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AZOCOUPLING PRODUCTS. III.[1] SPECTROSCOPIC INVESTIGATION AND SYNTHESIS OF SOME AZOCOUPLING PRODUCTS BETWEEN 1-(4-HYDROXY-6-METHYL-PYRIMIDIN-2-YL)-3-METHYL-PYRAZOLIN-5-ONE AND AROMATIC DIAZONIUM SALTS

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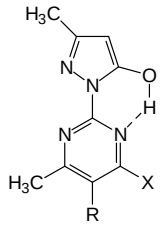
ABSTRACT. By azocoupling of 1-(4-hydroxy-6-methyl-pyrimidin-2-yl)-3-methyl-pyrazolin-5-one (11) with disubstituted benzene diazonium salts (3) three new dyes (12-14) were synthesized. The comparative electronic absorption and ^{1}H-NMR studies of these compounds (12-14) and of other azocoupling products (4-10, 15) of 11 with *ortho*-, respectively *para*- monosubstituted benzenediazonium salts support the manifestation of the azo-hydrazono tautomerism for the examined dyes. However, in aprotic solvents and in acidic medium only one species has been detected for the studied dyes. The ^{1}H-NMR spectra of these dyes recorded in deutero-chloroform prove the hydrazonic structure (4a-10a, 12a-15a) of the detected species. In methanolic solution the hydrazonic tautomer is favored with respect to the azohydroxy tautomer by the *ortho*-substituent in benzenic ring of the examined azocoupling products (8, e.g.), as a manifestation of the *ortho* effect of the substituent. It is described also the *ortho* effect of the substituent situated in the *ortho*-position of the benzenic ring of azocoupling products 8-10, 15 concerning the acidity and the chemical shift of their mobile hydrogen having the ^{1}H-NMR signal at about 14 ppm. The *ortho* effect of nitro group is unusually strong ($\Delta\delta_{o-p}$ =1.5 ppm).

1. INTRODUCTION



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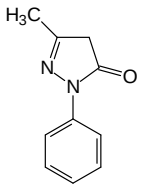

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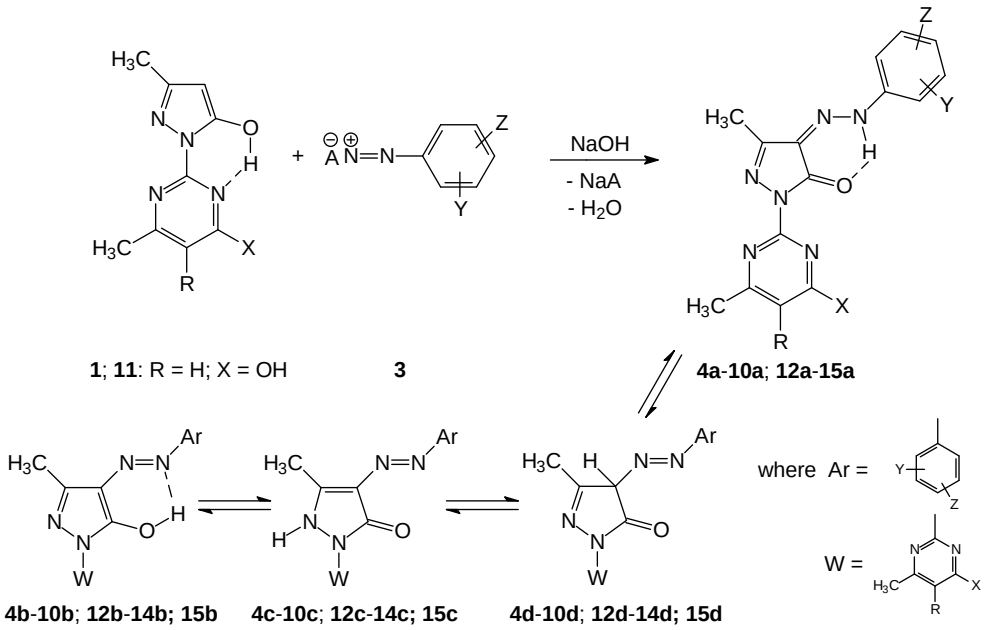
Taking into account the proved structural [1] and reactivity [1-3] analogy between 1-(6-methyl-5-R-4-X-pyrimidin-2-yl)-3-methyl-pyrazolin-5-ones (**1**) and 1-phenyl-3-methyl-pyrazolin-5-one (**2**) as well as the known utilisation of the latter to the manufacturing by azocoupling [4-6] of a series of commercial dyes, we have carried out [2,3,7,8] the azocoupling of **1** with aromatic diazonium salts (**3**).

