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Azocoupling products. V[1]. Electronic spectroscopy study of two azocoupling products of 1-(4-hydroxy-6-methyl-pyrimidin-2-yl)-3-methyl-pyrazolin-5-one

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Abstract

A systematic study of the effect of solvent, sample concentration, time and acid or alkali addition, respectively of pH′, upon the electronic absorption spectra of two dyes **7** and **8**, as well as the pK'_a determination of these dyes was carried out. In C_6H_6, $CHCl_3$, DMSO, and acidic media (AcOH, acidified EtOH) these dyes that theoretically may be involved in azo–hydrazone tautomerism have been detected only as hydrazone tautomers **7c** and **8c**. In exchange, in neutral and alkalized EtOH, respectively in DMF, in concentration range 10^{-4}–10^{-6} mol L^{-1} these tautomers are in equilibrium with monodeprotonated (**9**, **10**) and twice deprotonated (**13**, **14**) species. By increase of pH, or by dilution, the equilibrium shifts increasingly towards the deprotonated species. The monodeprotonated species, correspond also to a hydrazone structure **9**, **10**, whilst the doubly deprotonated species represent a common dianion that should be predominantly azo in character (**13**, **14**).

Keywords: Azocoupling products of 1-(4-hydroxy-6-methyl-pyrimidin-2-yl)-3-methyl-pyrazolin-5-one; Electronic absorption spectra; pK_a; Hydrazone- or deprotonated azo-structures

1. Introduction

Several data in our last studies [1,2] on azocoupling products (**1**) obtained from 1-(4-hydroxy-6-methyl-pyrimidin-2-yl)-3-methyl-pyrazolin-5-one (**2**) and aromatic diazonium salts (**3**) have suggested the manifestation in the case of these dyes (**1**) of interconnected azo–hydrazone (e.g. **1a–c**, **4a–c**, **5**) and acid–base (e.g. **1a**, **4a**, **6**) equilibria (Scheme 1). It must be underlined that such interconnected equilibria, as above [3,4,5a] or involving either in addition, [5b,6] or instead of acid–base equilibrium, [7,8] an aggregation equilibrium, were formulated also in the quoted studies [3–8] concerning other azocoupling products that theoretically may be involved in azo–hydrazone tautomerism. Therefore, the aim of this paper is to find new data in support of the proposed [1,2] interconnected equilibria and eventually even for the aggregation process.

With this object in view we studied the effect of the solvents, pH, dye concentration and time on the absorption spectra over 350 nm for two representative azocoupling products of 1-(4-hydroxy-6-methyl-pyrimidin-2-yl)-3-methyl-pyrazolin-5-one (**2**) namely **7** and **8** (see Scheme 1). These compounds **7** and **8** are differentiated principally by the substituent nature in the *para* position of their benzene ring with respect to the azo- (or hydrazone-) group: in **7** a weak electron-releasing substituent (CH_3) and in **8** a strong electron-withdrawing substituent (NO_2). In addition, **7** and **8** differ only by the position of a supplementary methyl group in their above mentioned benzene ring: *ortho*- in **7** but *meta*- in **8**.

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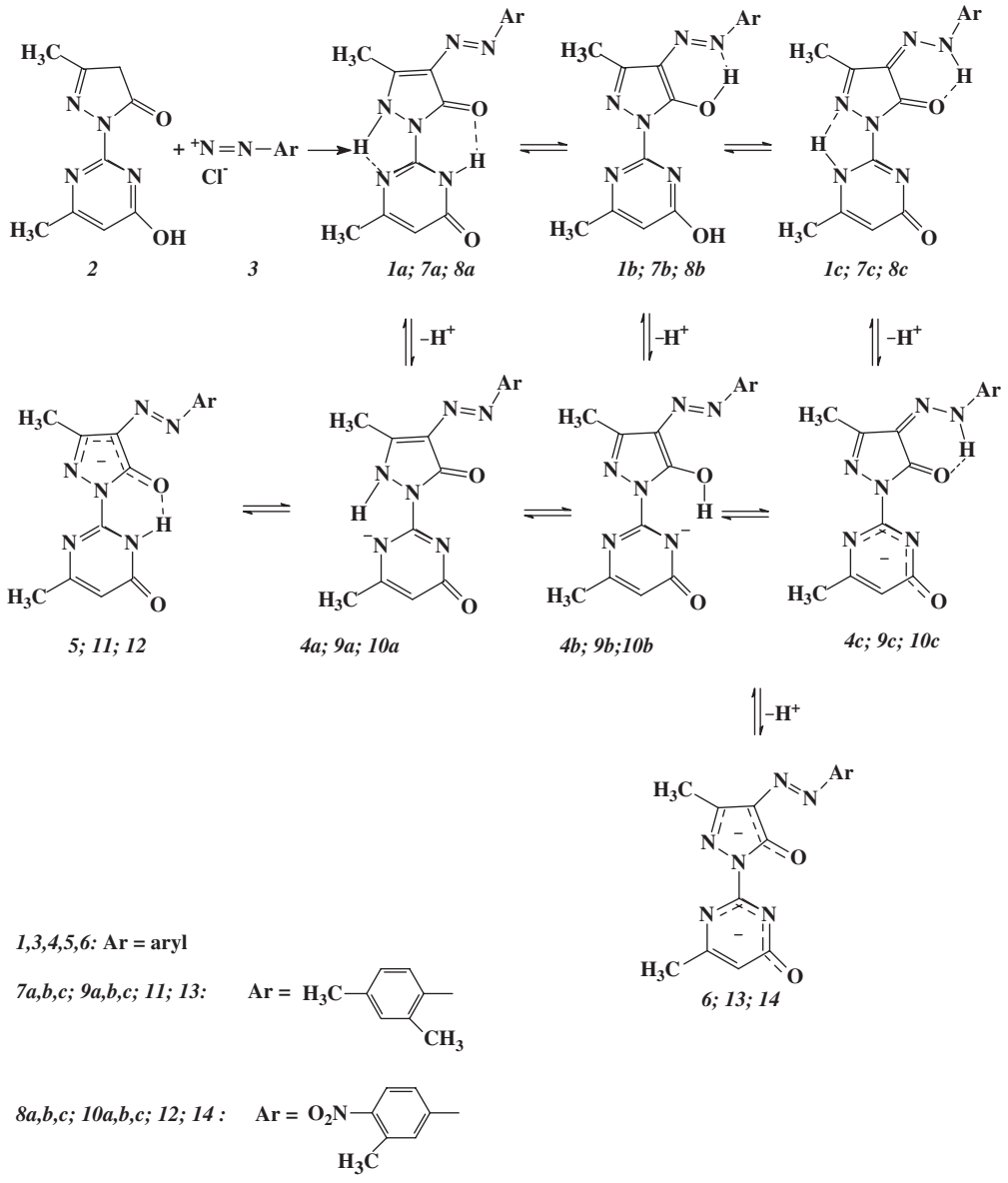

Scheme 1.

We mention that **7** is an 1-(4-hydroxy-6-methyl-pyrimidin-2-yl) analog of the CI-Food Yellow-12. Because most of the compounds discussed in this paper are those that theoretically may be involved in tautomerism (see Scheme 1), to indicate such compounds, in general, we will use figures without letters (e.g. **1**, **2**, **4**, **7**–**10**). In exchange, for each definite tautomer the figure is accompanied by a letter (e.g. **1a** or **1b**)

2. Results and discussion

2.1. General presentation of the electronic absorption spectra of the dyes 7 and 8

The spectra of **7**, **8** were recorded in various solutions using as solvent: glacial acetic acid (AcOH), benzene (C_6H_6), chloroform ($CHCl_3$) dimethylformamide (DMF), dimethylsulfoxide (DMSO) or ethanol (EtOH) (the last one inclusively aqueous, acidulated or alkalized) in a concentration range of 10^{-4}–10^{-6} mol L^{-1} dye. We mention that the dyes **7** and **8** have a very low solubility in all solvents but especially in water. Therefore, the spectra could not be recorded quantitatively in water as unique solvent.

