium dioxide, often used in the colouring power study of the dyes and pigments.

Results and discussions

The synthesis of the azo dyes 1-3 with structures shown in Figure 1 involved the diazotization of p-nitroaniline (PNA) followed by the coupling reaction of the resulted diazonium salt with salicylic acid derivatives: 2-amino-1,2,4(H)-triazole (I), 2-aminotiazole (II) and 2-amino-benztiazole (III) respectively.

The diazotization of p-nitroaniline was carried out by the direct method, in a HCl aqueous solution [17]. In the azo coupling reaction, the diazonium ions formed during diazotization give rise to azo compounds in an electrophilic aromatic substitution. Because diazonium ion is generally a weak electrophilic reagent, the phenolate ion (Ar–O-) and the free amine (Ar–NH$_2$) react more easily as coupling components than free phenol (Ar–OH) and the ammonium ion (Ar–NH$_3$ +). As a consequence, the coupling reactions were performed in an alkaline aqueous medium (*p*H around 8), in presence of Na$_2$CO$_3$ at room temperature. It was found that the direct addition of the diazonium salt to the coupling component was the optimum way for the azo-dyes (1-3, table 1) synthesis. The progress of the coupling reactions was monitorized. Purification was achieved by re-crystallization from hot distilled water and treatment with activated charcoal. A second purification involved a re-crystallization from hot dimethylsulfoxide (DMSO).

The newly synthesized disazo dyes 1-3 (table 1) were characterized by means of TLC, FT/IR, and UV- VIS spectroscopy. The analysis of the IR spectra permitted the assignment of the absorption bands with confidence. Each of the three compounds examined presents the three well-known characteristic bands corresponding to the secondary amide group (CONH–). The spectra of the dyes show two absorption bands, around 3500 and 1350 cm^{-1}, corresponding to the OH stretching and deformation vibrations of the phenolic function. The characteristic frequency of ías vibration for $–NO_2$ group appears at 1500-1520 cm^{-1} intense, overlapped with those of azo group; medium-intense for ís vibration at 1330-1345 cm^{-1} and medium intensity at 850-860 cm^{-1} (δNO_2).

The UV-VIS spectra were presented in table 1.

It is known that the description of colour is based on the interaction of three elements: illuminant - which is normally specified in terms of the relative energy tabulated for each wavelength or wavelength band, coloured object - which is normally specified by the reflection curves, and observer - characterized by the spectral distribution curves [18]. In order to describe a colour, three numerical components are necessary and sufficient, and that is because the human retina has three types of colour photoreceptors. A colour may be numerically described by three virtual stimulus X (an imaginary red source), Y (an imaginary green source), and Z (an imaginary blue source), which are specific for each colour, and identical to the fractions of three primary light sources; they do not represent real colours but are only size calculation numbers, and that is why they are called virtual stimulus [18]. The XYZ tri-stimulus values, can also predict if the colours are metamers - whether they appear exactly the same to the human eye, or whether a colour appears lighter than another, but they cannot predict perceived colour differences.