The electronic absorption spectra of the obtained azocoupling products (**4**) exhibit in the range of 350-600 nm one, two or three bands as a function of (i) the substituent in the benzenic, respectively pyrimidinic ring; (ii) the solvent and (iii) the acidity or basicity of the methanolic solution used for the recording of the spectra [8,9]. This behavior has been attributed [8,9] to the possible tautomerism of the azocoupling products (**4a**-**4d**).

[1] Part II: reference [8]



1: R = H, C_1-C_4 Alkyl; X = OH, OCH_3, Cl;
3: Y = H, CH_3, COOH, NO_2, Cl; Z = R, X, Y, $NHCOCH_3$, $N(CH_3)_2$, OC_2H_5, Br, $COOCH_3$, SO_2NH_2;
4: R, X as in **1**; Y, Z as in **3**;

5: R = H; X = OH; Y = H; Z = 4-NO_2;
6: R = H; X = OH; Y = H; Z = 4-CH_3;
7: R = H; X = OH; Y = H; Z = 4-Cl;
8: R = H; X = OH; Y = 2-CH_3; Z = H;
9: R = H; X = OH; Y = 2-Cl; Z = H;
10: R = H; X = OH; Y = 2-NO_2; Z = H;
12: R = H; X = OH; Y = 3-CH_3; Z = 4-NO_2;
13: R = H; X = OH; Y = 2-CH_3; Z = 4-CH_3;
14: R = H; X = OH; Y = 3-NO_2; Z = 4-C_2H_5;
15: R = H; X = OH; Y = 2-NO_2; Z = 4-CH_3.

SCHEME 1

In the above mentioned studies [8,9] we brought arguments especially for the hydrazono (**4a**) and the hydroxyazo (**4b**) tautomers. The hydrazono forms **4a** were sustained among other things by NOESY spectra [9]. These spectra recorded in $CDCl_3$ have showed an interaction and therefore a spatial close proximity of the mobile hydrogen atom (responsible for the ^{1}H-NMR signal at 13-14 ppm) with the hydrogen atoms situated on the benzenic ring in *ortho*- position with respect to the two nitrogen atoms bridge between the rings of the azocoupling products **4**. Such a spatial arrangement is compatible only with the hydrazono tautomer **4a** when one takes also into account the expected electronic absorption spectra of all tautomers **4a**-**4d** and that observed in fact for **4** in $CHCl_3$ [9]. The lowest field ^{1}H-NMR signal (13-14 ppm) of the azocoupling products **4** corresponds to strongly chelated hydrazonic N-H of **4a** (compare [10]). As a consequence of these observations it was of interest to examine the effect of the substituent in the mentioned *ortho*-position of the benzenic

ring on the lowest field ^{1}H-NMR signal of the azocoupling products **4**. This effect may give useful information on the structure of tautomeric azocoupling products **4** (see [11]). On the other hand, the azohydroxy tautomers **4b** were supported especially by the effects of the alkali or acid addition on the electronic absorption spectra of the azocoupling products **4** in methanolic solutions. These effects have been totally different [9] for the azocoupling product substituted with a nitro group in *para* position of the benzenic ring (**5**) comparative to other azocoupling products of this series (e.g. **6**, **7**). Therefore, it was interesting to examine whether these effects manifest themselves for the azocoupling products substituted in *ortho*- position of the benzenic ring (e.g. **8**-**10**) in a similar manner as for the *para*- isomers (e.g. **5**-**7**). Consequently, a purpose of this work is the comparative study of the electronic and ^{1}H-NMR spectra of three pairs consisting of isomeric products (**5**-**10**) obtained by azocoupling of 1-(4-hydroxy-6-methyl-pyrimidin-2-yl)-3-methyl-pyrazolin-5-one (**11**) with *ortho*-, and with *para*-substituted benzenediazonium salts (**3**), respectively. This study should contribute to the elucidation of the tautomerism of the azocoupling products **4** and of the *ortho* effect of some substituents. Another aim is the synthesis of three new in benzenic ring disubstituted azocoupling products (**12**-**14**)[2] and their spectroscopic (electronic and ^{1}H-NMR) study, comparative to other already studied [8,9] similar dyes (**4**).