The spectra were analyzed only in the wavelength range over 350 nm which is significant for the applicability of the azocoupling products **7** and **8** as dyes. These spectra of **7** and **8** show a dependence by the solvent nature, acid or alkali presence and in certain solvents (EtOH, DMF) also by the dye concentration (Figs. 1–12a_1, a_2, Table 1). Thus, the spectra of the dye **7** (Figs. 1, 2, 4a, 5, 6, 9–11, Table 1) have under some conditions

one absorption band over 350 nm whilst in other conditions two such bands even if sometimes one of these appears only as shoulder. Each of the two bands has a well delimited wavelength range for its absorption maximum, namely, between 388 and 395 nm for that of shorter wavelength and 420–440 nm, respectively, for that of longest wavelength. Also, the intensity of the two maxima corresponding to these bands depends on conditions. Moreover, the relative intensity of one maximum decreases on account of simultaneous increase of the intensity of the other. For example, the spectra of dye **7** in EtOH solution at a concentration of circa 2×10^{-5} mol L^{-1} – has usually two bands over 350 nm: one with the maximum between 420 and 430 nm and the other about 390 nm (Fig. 1). The replacement of EtOH as solvent with AcOH, C_6H_6, $CHCl_3$ or DMSO caused in the spectra of **7** a reinforcement and a slight bathochromic shift (at circa 435 nm) of the longest wavelength band simultaneously with the disappearance of the shorter wavelength band (Fig. 1, Table 1). A similar effect is caused also by a large increase of the water content in EtOH solution of **7** (Fig. 2). On the contrary, by the replacement of EtOH as solvent for **7** with DMF, the band of shorter wavelength is reinforced and the longest wavelength band is strongly weakened (Fig. 1).

Anyway, the presented behavior of **7** is compatible with the existence of at least two species in equilibrium. Otherwise, this behavior of **7** (Figs. 1, 2) is very similar to that of the first proved example of azo–hydrazone tautomerism (cf. [5,9]), respectively to that of an other standard example of azo–hydrazone tautomerism, namely that of the azocoupling product between 1-naphthol and the diazonium salt obtained from 2-methoxy-aniline (cf. [10]). The similar spectroscopic behaviors of **7** (Figs. 1, 2) and of the mentioned

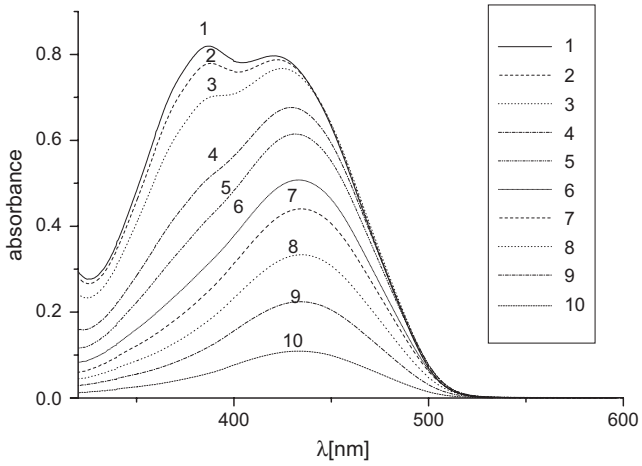

Fig. 2. The UV–VIS absorption spectra of the dye **7** in EtOH with increasing water content, at 25 °C. 1 – EtOH solution with a 4.6×10^{-5} mol L^{-1} dye concentration; 2 – mixture of 9 ml solution (1) with 1 ml water; 3 – mixture of 8 ml solution (1) with 2 ml water; 4 – mixture of 7 ml solution (1) with 3 ml water; 5 – mixture of 6 ml solution (1) with 4 ml water; 6 – mixture of 5 ml solution (1) with 5 ml water; 7 – mixture of 4 ml solution (1) with 6 ml water; 8 – mixture of 3 ml solution (1) with 7 ml water; 9 – mixture of 2 ml solution (1) with 8 ml water; 10 – mixture of 1 ml solution (1) with 9 ml water.

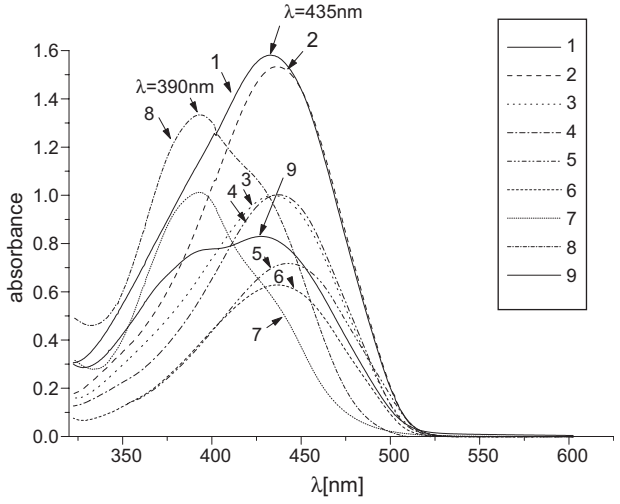

Fig. 1. The UV–VIS absorption spectra of the dye **7** in different solutions at 25 °C. For each curve (1–9) is given the solvent, the dye concentration in mol L^{-1}, the path length of the cuvette in cm and the concentration of the added HCl or KOH (curve 2, respectively 8). 1 – Absolute EtOH, 1.5×10^{-5}, 5; 2 – absolute EtOH, 1.4×10^{-5}, 5, [HCl] = 6×10^{-4} mol L^{-1}; 3 – DMSO, 4.73×10^{-5}, 1; 4 – AcOH, 3.55×10^{-5}, 1; 5 – $CHCl_3$, 2.81×10^{-5}, 1; 6 – C_6H_6, 2.96×10^{-5}, 1; 7 – DMF, 3.84×10^{-5}, 1; 8 – absolute EtOH, 1.4×10^{-5}, 5, [KOH] = 6×10^{-4} mol L^{-1}; 9 – EtOH, 4.38×10^{-5}, 1.

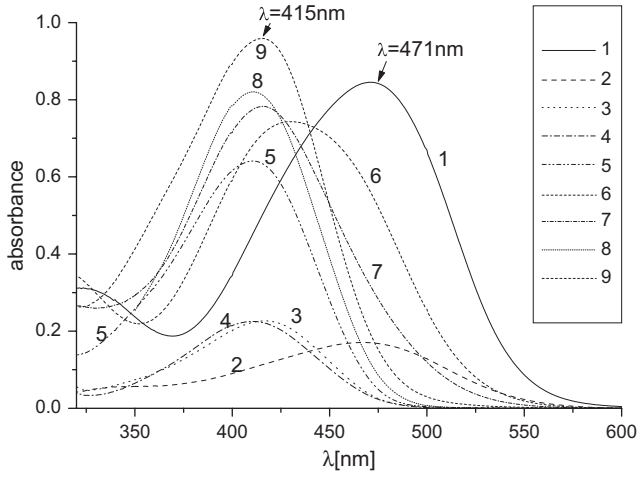

Fig. 3. The UV–VIS absorption spectra of the dye **8** in different solutions at 25 °C. For each curve (1–9) is given the solvent, the dye concentration in mol L^{-1}, the path length of the cuvette in cm and the pH value established with universal buffer solution added in proportion 1 v/1 v to solvent (curves 2, 3). 1 – DMF, 4.06×10^{-5}, 1; 2 – EtOH–water (2 v/3 v), 2.71×10^{-6}, 5; pH = 10.87; 3 – EtOH–water (2 v/3 v), 2.71×10^{-6}, 5; pH = 1.88; 4 – C_6H_6, 5.69×10^{-6}, 1; 5 – AcOH, 2.71×10^{-5}, 1; 6 – Absolute EtOH, 7.58×10^{-6}, 5; 7 – Absolute EtOH, 3.79×10^{-5}, 1; 8 – $CHCl_3$, 2.71×10^{-5}, 1; 9 – DMSO, 3.12×10^{-5}, 1.