CIE 1976 (L*, a*, b*) or CIELAB colour space is an approximately uniform colour space. The difference between points plotted in this space agrees with visual difference between the colours plotted. In the CIELAB colour space each colour has a unique location defined by its Cartesian co-ordinates with respect to the axes L*, a*, and b* - obtained from the XYZ tri-stimulus values according to the CIE 1976 equations, where L* is the degree of lightness and covers a range from white (100) to black (0) along a greyscale, a* is the degree of redness and greenness and b* is the degree of yellowness and blueness. The chromaticity coordinates (a*, b*) are represented in polar co-ordinates by the chroma (C*), the Euclidian distance from the lightness axis and the hue angle (h*) expressed in degrees starting from the positive a* axis (red) and turning in an anti-clockwise direction. Most colour scientists agree that three attributes can be identified in the description of colours: hue (h*), chroma (C*) and lightness (L*) [14-17, 18]. It is obvious that the CIELAB system can be represented either in terms of the three orthogonal co-ordinates L*, a*, and b* or of the cylindrical co-ordinates L*, C*, and h*. It is well known that colour differences are always calculated as sample standard values. DEab* colour difference (the total colour difference) is based on L*, a*, b*, colour differences and was intended to be a single number metric for pass/fail decision [18]. Colour Measuring Committee of the Society of Dyers and Colourists (DECMC) is a single number measurement that defines an elliptical colour difference space around the product standard. The DECMC equation defines an ellipsoid with semi axis corresponding to lightness (L*), chroma (C*) and hue (h*), which approximates much better the colour tolerance system of the human eye [18]. Usually, the colour differences DEab* present a ±0.2 units error, comparable with the sensibility of the human eye. At the same time, the observed disagreements depend on the size and orientation of the colour difference vector ΔEab*. It was remarked that the DECMC equation builds a tolerance system (pass/fall), performing better at the Gray centre by including the well-known adjustable parameters (commercial factor, lightness to chroma ratio) [18]. Generally, the metamerism is considered with respect to the human visual system. This phenomenon is broadly defined as the production of identical spectrally integrated responses from disparate spectral power distributions.

Table 3 features dye I, concentrated [1...4] %, under the three illuminants mentioned above. For each illuminant cylindrical, orthogonal and tri-stimulus coordinates are indicated. Also colour differences are shown.

Tables 4 and 5 refer to dyes II and III, in different concentrations, under the three illuminants.

Studying data in the tables above, the following remarks on luminosity course are important:

- under illuminant D65, the luminosity decreases inversely to concentration. In addition, the down-going slope of luminosity is more abrupt as the dye concentration grows;

Table 2
PERCENTAGE REFLECTANCE OF STANDARD SAMPLE AND DYE SAMPLES UNDER ILUMINANT D65

λ [nm]	*standard*	*I*	*II*	*III*
400	15.82	7.78	5.59	5.77
420	25.53	10.04	6.23	6.38
440	32.86	12.03	7.2	7.15
460	37.81	13.83	8.51	7.93
480	41.90	15.57	10.03	8.78
500	45.48	17.55	11.81	9.82
520	49.27	20.70	14.57	11.72
540	52.97	25.24	18.45	14.82
560	56.76	31.84	23.56	19.48
580	60.81	40.13	29.95	25.51
600	64.72	49.16	36.70	31.95
620	68.46	58.00	44.04	38.46
640	71.65	64.94	51.05	44.36
660	74.46	70.24	57.46	50.03
680	76.59	73.83	62.98	55.33
700	78.79	76.60	67.93	60.60