RESULTS AND DISCUSSIONS

A. Electronic absorption study

Table 1

Some chemical and physical data of the newly synthesized dyes (**12**-**14**).

Substituents Y, Z; compound no.	**Yield (%)**	**Melting point (°C)**	**Elemental analysis data Calcd./found (%)**			**UV-VIS data in methanol λ[nm], (ε, mol^{-1}·cm^{-1})**
			C	**H**	**N**	
Y=3-CH_3, Z=4-NO_2 **12**	92	289-290	52.03/ 52.10	4.06/ 4.20	26.56/ 26.30	425 (38.000)
Y=2-CH_3, Z=4-CH_3 **13**	95	254-255	60.35/ 59.90	5.32/ 5.50	24.85/ 24.70	392 (15.800) 428 (17.200)
Y=3-NO_2, Z=4-C_2H_5 **14**	95	246-247	53.26/ 53.30	4.43/ 4.60	25.58/ 25.50	388 (16.200)

The Table 1 and Figure 1 report some data for the newly synthesized azocoupling products **12**-**14**. The electronic absorption spectra of these, similarly to other studied [8,9] 1-(pyrimidin-2-yl)-3-methyl-pyrazolin-5-one azocoupling products (e.g. **5**-**7**; see Figure 2, curves 1-3), exhibit in the range 350-600 nm (Figure 1) one (**12**-**14**), two (**13**) or three (**14**) absorption bands (even if some of them appear only as shoulders) as a function of the substituents on the benzenic ring, of the solvent and of the acidity or the basicity of the methanolic solutions used for recording the

[2] The compounds for which several tautomers are possible are indicated in the corresponding figure **1**, **2**, **4**-**15** not accompanied by letters, except when a definite tautomer is under discussion. The examined azocoupling products **5**-**10**, **12**-**15** differentiate only by the substituents in the benzenic ring. The substituent positions are related to the hydrazono (or azo) bridge.

spectra. Also, the effect of acid or alkali addition to the methanolic solution of each new dye (**12**-**14**) is similar to that observed [8,9] for the azocoupling products **4** unsubstituted or mono-substituted in the benzenic ring (e.g. **5**-**7**; compare Figure 1 with Figure 2). On this basis one can assume that the newly synthesized azocoupling products (**12**-**14**) manifest very probably the azo-hydrazono tautomerism that was already assigned for similar reasons [8,9], in the case of some analogues dyes. However, since the visible spectra of these dyes recorded in chloroform, acetic acid and acidified methanol show practically the same unique absorption maximum (e.g. Figure 1a) the examined azocoupling products have been detected in mentioned solvents as a unique species, namely the hydrazono tautomer (**12a**-**14a**).