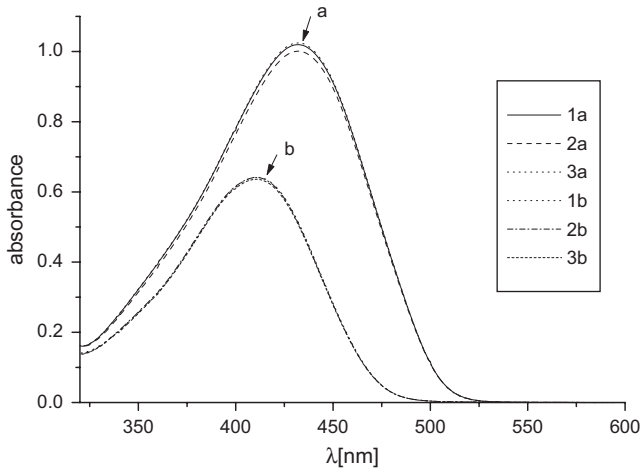

Fig. 4. The UV–VIS absorption spectra of the dye **7** in DMSO in a range of different concentrations from 9.46×10^{-5} to 2.36×10^{-5} mol L^{-1}, keeping the value $c_0 \times l = \text{const} = 4.73 \times 10^{-5}$ mol L^{-1} (curves "a") and of the dye **8** in AcOH in a range of different concentrations from 5.42×10^{-5} to 1.35×10^{-5} mol L^{-1}, keeping the value $c_0 \times l = \text{const} = 2.71 \times 10^{-5}$ mol L^{-1} (curves "b") at 25 °C. 1a, 1b $-l = 0.5$ cm; 2a, 2b $-l = 1$ cm; 3a, 3b $- l = 2$ cm.

examples [5b,9,10] of azo–hydrazone tautomerism consists in the existence, depending on the used solvent, of one or two absorption bands and in fact that the intensity of one band increases on account of the decrease – eventually up to disappearance of the other band. These similarities may suggest that the two

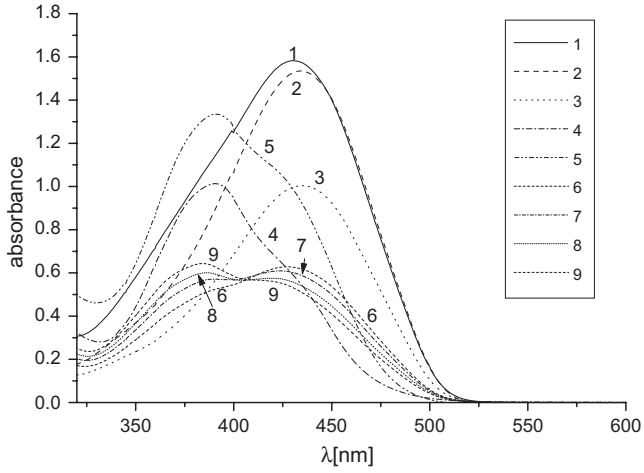

Fig. 5. The UV–VIS absorption spectra of the dye **7** in different solution at 25 °C. For each curve (1–9) is given the solvent, the dye concentration in mol L^{-1}, the path length of the cuvette and the concentration of the added HCl or KOH (curve 2, respectively 5). 1 – absolute EtOH, 1.5×10^{-5}, 5 cm; 2 – absolute EtOH, 1.4×10^{-5}, 5 cm; [HCl] = 6×10^{-4} mol L^{-1}; 3 – AcOH, 3.55×10^{-5}; 1 cm; 4 – DMF, 3.84×10^{-5}, 1 cm 5 – absolute EtOH, 1.4×10^{-5}, 5 cm; [KOH] = 6×10^{-4} mol L^{-1}; 6 – absolute EtOH, 7.69×10^{-5}, 0.5 cm; 7 – absolute EtOH, 3.85×10^{-5}, 1 cm; 8 – absolute EtOH, 1.92×10^{-5}, 2 cm; 9 – absolute EtOH, 7.69×10^{-6}, 5 cm.

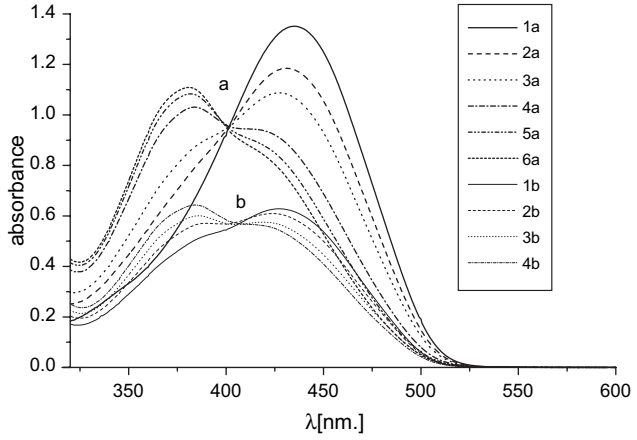

Fig. 6. The dependence of the spectra of the dye **7** by the pH′ of its isomolare (5.34×10^{-5} mol L^{-1}) solutions in EtOH–water (1 v/1 v) at ionic strength 0.01 mol L^{-1} KCl (curves "a"), respectively by the dye concentration of its solutions in absolute EtOH (curves "b") at 25 °C. For each curve "1a–6a" is given the pH′ value that was established with HCl- or KOH-solution (10^{-2} mol L^{-1}). By the curves "1b–4b" the product $c_0 \times l$ was constant (3.85×10^{-5} mol L^{-1}) and for each curve is given the dye concentration (c_0) in mol L^{-1} and path length (l) of the cuvette in cm. 1a – 5.16; 2a – 6.59; 3a – 7.03; (the initial EtOH–water solution with ionic strength 0.01 mol L^{-1} KCl) 4a – 7.49; 5a – 7.99; 6a – 9.15 1b – 7.69×10^{-5}, 0.5; 2b – 3.85×10^{-5}, 1; 3b – 1.92×10^{-5}, 2; 4b – 7.69×10^{-6}, 5.

different bands from the absorption spectra over 350 nm of **7** in EtOH correspond eventually one to the azo-tautomer (**7a** or **7b**), that at lower wavelength (λ_{max} circa 390 nm) and the other to the hydrazone tautomer **7c** – that at longest wavelength (λ_{max} circa 430 nm) so as

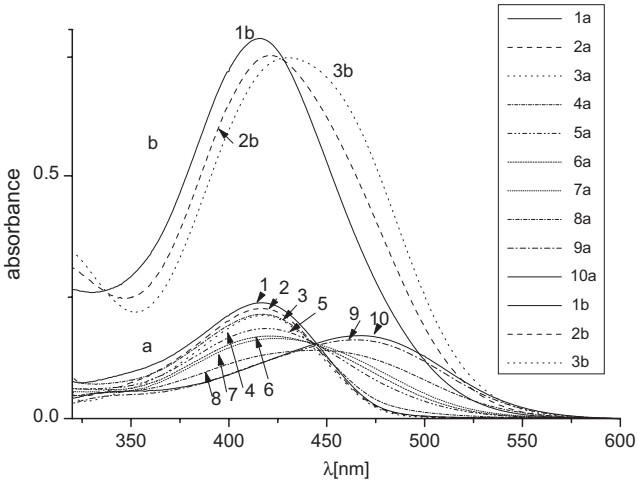

Fig. 7. The dependence of the spectra of the dye **8** by the pH′ of its isomolare (2.71×10^{-6} mol L^{-1}) universal buffer solutions with a 20% (v/v) EtOH content (curves "a",) respectively by the dye concentration of its solutions in absolute EtOH (curves "b") at 25 °C. For each curve "1a–9a" is given the pH′ value. By the curves "1b–3b" the product $c_0 \times l$ was constant (3.79×10^{-5} mol L^{-1}) and for each curve is given the dye concentration (c_0) in mol L^{-1} and the path length (l) of the cuvette in cm. 1a – 1.88; 2a – 3.41; 3a – 4.37; 4a – 5.62; 5a – 6.64; 6a – 7.3; 7a – 8.28; 8a – 9.51; 9a – 10.23; 10a – 10.87; 1b – 3.79×10^{-5}, 1; 2b – 1.89×10^{-5}, 2; 3b – 7.58×10^{-6}, 5.