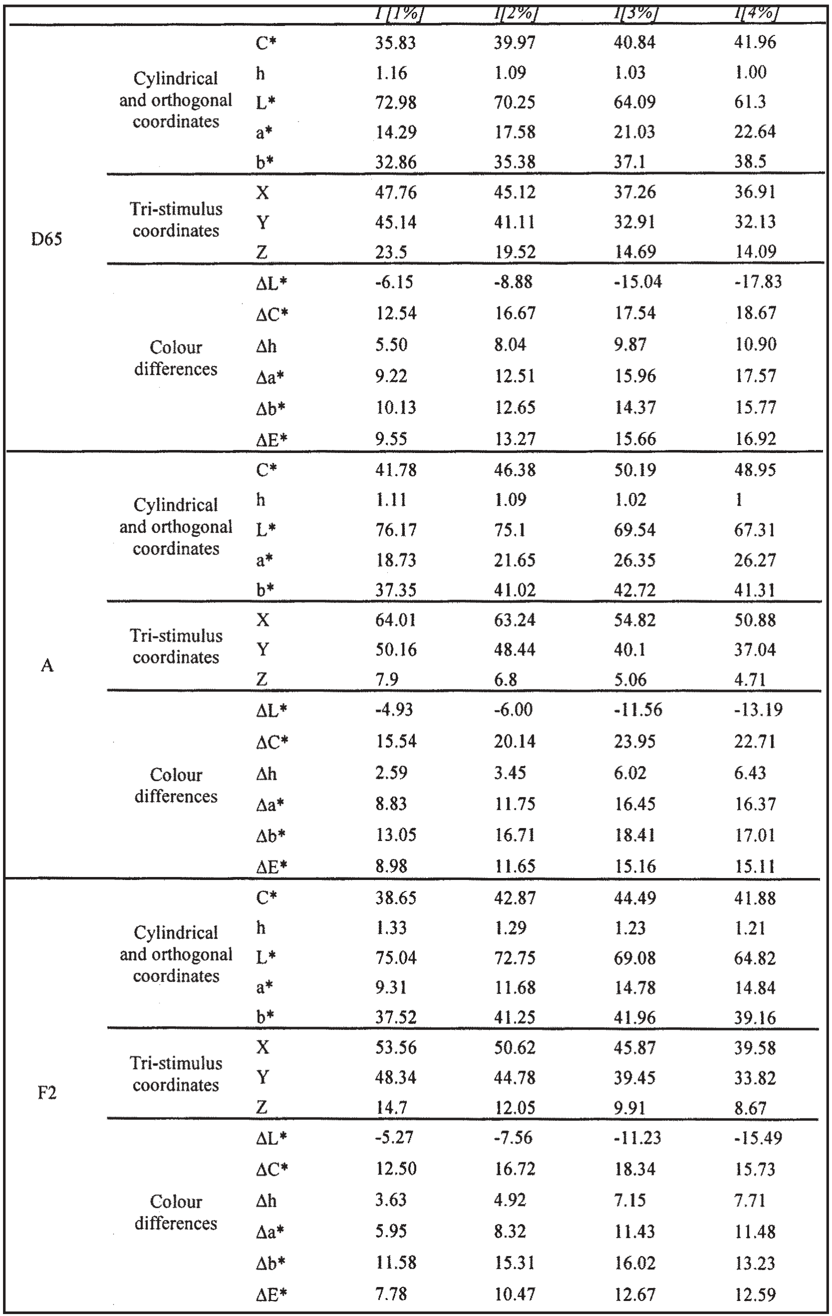

Table 3
COLOUR COORDINATES
OF DYE I

			I [1%]	*I[2%]*	*I[3%]*	*I[4%]*
D65	Cylindrical and orthogonal coordinates	C*	35.83	39.97	40.84	41.96
		h	1.16	1.09	1.03	1.00
		L*	72.98	70.25	64.09	61.3
		a*	14.29	17.58	21.03	22.64
		b*	32.86	35.38	37.1	38.5
	Tri-stimulus coordinates	X	47.76	45.12	37.26	36.91
		Y	45.14	41.11	32.91	32.13
		Z	23.5	19.52	14.69	14.09
	Colour differences	ΔL*	-6.15	-8.88	-15.04	-17.83
		ΔC*	12.54	16.67	17.54	18.67
		Δh	5.50	8.04	9.87	10.90
		Δa*	9.22	12.51	15.96	17.57
		Δb*	10.13	12.65	14.37	15.77
		ΔE*	9.55	13.27	15.66	16.92
A	Cylindrical and orthogonal coordinates	C*	41.78	46.38	50.19	48.95
		h	1.11	1.09	1.02	1
		L*	76.17	75.1	69.54	67.31
		a*	18.73	21.65	26.35	26.27
		b*	37.35	41.02	42.72	41.31
	Tri-stimulus coordinates	X	64.01	63.24	54.82	50.88
		Y	50.16	48.44	40.1	37.04
		Z	7.9	6.8	5.06	4.71
	Colour differences	ΔL*	-4.93	-6.00	-11.56	-13.19
		ΔC*	15.54	20.14	23.95	22.71
		Δh	2.59	3.45	6.02	6.43
		Δa*	8.83	11.75	16.45	16.37
		Δb*	13.05	16.71	18.41	17.01
		ΔE*	8.98	11.65	15.16	15.11
F2	Cylindrical and orthogonal coordinates	C*	38.65	42.87	44.49	41.88
		h	1.33	1.29	1.23	1.21
		L*	75.04	72.75	69.08	64.82
		a*	9.31	11.68	14.78	14.84
		b*	37.52	41.25	41.96	39.16
	Tri-stimulus coordinates	X	53.56	50.62	45.87	39.58
		Y	48.34	44.78	39.45	33.82
		Z	14.7	12.05	9.91	8.67
	Colour differences	ΔL*	-5.27	-7.56	-11.23	-15.49
		ΔC*	12.50	16.72	18.34	15.73
		Δh	3.63	4.92	7.15	7.71
		Δa*	5.95	8.32	11.43	11.48
		Δb*	11.58	15.31	16.02	13.23
		ΔE*	7.78	10.47	12.67	12.59