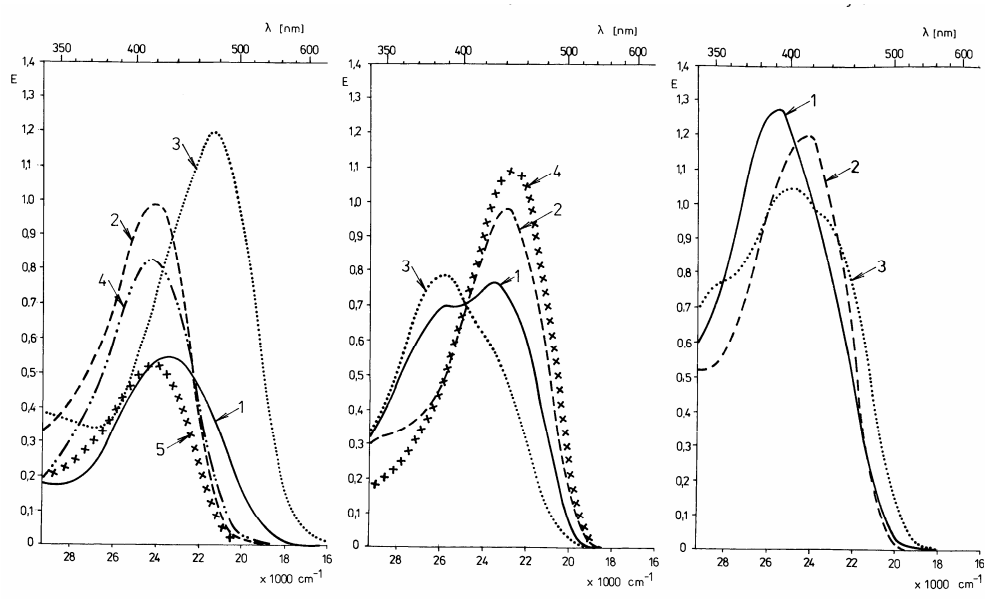


Figure 1. *The electronic absorption spectra of the newly synthesized compounds: a) **12**; b) **13**; c) **14**. Curves 1: methanolic solution; curves 2: methanolic 0.1 mol/dm^3 HCl solution; curves 3: methanolic 0.1 mol/dm^3 KOH solution; curves 4: chloroformic solution; curves 5: acetic acid solution.*

The Figure 2 presents the absorption spectra of three pairs of isomeric azocoupling products (**5**, **10**; **6**, **8**; **7**, **9**) in the range 350-600 nm. One isomer of each pair has the substituent of the benzenic ring in *para* position (**5**-**7**) while the other bears the same substituent in the *ortho* position (**8**-**10**). These spectra in absolute methanol present for every pair practically the same absorption maxima. However, for the azocoupling products having the substituent in *ortho*-position the absorption band, corresponding to the longest absorption maximum, is a little narrower and lacks the shoulder that can appear for *para* substituted isomers (e.g. **6**) at lower wavelength (Figure 2b, curves 1 and 4). This shoulder was assigned [9] to the hydroxyazo tautomer (e.g. **6b**). Consequently, the absence of the shoulder for the *ortho*-isomers (e.g. **8**, Figure 2b) can signify the increase of the content of hydrazono tautomer (e.g. **8a**) in these cases (compare [11]).