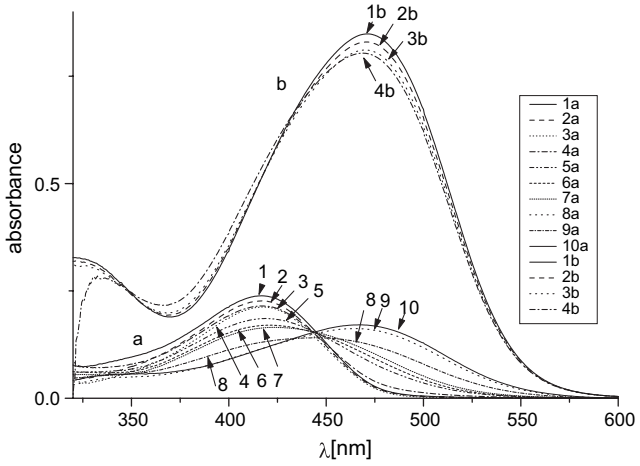

Fig. 8. The dependence of the spectra of the dye **8** by the pH′ of its isomolare (2.71×10^{-6} mol L^{-1}) universal buffer solutions with a 20% (v/v) EtOH content (curves "a"), respectively by dye concentration of its solutions in DMF (curves "b") at 25 °C. For each curve "1a–9a" is given the pH′ value. By the curves "1b–4b" the product $c_0 \times l$ was constant (4.06×10^{-5} mol L^{-1}) and for each curve is given the dye concentration (c_0) in mol L^{-1} and path length (l) of the cuvette in cm. 1a – 1.88; 2a – 3.41; 3a – 4.37; 4a – 5.62; 5a – 6.64; 6a – 7.3; 7a – 8.28; 8a – 9.51; 9a – 10.23; 10a – 10.87; 1b – 8.13×10^{-5}, 0.5; 2b – 4.06×10^{-5}, 1; 3b – 2.03×10^{-5}, 2; 4b – 8.13×10^{-6}, 5.

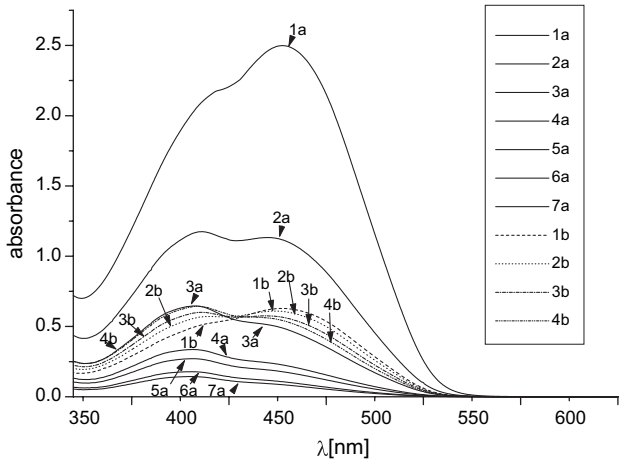

Fig. 10. The concentration dependence of the spectra of the dye **7** in absolute ethanol at 25 °C. Curves "a" correspond to measurements in cuvette with the same path length (1 cm) but having different concentration, which is given for each curve "1a–7a". Curves "b" have the same product $c_0 \times l = \text{const} = 3.85 \times 10^{-5}$ mol L^{-1} and for each curve "b" is given the dye concentration (c_0) in mol L^{-1} and the path length of the cuvette in cm. 1a – 1.54×10^{-4}; 2a – 7.7×10^{-5}; 3a – 3.85×10^{-5}; 4a – 1.92×10^{-5}; 5a – 1.54×10^{-5}; 6a – 9.6×10^{-6}; 7a – 7.7×10^{-6}; 1b – 7.69×10^{-5}, 0.5; 2b – 3.85×10^{-5}, 1; 3b – 1.92×10^{-5}, 2; 4b – 7.69×10^{-6}, 5.

has been observed [5b,9–14] for the standard examples of azo–hydrazone tautomerism.

This suggestion seems to be supported also by the appearance, particularly in EtOH, of the band tentatively assigned to the azo-tautomer **7a** or **7b** since it is known [5b,9,10,12,13] that EtOH favors comparative to AcOH, H_2O or $CHCl_3$, the azo-tautomers, whilst the last three solvents favor the hydrazone tautomers.

On the other hand, it must be underlined that of late [3b,4b] very similar electronic absorption spectroscopy behaviors with those of the mentioned standard

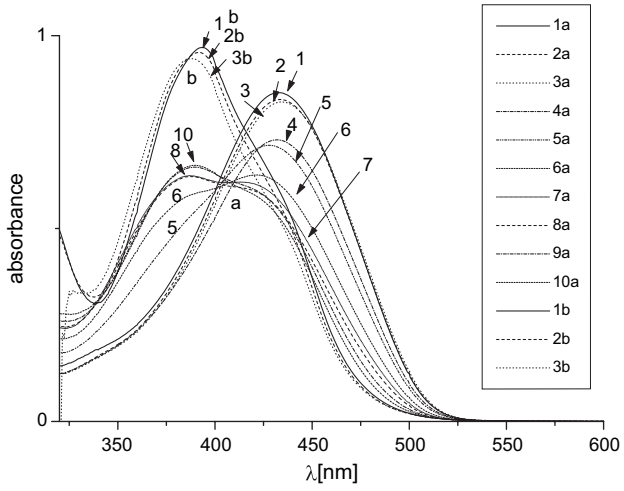

Fig. 9. The dependence of the spectra of the dye **7** by the pH′ of its isomolare (3.9×10^{-5} mol L^{-1}) universal buffer solutions with a 20% (v/v) EtOH content (curves "a"), respectively by dye concentration of its solutions in DMF (curves "b") at 25 °C. For each curve "1a–9a" is given the pH′ value. By the curves "1b–3b" the product $c_0 \times l$ was constant (4.43×10^{-5} mol L^{-1}) and for each curve is given the dye concentration (c_0) in mol L^{-1} and path length (l) of the cuvette in cm. 1a – 2.02; 2a – 3.5; 3a – 4.53; 4a – 5.6; 5a – 6.76; 6a – 7.37; 7a – 8.45; 8a – 9.6; 9a – 10.36; 10a – 10.92; 1b – 8.87×10^{-5}, 0.5; 2b – 2.22×10^{-5}, 2; 3b – 8.87×10^{-6}, 5.

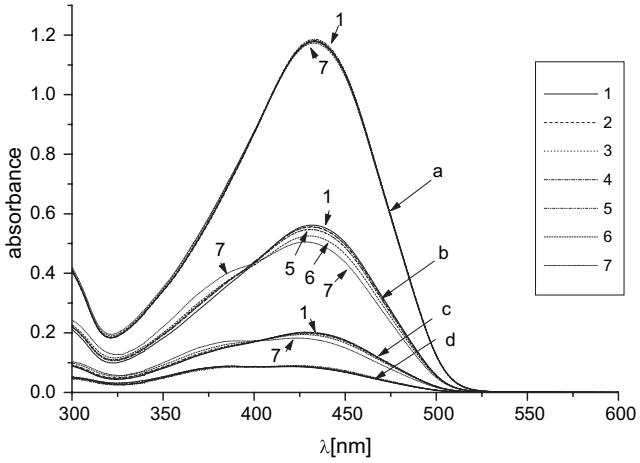

Fig. 11. The dependence of spectra of dye **7** by the concentration (curves of type "a", "b", "c", "d"), respectively by the time (curves 1–7 for each concentration "a–d"). It is given the concentration in mol L^{-1} for each tip "a–d", respectively the time interval (for curves 2–7) after the initial registration (1), that is the same for each concentration ("a–d"). a – 5.2×10^{-5}; b – 2.6×10^{-5}; c – 1.04×10^{-5}; d – 5.2×10^{-6}; 1 – initial registration; 2 – after 24 h; 3 – after 48 h; 4 – after 5 days; 5 – after 9 days; 6 – after 15 days; 7 – after 22 days.