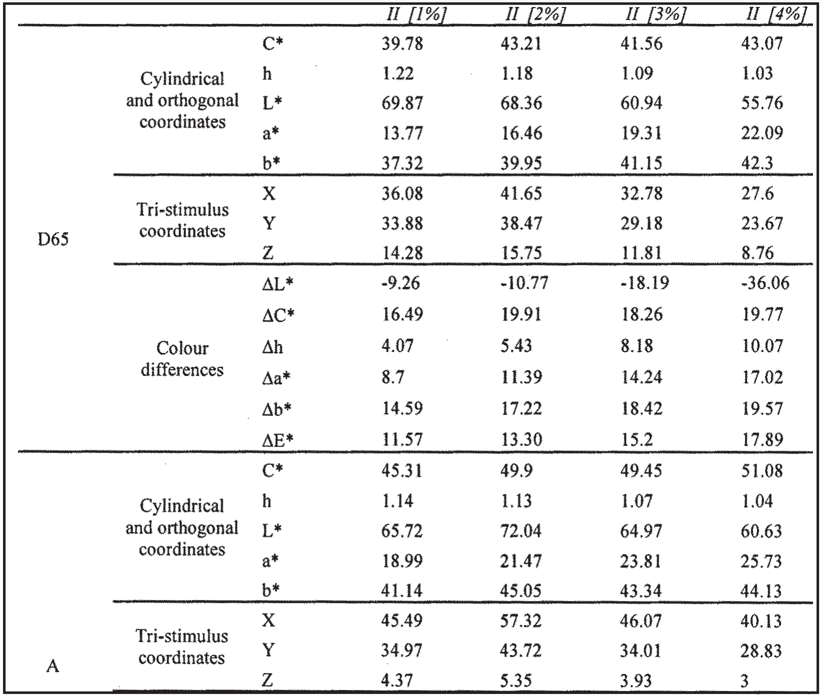

Table 4
COLOUR COORDINATES
OF DYE II

			II [1%]	*II [2%]*	*II [3%]*	*II [4%]*
D65	Cylindrical and orthogonal coordinates	C*	39.78	43.21	41.56	43.07
		h	1.22	1.18	1.09	1.03
		L*	69.87	68.36	60.94	55.76
		a*	13.77	16.46	19.31	22.09
		b*	37.32	39.95	41.15	42.3
	Tri-stimulus coordinates	X	36.08	41.65	32.78	27.6
		Y	33.88	38.47	29.18	23.67
		Z	14.28	15.75	11.81	8.76
	Colour differences	ΔL*	-9.26	-10.77	-18.19	-36.06
		ΔC*	16.49	19.91	18.26	19.77
		Δh	4.07	5.43	8.18	10.07
		Δa*	8.7	11.39	14.24	17.02
		Δb*	14.59	17.22	18.42	19.57
		ΔE*	11.57	13.30	15.2	17.89
A	Cylindrical and orthogonal coordinates	C*	45.31	49.9	49.45	51.08
		h	1.14	1.13	1.07	1.04
		L*	65.72	72.04	64.97	60.63
		a*	18.99	21.47	23.81	25.73
		b*	41.14	45.05	43.34	44.13
	Tri-stimulus coordinates	X	45.49	57.32	46.07	40.13
		Y	34.97	43.72	34.01	28.83
		Z	4.37	5.35	3.93	3