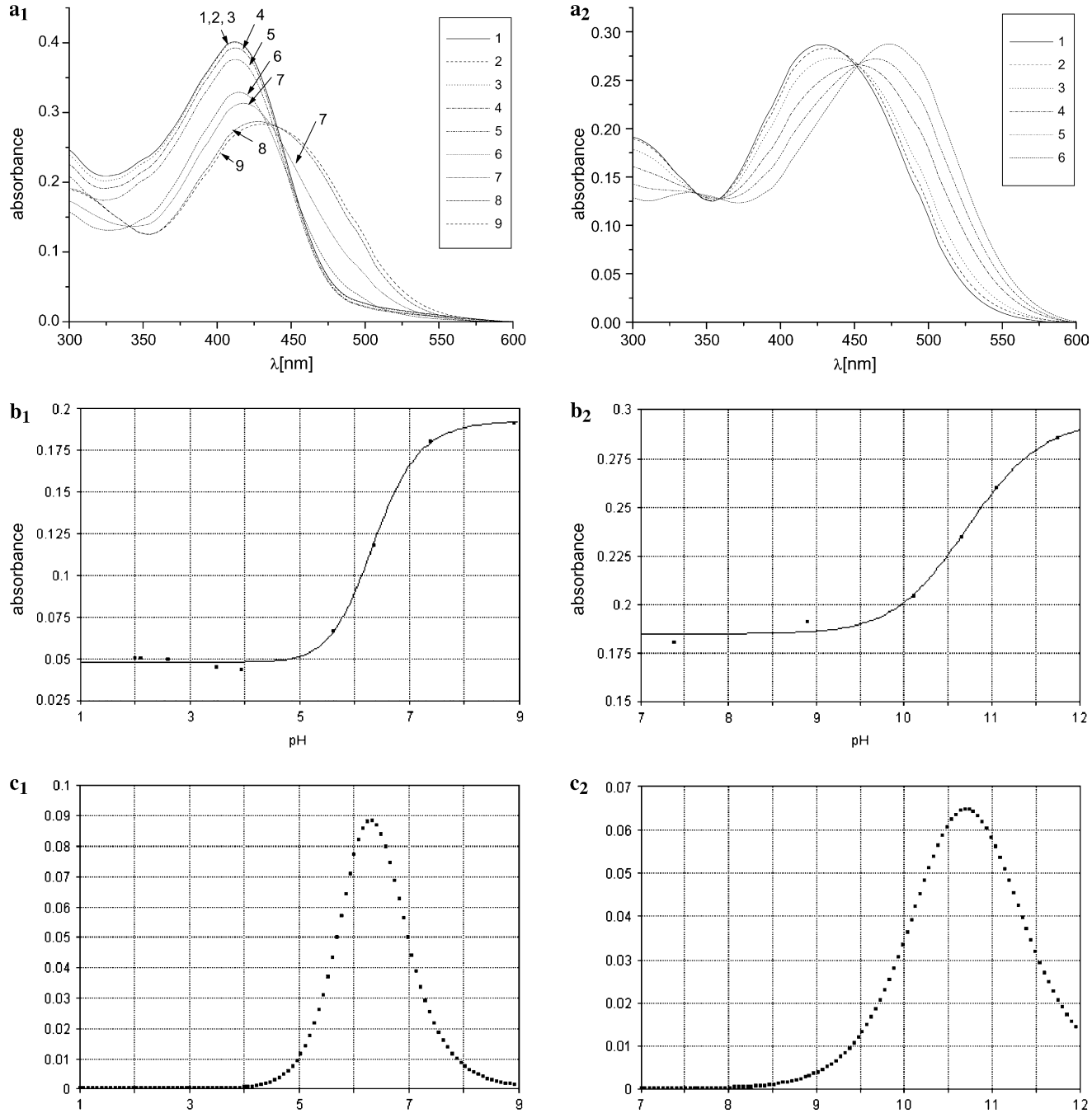

Fig. 12. (a_1, a_2) The absorption spectra of the dye **8** in its isomolare (7×10^{-6} mol L^{-1}) EtOH–water (1 v/1 v) solutions at ionic strength 0.01 mol L^{-1} KCl and 25 °C in the pH′ range from 2 to 9 (Fig. 12a_1), respectively from 7 to 12 (Fig. 12a_2). The path length of the cuvette: 2 cm. The pH′ values by the curves "1–9" from Fig. 12a_1 are:1 − 1.99; 2 − 2.1; 3 − 2.6; 4 − 3.48; 5 − 3.94; 6 − 5.6; 7 − 6.35; 8 − 7.38; 9 − 8.9; The pH′ values by the curves "1–6" from Fig. 12a_2 are: 1 − 7.38; 2 − 8.9; 3 − 10.11; 4 − 10.65; 5 − 11.05, 6 − 11.75. (12b_1, b_2). The plots absorbance vs. pH′ corresponding to the above curves in the pH′ range from 2 to 9 (Fig. 12b_1), respectively from 7 to 12 (Fig. 12b_2) at analytical wavelength (480 nm). (12c_1, c_2) The first derivative for the plot from Fig. 12b_1 (Fig. 12c_1), respectively from Fig. 12b_2 (Fig. 12c_2).

examples of azo–hydrazone tautomerism [5b,9,10] and of course of the dye **7**, were regarded, in the case of other azocoupling products, to be rather consistent with an acid dissociation equilibrium than with azo–hydrazone tautomerism. On the basis of one such last assessment the two different bands in the spectra over 350 nm of **7** in EtOH, should correspond to the hydrazone tautomer **7c** (λ_{max} circa 430 nm) and to the common anion with predominant azostructure **11** (λ_{max} circa 390 nm), respectively (cf. [3b,4b]).

Also, the electronic absorption spectroscopy behavior of the dye **8** is compatible with an equilibrium, although its spectra in all examined conditions show apparently only one absorption band over 350 nm. But the

Table 1
The position of the absorption maxima (λ_{max} in nm) over 350 nm for the dyes **7** and **8**, in different solutions

Dye	Solution in							
	AcOH	C_6H_6	$CHCl_3$	DMSO	EtOH[a]	EtOH + HCl	EtOH + KOH	DMF
7	434.5	434	440.5	432	420–430 and 390	435	390 and 425 (sh)	394[b] and 425 (sh)
8	411	410	410.5	415	416[b]	412	470	472[b]

sh = Shoulder.
[a] In EtOH may appear one or two absorption maxima having a variable position and intensity as a function of the dye concentration and of water content (see Section 2).
[b] Also the position and intensity of these maxima are a function of the dye concentration (see Section 2).

wavelength of the maximum of this band changes progressively between 412 and 472 nm depending on conditions (solvent, dye concentration, pH value) (Figs. 3, 4b, 7, 8, Table 1). Thus, e.g., the wavelength of the maximum in spectra over 350 nm of the solution of **8** in AcOH, C_6H_6, or $CHCl_3$ is equal with 410.5 nm, whilst in DMSO, EtOH and DMF, respectively, it is equal with 415, 416 and 472 nm, respectively (Fig. 3, Table 1).

With a view to decide if the dyes **7** and **8** are involved into acid–base and/or azo–hydrazone equilibrium and to assign the involved species, respectively, further is presented a systematic study of the effects of the solvent, dye concentration, pH and time on the electronic absorption spectra of these dyes.

2.2. Effect of the solvent

2.2.1. Spectra in AcOH, C_6H_6, $CHCl_3$ or DMSO

The spectra over 350 nm of the dye **7** or **8** in AcOH, C_6H_6, $CHCl_3$ or DMSO solution, in the concentration range 10^{-4}–10^{-6} mol L^{-1} (Figs. 1, 3, 4) have only one absorption band with a maximum at approximately the same wavelength for each dye, namely at circa 435 nm for **7** and 412 nm for **8**, respectively (Table 1). Also, the above solutions follow Lambert–Beer's law (Fig. 4). Therefore, it is reasonable to conclude that under these conditions each dye **7** or **8** is detected as the same unique species. Because in the case of the azocoupling products that theoretically may be involved in azo–hydrazone tautomerism, the AcOH strongly shifts the equilibrium towards the hydrazone form [1,2,3b,5b,9a,10–13,15–17] the same is to be expected also for the dyes **7** and **8**. Consequently, these dyes should appear in AcOH solution as hydrazone tautomers **7c** and **8c**. A similar situation should occur in C_6H_6, $CHCl_3$ or DMSO solution since the dyes **7** and **8** are detected in these solvents in the form of the same species as in AcOH (see above).

The hydrazone nature **7c** or **8c** of the single species detected in AcOH, C_6H_6, $CHCl_3$ or DMSO solution of each dye **7** or **8** is supported also by the effect of the substituent from the *para* position of the benzene ring with respect to the azo (or hydrazone) group of these azocoupling products on their unique absorption maximum over 350 nm in the mentioned solvents. As with other hydrazone tautomers (cf. [1,3b,12,13,18,19]) the electron-releasing substituent ($-CH_3$) in the above mentioned position determines an absorption maximum at longer wavelength (circa 435 nm, Table 1) than the electron-withdrawing substituent ($-NO_2$) (circa 412 nm, Table 1). For the azo-tautomers the opposite is to expect (cf. [12,13]). Thus, the data of the electronic spectra in AcOH, C_6H_6, $CHCl_3$ or DMSO solution of the dye **7** or **8** are in agreement with the single hydrazone species **7c** or **8c** detected for these dyes also by ^1H RMN spectra in $CDCl_3$ or hexadeuterated DMSO [2].

2.2.2. Spectra in EtOH or DMF solutions. The effect of the presence of acid or alkali in ethanol solutions of 7 or 8

The electronic absorption spectra of the dye **7** or **8** in EtOH or DMF solution usually differ significantly from those in AcOH, C_6H_6, $CHCl_3$ or DMSO (Figs. 1, 3). Thus, e.g. the spectra of **7** may present, depending on conditions (EtOH or DMF, water content in EtOH, dye concentration or the presence of acid or base even as traces that can arise by an accidental contamination) one or two absorption bands over 350 nm (Figs. 2, 5, 6, 9–11). One band is present only in certain spectra of **7** in absolute or p.a. EtOH usually at a concentration greater than 5×10^{-5} mol L^{-1} and always in acidulated EtOH, respectively (Figs. 5, 6a, 9a, 11). The position (circa 432 nm) of the maximum of this unique band over 350 nm in EtOH solution of **7** and especially in acidulated EtOH (circa 435 nm) is practically identical with that of the correspondent unique maximum over 350 nm (circa 435 nm) in AcOH, C_6H_6, $CHCl_3$ or DMSO solution (Figs. 1, 5, 6a). Because this last maximum has been assigned (see Section 2.2.1.) to the hydrazone tautomer **7c** the same must be done also for the unique maximum in above EtOH solution of **7**. But usually the spectra over 350 nm of the dye in various EtOH (especially at concentrations lower than 5×10^{-5} mol L^{-1}, at lower water content and in presence of alkali, respectively) or DMF solution (Figs. 1, 2, 5, 6, 9, 11) show two bands over 350 nm: one of longest wavelength (maximum between 430 and 420 nm) and the other of lower wavelength (maximum between

395 and 388 nm). However, the spectra of EtOH or EtOH–water solution of **7** with two bands over 350 nm are converted by addition of acid or larger quantity of water in spectra with only one band over 350 nm, namely with maximum at 435 nm (Figs. 1, 2, 5). This maximum has been already assigned to the hydrazone tautomer **7c** (see above).

In fact, the acid or water addition to the EtOH solution of **7**, that initially had one or two absorption bands over 350 nm determines (Figs. 1, 2, 5) the disappearance of the lower wavelength band (maximum at circa 390 nm) – if before the addition have been two bands – and in all cases slight bathochromic shifts (namely from 420–430 nm to 435 nm) for the longest wavelength band. All of the experimental facts for the EtOH or EtOH–water solution of **7** agree with the assignment of the longest wavelength band from the spectra with one or two bands over 350 nm of these solutions to the hydrazone tautomer **7c**. This assignment is supported also by the presence of the longest wavelength band from the EtOH solution of **7** as the unique band in acidic medium (Figs. 1, 5) or in water (Fig. 2) because it is known [1,2,3b,4a,4c,5,9–12,15–17] that the last media favor strongly the hydrazone tautomer. Moreover, this assignment is supported also by the alkali addition effect on the spectra of EtOH solution of **7**. The alkali addition converts the spectra of **7** with one band over 350 nm, namely with the maximum at 430 nm into spectra with two bands over 350 nm, namely with the maxima at circa 390 and 420–430 nm, respectively. The alkali addition changes also the spectra of **7** with two bands over 350 nm in EtOH. In this case, the alkali addition determines (Figs. 1, 5, 6a) an increase of intensity of the maximum of lower wavelength band on the account of the decrease in intensity of the longest wavelength one – which has been assigned above to the hydrazone tautomer. As it is known [1–4,9,11,12,14–19] the alkali addition causes just the transformation of the hydrazone tautomer in other species.

Concerning the electronic spectra in EtOH or DMF solution of the dye **8** although these have each only one absorption band over 350 nm, the position and shape of this band is quite different (Figs. 3, 7, 8). Thus, in EtOH at a concentration of about 4×10^{-5} mol L^{-1} for **8** the band (maximum at circa 415 nm) is very similar to that in AcOH, C_6H_6, $CHCl_3$ or DMSO solution (maximum at circa 412 nm) whilst in DMF it is strongly shifted bathochromically (maximum at 472 nm) and broadened relative to that from the other mentioned solvents. In acidulated EtOH this unique band over 350 nm of **8** is only slighty shifted hypsochromically (maximum at 412 nm) comparative to that in neutral EtOH and it corresponds to the band in visible of **8** in AcOH, C_6H_6, $CHCl_3$ or DMSO, band wich has been assigned to the hydrazone tautomer **8c** (see Section 2.2.1).

Consequently, the spectrum over 350 nm of **8** in acidulated EtOH – which is identical to that in AcOH, C_6H_6, $CHCl_3$ or DMSO – as well as that in neutral EtOH, with a maximum below 420 nm – which is very similar to the foregoing spectra – should correspond in all and at least principally, respectively, to the hydrazone tautomer **8c**. On the other hand, the alkaline medium determines an opposite shift of the absorption maximum of **8** relative to that caused by the acid medium (Figs. 3, 7a) similar to the corresponding shifts in the case of the dye **7**. Thus, if the acid medium determines a slight hypsochromic shift (from 415 to 412 nm) of the maximum assigned to the hydrazone tautomer **8c**, the alkaline medium causes a progressive transformation of the initial absorption band from neutral medium (415 nm) into a bathochromically shifted (eventually up to 470 nm) and broader absorption band comparative to that in neutral medium. However, the shift determined by acid or alkali addition to the EtOH solution of **8** is each opposite to the corresponding shift in the case of EtOH solution of **7**.

It is also interesting that the absorption spectra over 350 nm obtained in alkaline medium for the dye **7** or **8** are very similar to the corresponding spectra registered in DMF (Figs. 1, 3, 5, 8, 9). Therefore, it is possible that the different spectra in DMF comparative to those in AcOH, C_6H_6, $CHCl_3$ DMSO or unalkalized EtOH to be caused just by the traces of base impurities which may be present (cf. [20]) in DMF. A particularity of the spectra of **7** or **8** in EtOH (Figs. 6b, 7b, 10, 11) or DMF (Figs. 8b, 9b) solution in the concentration range 10^{-4}–10^{-6} mol L^{-1} is the fact that apparently (cf. [18]) these do not obey the Lambert–Beer's law if the absorbance (A) is measured at the absorption maximum assigned to the hydrazone tautomer.