Table 4
(continuated)
COLOUR COORDINATES
OF DYE II

	Colour differences	ΔL*	-15.38	-9.06	-16.13	-20.47
		ΔC*	19.07	23.66	23.21	24.64
		Δh	1.58	2.10	4.16	5.16
		Δa*	9.10	11.57	13.91	15.83
		Δb*	16.84	20.74	19.03	19.83
		ΔE*	11.73	13.22	14.51	16.34
F2	Cylindrical and orthogonal coordinates	C*	44.93	47.97	45.47	45.32
		h	1.36	1.34	1.28	1.24
		L*	69.08	70.25	63.31	57.01
		a*	9.37	10.85	12.95	14.91
		b*	43.94	46.73	43.59	42.79
	Tri-stimulus coordinates	X	43.96	46.27	36.89	29.59
		Y	39.46	41.1	31.95	24.94
		Z	9.36	9.15	6.97	4.95
	Colour differences	ΔL*	-11.23	-10.06	-17.0	-23.3
		ΔC*	18.78	7.49	19.32	19.16
		Δh	2.79	3.52	5.51	7.09
		Δa*	6.02	7.49	9.59	11.55
		Δb*	18.0	20.79	17.65	16.86
		ΔE*	11.14	12.65	13.16	14.99

Table 5
COLOUR COORDINATES
OF DYE III

			III [2%]	*III [3%]*	*III [4%]*	*III [5%]*
D65	Cylindrical and orthogonal coordinates	C*	37.23	41.85	48.58	39.49
		h	1.25	1.19	1.08	0.94
		L*	72.4	70.32	62.94	51.83
		a*	11.84	15.51	22.01	23.23
		b*	35.3	38.87	42.79	43.5
	Tri-stimulus coordinates	X	44.5	44.17	36.36	23.85
		Y	42.77	41.21	31.51	20
		Z	20.61	17.83	10.9	8.24
	Colour differences	ΔL*	-6.73	-8.81	-16.19	-27.3
		ΔC*	13.94	18.56	25.29	16.2
		Δh	3.07	4.99	9.19	12.33
		Δa*	6.41	10.44	16.94	18.16
		Δb*	12.57	16.14	20.06	20.77
		ΔE*	9.00	12.23	18.43	19.16
A	Cylindrical and orthogonal coordinates	C*	43.38	47.5	54.28	47.92
		h	1.15	1.13	1.05	0.99
		L*	75.23	73.81	64.79	58.12
		a*	17.7	20.19	27.19	26.16
		b*	39.6	42.99	46.98	40.15
	Tri-stimulus coordinates	X	61.71	60.06	47.05	36.72
		Y	48.65	46.39	33.79	26.09
		Z	7.17	6.15	3.46	2.96
	Colour differences	ΔL*	-5.87	-7.30	-16.31	-22.98
		ΔC*	17.14	21.26	28.04	21.68
		Δh	1.14	1.85	5.20	6.75
		Δa*	7.81	10.29	17.29	16.26
		Δb*	15.30	18.69	22.68	15.85

Table 5
(continuated)
COLOUR COORDINATES
OF DYE III

		ΔE*	9.44	11.80	17.17	16.33
F2	Cylindrical and orthogonal coordinates	C*	42.02	48.26	48.23	41.76
		h	1.38	1.34	1.22	1.19
		L*	73.1	71.59	61.1	56.44
		a*	7.85	11.01	16.6	15.35
		b*	41.28	46.99	45.28	38.83
	Tri-stimulus coordinates	X	49.72	48.47	35.1	29.04
		Y	45.31	43.05	29.36	24.35
		Z	12.23	9.71	5.81	5.5
	Colour differences	ΔL*	-7.21	-8.72	-19.21	-23.87
		ΔC*	15.87	22.11	22.08	15.61
		Δh	1.96	3.60	7.89	8.17
		Δa*	4.49	7.66	13.24	12.00
		Δb*	15.34	21.05	19.35	12.90
		ΔE*	9.05	12.68	15.70	14.45