Moreover, the absorption curves of **7** (Figs. 6b, 9b, 10) or **8** (Figs. 7b, (8b) in EtOH or DMF solution at different concentration keeping constant the value $c_0 \times l$ (from the Lambert–Beer's law $A = \varepsilon \times c_0 \times l$) show isosbestic points. These isosbestic points suggest (cf. [3b,7]) the existence of an equilibrium. Otherwise, all presented spectroscopic behaviors for the dyes **7** and **8**, but especially those in EtOH at the variation of the pH, dye concentration or of water content (Figs. 1–3, 5–11) can be explained most reasonably by the assumption of an equilibrium between the assigned hydrazone tautomer **7c** or **8c** and at least an other species (cf. [1–19,21,22]). The proposed other species are transformed by addition of acid or water into the hydrazone tautomer and the hydrazone tautomer is converted by addition of alkali in the proposed other species at least partially (Figs. 1–3, 5, 6a–9a). In AcOH, C_6H_6, $CHCl_3$ DMSO or acidulated EtOH, the equilibrium is apparently completely shifted towards the hydrazone tautomers **7c** and **8c**. In neutral EtOH the hydrazone tautomers are usually predominant and by addition of acid or water the equilibrium is increasingly shifted towards hydrazone tautomers. On the contrary, the

addition of alkali to the EtOH solution of **7** or **8**, shifts the equilibrium in the opposite direction, so that the hydrazone tautomer content decreases (Figs. 1–3, 5, 6a–9a) and that of the proposed other species increased. Also, in DMF, the equilibrium is strongly shifted towards the other species, like in the presence of alkali (Figs. 1, 3, 5, 8, 9). The above equilibrium is supported also (cf. [14]) by the experimental observation that for each dye **7** or **8** the absorbances at the isosbestic points obey the Lambert–Beer's law (see e.g. Fig. 11). Because this equilibrium is very sensitive to acid or base it may be firstly an acid–base equilibrium (cf. [3b,4,16]) between the assigned hydrazone tautomer **7c**, respectively **8c**, and the corresponding common anion **11**, respectively **12**, resulted by the acid dissociation of the hydrazone NH group. For such an anion an azo-structure is expected (cf. [3b,4a,12,14,16,21]). But the dyes **7** and **8** may exhibit also another acid–base equilibrium due to the acid dissociation of the pyrimidinic NH (or OH) group (cf. [1,2,23]) to the anions **9** and **10**. At the same time, it must be underlined that also the azo–hydrazone equilibrium (**7a** ⇔ **7b** ⇔ **7c** or **8a** ⇔ **8b** ⇔ **8c**) is expected to be sensitive to acid or to base (cf. [1,5b,9a,11,17]). The eventual presence of this tautomeric equilibrium seems to be sustained by the discussed effect of the solvent and of the increasing water content in EtOH solution on the spectra of dyes **7** and **8** (see Section 2.1) (cf. [5,9,10,13]).

To obtain more information concerning the effect of acid or base and thus to decide the nature of the equilibria in the solution of dyes **7** and **8** we examined the influence of the systematic variation of pH on their spectra in aqueous EtOH (Figs. 6a, 7a, 8a, 9a, 12a$_1$,a$_2$).

2.3. Effect of the pH. Determination of the pK'_a

The pH dependence of spectra of the dye **7** or **8** was examined in the pH range 2–12, in ethanol–water solution. To indicate that the measurements have been effected not in water the notation pH′ and pK'_a are utilized. The pH′ of the solutions were established with universal buffer solutions (Figs. 7a, 8a, 9a) or only by the addition of either HCl or KOH, respectively (Figs. 6a, 12a$_1$, a$_2$). The last procedure has been used to discourage dye aggregation (cf. [14]). The absorption curves of isomolare solutions of the dye **7** or **8** in the examined pH range have given distorted isosbestic points (Figs. 7a, 8a, 9a,12a$_1$). The isosbestic points are however better defined for the absorption curves registered at pH′ values greater than 5 and in unbuffered 50% (v/v) ethanol–water solutions (Figs. 6a, 12a$_2$) comparative to buffered solutions. The above situation is compatible with a normal ionization step corresponding to pH′ values where quite well definite isosbestic points were obtained and a non-simple ionization step (cf. [8]) at lower pH′ values with distorted isosbestic points (e.g. Fig. 12a$_1$). Anyway, the pH′ dependences of the spectra of the dye **7** or **8** (Figs. 6a, 8a, 9a, 12a$_1$,a$_2$) may correspond to acid–base equilibria (cf. [3b,4b,5a,8,13,22]) (see also Section 2.2.2). On the other hand, the existence of two ionization steps is confirmed by the plots absorbance vs. pH′ at a certain analytical wavelength for each dye **7** or **8** because there were obtained sigmoidal curves in two pH′ ranges (see e.g. Fig. 12b$_1$, b$_2$). As it is known [5a,22] such sigmoidal curves are characteristic for acid–base equilibria, they being in fact spectrophotometric titration curves [22a]. The obtained sigmoidal curves enabling to determine the pK'_a values with half curve height method (cf. [22b]) and by means of the first derivative (e.g. Fig. 12c$_1$, c$_2$) for each curve.

Thus, we obtained two pK'_a values for each dye **7** or **8**. This fact is in accordance with the presence of two mobile (acidic) hydrogen atoms of the two NH (or OH) groups in these dyes. Consequently, they correspond to dibasic acids (H_2A) and can ionize in two steps (e.g. **8** ⇔ **10** and **10** ⇔ **14**, see Scheme 1), similar [23] to 1-(4-hydroxy-6-methylpyrimidin-2-yl)-3-methyl-pyrazolin-5-one (**2**), which has been used as a coupling component for the synthesis of these dyes by azocoupling [2]. The pK'_a values determined for dye **7** are: pK'_{a1}= 5.4 and pK'_{a2}= 7.2 in universal buffer solutions with 20% (v/v) ethanol, respectively pK'_{a1}= 5.1 and pK'_{a2}= 6.9 in 50% (v/v) unbuffered ethanol–water solutions. The pK'_a values for dye **8** are: pK'_{a1}= 6.1 and pK'_{a2}= 10.3 in universal buffer solutions with 50% (v/v) ethanol, respectively pK'_{a1}= 6.3 and pK'_{a2}= 10.7 in 50% (v/v) unbuffered ethanol–water solutions. The error in determination of pK'_a values has been ±0.1 pH units. We ascribe the pK'_a values – that are determined on the basis of the sigmoidal curves obtained at lower pH′ values (see e.g. Fig. 12b$_1$) for the deprotonation step of the group NH (or OH) from the pyrimidinyl moiety, similar to the case of 1-(4-hydroxy-6-methylpyrimidin-2-yl)-3-methyl pyrazolin-5-one (**2**) (cf. [23]). This assignment is supported by the experimental observation that the λ_{max} of the single absorption band over 350 nm afferent to the corresponding ionization equilibrium (e.g. Fig. 12a$_1$) is not changed significantly (maximum 15 nm). Such a situation is compatible even with the deprotonation equilibrium **7** ⇔ **9** or **8** ⇔ **10** (see Scheme 1) because this does not change essentially the chromophore system, which remains principally a hydrazone one. On the contrary, in the equilibrium corresponding to the determination of pK'_{a2} (e.g. Fig. 12a$_2$,b$_2$,c$_2$) a more significant change of λ_{max} takes place (37, respectively 50 nm). This is in agreement with the change of the chromophore system in the equilibria enabling to calculate the pK'_{a2}values, namely the deprotonation of mobile (acidic) hydrogens of the NH (or OH) groups that may be eventually involved in azo–hydrazone tautomerism and therefore to lead to the common anion with azo-structure (**9** ⇔ **13**, respectively **10** ⇔ **14**; Scheme 1).

A similar explanation was given for other azocoupling products that theoretically may be involved in azo–hydrazone tautomerism [3c,d,4b,12,14,16,19].

But the determined pK'_{a1} and pK'_{a2} values for dyes **7** and **8**, are not in accordance with the usual effect of substituents upon acidity. Thus, the pK'_a values of the dye **7** having an electron-releasing substituent (CH_3) in the *para* position of the benzene ring relative to the hydrazone (or azo) group are lower than those of the dye **8** which have a strong electron-withdrawing substituent (NO_2) in the same position. It is noteworthy that the discussed *para* position is connected by a delocalized π-electron system to the acidic NH or OH group involved in the azo–hydrazone tautomerism, respectively, in the second step of ionization of the dye **7** or **8** (see Scheme 1). Consequently, in ordinary ionization equilibria (cf. [15,24]) at least the value of the pK'_{a2} should be lower for **8** than that for **7**. The above unexpected inversion of the pK'_a values may be eventually explained (cf. [5b,19]) by the fact that the *para* nitrosubstituent in the case of dye **8** favors (cf. [5,10,13]) strongly the less acidic (cf. [25]) hydrazone tautomer **8c**, respectively, an aggregated form of this (cf. [5b]), whilst the methyl substituent in the case of dye **7** favors, on the contrary (cf. [5,10,13]), the more acidic (cf. [25]) azotautomer **7b**. Thus, in the ionization equilibria of the dyes **7** and **8** the azo–hydrazone (cf. [5b,19]) and/or aggregation equilibria (cf. [5b,6]) may be eventually involved . This suggestion seems to be sustained also (cf. [4c,6]) by the above mentioned distorted isosbestic points in the pH′-dependent absorption curves (e.g. Fig. 12a$_1$).