- the paint shifts to dark, thus the presence of black is more accented. Considering the structure of the dyes, one can notice that the dye containing nitrogen in the coupling compound provides higher luminosity than the dyes containing sulphur. Among the two dyes containing sulfur, the one with benzenic nucleus is less luminous. This is the result of aromatic conjugation growth, which determines a batochrome displacement and, thus, a shift to dark and decrease in luminosity;

- parameter a* depends directly on the concentration. This means that as the concentration grows, the hue turns towards red, for all three dyes. This effect is stronger for the dye containing nitrogen and weaker for the dye with sulphur and coupling compound with higher conjugation. The last one tends to show less red, which determines a shift to green in colour space;

- parameter b* decreases as concentration grows. This means that the hue turns to blue proportionally with concentration. The dye with nitrogen contains more yellow than the ones containing sulphur. The course is similar for all three dyes. At small concentrations the yellow is more pronounced. As concentration grows, the yellow fades and the hue shifts towards blue in the colour space. The effect is more obvious at the dye containing a coupling component with higher conjugation;

- furtheron, the colouring power will be referred to as the relative ability of a dye to modify the colour of a white pigment to which it is added. The colouring power was quantified by the colour difference DE. As the concentration grows, the colour difference to the white sample increases significantly. An important conclusion is that the colouring power of the dyes is strong;

- the nature of illuminant influences colour. The apparent change in colour is dichotic-type. In the case of the studied dyes, the dichroism was evaluated through the colour difference HE of samples under the three illuminants (tables 3-5). One can notice that as the concentration increases, the colour difference also gets higher for all three illuminants. The colour difference is given by the relationship:

$$\Delta E^*_{ab} = \sqrt{\left(\Delta L^*\right)^2 + \left(\Delta a^*\right)^2 + \left(\Delta b^*\right)^2} \quad (1)$$

It is also of some scientific and technical interest to learn which parameter among L*, a* and b* are most significant in colour difference variation. For this purpose the values ΔL*, ΔC*, Δh*, Δa* and Δb* in table 1 are analyzed. The following remarks can be made:

- ΔE* does not differ much enough to allow distinction of colours with the naked eye. This applies to all dyes under a certain illuminant;

- the values of ΔL* are also close within a small range for all concentrations;

- parameter Δa* is very different for illuminants D65 and F2 compared to A. Under illuminant A the samples seem to contain more red;

- parameter Δb* varies a lot from illuminants D65 and A to F2. Under illuminant F2 the samples seem to be more yellowish;

- parameter ΔC* varies a lot from illuminants D65 and A to F2. Under illuminant F2 the colour appears more saturated;

- parameter Δh* shows small variations with concentration, which means the hues are close.

Conclusions

Three new azo direct dyes using p-nitroaniline as diazotized component were synthesized and characterized. As coupling component were used N-substituted amides of salicylic acid with 2-amino-1,2,4(H)-triazole, 2-aminothiazole and 2-aminobenztiazole respectively. The compounds were characterized and UV-VIS, FT/IR and TLC data were presented.

The colorimetric study conducted on three azoic dyes showed that the higher the concentration gets, the lower the luminosity becomes. Considering the structure of the dyes, the dye containing nitrogen in the coupling compound provides higher luminosity than the dyes containing sulphur. Among the two dyes containing sulphur, the one with benzenic nucleus is less luminous.

The dye containing nitrogen and the dye with sulphur and lower conjugation tend to have more red as the concentration increases. The third dye, containing a coupling compound with higher conjugation, gets less red as the concentration increases and its colour sifts toward green in colour space.

The dye with nitrogen seems to be more yellow than the dyes with sulphur. The yellow component is present for all dyes at small concentrations, but it starts to fade as the concentration increases.

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