Therefore, the determined pK'_a values are apparent pK'_a values (cf. [6]) that may correspond (cf. [1,5b,6]) to ionization equilibria eventually connected with (or supraimposed on) azo–hydrazone or/and aggregation equilibria.

On the basis of pK'_a determination it may be concluded that:

- the species present in acidic media (pH < 4) are the hydrazones **7c** (λ_{max} circa 435 nm) and **8c** (λ_{max} circa 412 nm).
- the monodeprotonated species correspond firstly to **9c** (λ_{max} circa 430 nm and ε_{max} circa 80% from that of **7c**) or **10c** (λ_{max} circa 425 nm and ε_{max} circa 70% from that of **8c**) but these are eventually in equilibrium with their tautomers **9a**, **9b**, respectively **10a**, **10b** and even with **11**, respectively **12**. However, the equilibrium is apparently shifted towards hydrazone forms **9c** and **10c**, similar to the initial undeprotonated species (cf. [4c,6]). Hence the azo-tautomers of the undeprotonated- and monodeprotonated-forms of the dyes **7** and **8** could not be detected directly. As was already shown for these forms may be detected only the hydrazone tautomers.
- the doubly deprotonated species correspond apparently only to a single species, **13** (λ_{max} circa 390 nm) or **14** (λ_{max} circa 470 nm), with an azo-structure. This azo-structure of dianions is supported by the effect of the substituents in benzene ring of the dyes **7** and **8** on the position of the maximum on their absorption band over 350 nm in strong alkaline media (pH circa 11). As with other azoanions (cf. [1,12,16,18,19,21]) the electron-releasing substituent (CH_3) in the *para* position of the benzene ring with respect to the azo group of these dyes determines an absorption maximum at lower wavelength (circa 390 nm) than that caused by the electron-withdrawing substituent (NO_2) (circa 470 nm).

2.4. Effect of the sample concentration and time on the spectra of dyes 7 and 8, in EtOH or DMF solution

As was already shown (Section 2.2.2) the absorption spectra of the dye **7** (Figs. 6b, 9b) or **8** (Figs. 7b, 8b) at different concentrations in ethanol or DMF, keeping constant the value of the '$c_0 \times l$' product, present the isosbestic points that indicate the existence of an equilibrium. In principle this may be both an aggregation, azo–hydrazone- or ionization-equilibrium and one that involves two or all mentioned equilibria (cf. [3b,4b,5–8]). At the same time it may be observed that the decrease of the concentration from 10^{-5} to 10^{-6} M of the dye **7** or **8** in EtOH or DMF solution causes a similar effect upon the electronic absorption spectra of each dye to that determined by the increase of pH′ on the spectra of these dyes in aqueous ethanol solution (compare the curves 'a' with curves 'b' in Figs. 6–9).

The similar effect determined either by the decrease of the concentration or by the increase of pH′ on the spectra of the dye **7** or **8** support the involvement in both effects of the same type of equilibria, respectively the presence of the same species. As was shown (see Section 2.3) the equilibria compatible with the pH′ effect on the spectra of **7**, **8** are the ionization equilibria (e.g. **7** ⇔ **9**, **9** ⇔ **13**) eventually coupled with azo–hydrazone equilibria (e.g. **9a** ⇔ **9b** ⇔ **9c**). Consequently, also by the effect of the concentration variation on the spectra of dyes **7** and **8** should be involved the above mentioned ionization- and eventually azo–hydrazone equilibria. Otherwise, both the dilution and the increase of pH favors also in the case of other dyes that theoretically may be involved in azo–hydrazone tautomerism the similar shifts of ionization equilibrium towards ionized forms [3b,4b,6] and of azo–hydrazone equilibrium towards azo-form [6,8]. We mention however that the determined effect on the spectra of the dye **7** in EtOH solution by simple concentration variation (Fig. 10, curves 'a') is very similar to that obtained by other authors for another

dye that theoretically may be involved in azo–hydrazone tautomerism. But in the last case the effect was ascribed [8] to an aggregation equilibrium coupled with azo–hydrazone equilibrium. With a view to detect the eventual involvement of the aggregation of the dye **7** in EtOH solution we have examined also the dependence of the absorption spectra upon time (up to one month), at different concentration (Fig. 11), since it is known [8] that the aggregation is also a function of time. The absorption curves at a certain registration time show again the above discussed dependence upon concentration. But the time dependence of the spectra of **7** is irregular. In any way the time dependence of the spectra of **7** in EtOH is similar to the concentration or pH dependence of these spectra. Therefore, also by time dependence should be involved again the ionization and eventually azo–hydrazone equilibria presented by pH′ dependence. The irregular variation with time of these equilibria may be caused by accidental contamination of the solution with traces of acid or base. Owing to the great sensitivity to acid or base of the discussed equilibria of **7** (see Sections 2.2.2 and 2.3) these traces become relatively very important at low concentrations of the dye (cf. [3b]). Thus, it may be concluded that the studied dependence of the spectra of the dyes **7** and **8** upon concentration or time does not sustain, although it also does not exclude definitively, the aggregation of these.

2.5. Conclusions

The systematic investigation of the effect of solvent, sample concentration, time and acid or alkali addition, respectively of pH′, upon the electronic absorption spectra of the dyes **7** and **8**, together with pK'_a values determination of these, have proved that in some solvents (C_6H_6, $CHCl_3$, DMSO) and in acidic media (AcOH or acidified EtOH) the structures of dyes correspond to hydrazone tautomers **7c** and **8c**, whilst in neutral and alkalinized EtOH, respectively DMF, these are in equilibrium with monodeprotonated (**9**, **10**) and twice deprotonated species (**13**, **14**). By increase of pH or by dilution the equilibrium shifts increasingly towards the deprotonated species. The monodeprotonated species (**9**, **10**) correspond also to a hydrazone structure whilst the twice deprotonated species (**13**, **14**) to a common dianion with azo-structure. The inversed pK'_a values with respect to the usual substituent effect upon pK_a may be explained reasonably in the case of the dyes **7** and **8** on the basis of the eventual involvement of azo–hydrazone equilibria alongside of ionization equilibria of these.

3. Experimental

The synthesis and purification of the dyes **7** and **8** were made as previously described [2]. Analytical grade reagents and solvents were provided by Chimapur or Remed (Bucharest), Merck (Darmstadt) and Fluka (Buchs). These were used without further purification. The water used was doubly distilled. As a rule a relatively concentrated (10^{-4}–10^{-6} mol L^{-1}) stock solution of the dye in certain organic solvent was prepared. This solution was used as such, or diluted with the initial solvent, or water, or universal buffer, HCl or KOH solution to the concentration needed in spectroscopic measurements (10^{-5}–10^{-6} mol L^{-1}). The ionization constants (pK'_a values) were determined at 25 °C in presence of 0.01 mol L^{-1} KCl, on the basis of correlation between pH′ and absorbance (Fig. 12b_1, b_2) at analytical wavelength (cf. [22]). The correlation was fitted with the aid of the programme Table Curve Windows v.1.10, Table Curve™, Jandel Scientific, Copyright 1989–1993 AISN Software. The electronic absorption spectra were performed on a Jasco V-530 spectrophotometer. There were used matched glass cells of 0.5, 1.0, 2.0 and 5.0 cm. The experimental pH′ values corresponding to the working conditions were measured by a digital Pracitronic MV-870 pH-meter equipped with a combined pH-reference electrode ESHC-02, produced by Naposenz SRL Cluj-Napoca; temperature was controlled with an ultrathermostat.

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