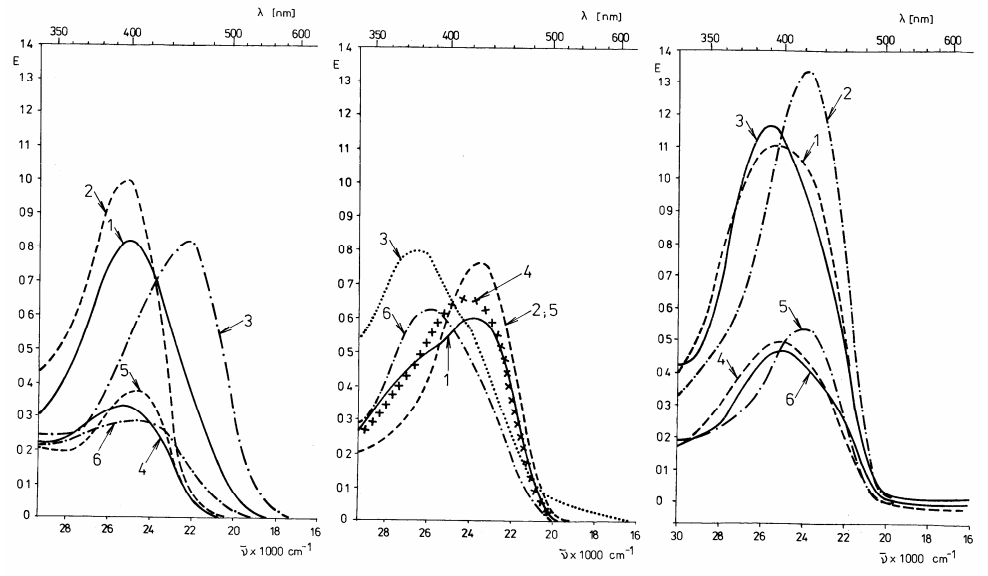


Figure 2. *The electronic absorption spectra of three pairs of isomeric para- and ortho-substituted azocoupling products: a) nitro-substituted (**5**, **10**); b) methyl-substituted (**6**, **8**); c) chloro-substituted (**7**, **9**). Curves 1, 2, 3: for para-substituted products (**5**-**7**); curves 4, 5, 6: for ortho-substituted products (**8**-**10**). Curves 1, 4: methanolic solution; curves 2,5: methanolic 0.1 mol/dm^3 HCl solution; curves 3, 6: methanolic 0.1 mol/dm^3 KOH solution.*

The effects of the addition of acid respectively of alkali, up to a concentration of 0.1 mol/dm^3 on the electronic absorption spectrum of the azocoupling product **8** (methyl substituted in *ortho*-position) recorded in methanol are practically identical to those observed for the corresponding *para* substituted isomer **6** (Figure 2b). Also, these effects are very similar for the *para* (**7**) and *ortho* (**9**) chloro-substituted azocoupling products (Figure 2c). On the contrary, these effects on the methanolic solution of the *ortho*-nitro-substituted azocoupling product (**10**) are different from those observed for the *para*-substituted isomer (**5**). Thus, while the HCl addition up to 0.1 mol/dm^3 over the methanolic solution of the *para* isomer **5** causes a very weak (~ 5nm) hypsochromic shift of the longest wavelength band, the same addition to the absolute methanolic solution of the *ortho* isomer **10** determines a bathochromic shift (~ 10 nm) of the longest wavelength band of **10**. The different behaviour of *ortho*-nitro substituted azocoupling product comparative to the *para* isomer **5** may be caused by the *ortho*-effect of the nitro group. This effect may be exerted in **10** by the formation of intramolecular hydrogen bonding (compare [12]) between *ortho*-nitro group and hydrazonic N-H of the hydrazono tautomer **10a**.

On the other hand, KOH addition up to 0.1 mol/dm^3 in methanolic solution of **5** and **10**, respectively, has induced in both cases a bathochromic shift which is much stronger for **5** (~60 nm) than for **10** (~10 nm). The strong bathochromic shift in the case of **5** may be explained [9] by the dissociation *via* deprotonation of the more acidic pyrazolic –OH (compare [13]) of the azohydroxy tautomer **5b**. Only the

very extensively delocalized anion resulted by the described dissociation of the pyrazolic –OH in the azohydroxy tautomer **5b** (the delocalization being extended between *para* nitro group of the benzenic ring and the pyrazolic oxygen) is compatible with such an absorption at much greater wavelength as compared to the undissociated species. The acidifying is due to the conjugation of the donor pyrazolic –OH with the strong withdrawing -NO_2 group in *para* position of the benzenic ring of the azohydroxy tautomer **5b**. Thus, the much lower bathochromic shift determined by addition of KOH to the methanolic solution of **10** can signify a much lower acidity of **10**. This low acidity of **10** may determine its decreased dissociation to form an extensive delocalized anion of the type resulted by deprotonation of **5** and implies a lower bathochromic shift. This low acidity of **10** may be explained by a possible stabilization of the low acidity (compare [13]) hydrazonic tautomer **10a** by the already presumed intramolecular hydrogen bonding between hydrazonic N-H and the *ortho*-nitro group of the benzenic ring, as a manifestation of the *ortho*-effect of the nitro group. The implication of the tautomeric azohydroxy-hydrazono equilibrium in the explanation of acidity difference (and on this basis of longest wavelength band position in alkaline medium) between *para*- (**5**) and *ortho*- (**10**) nitro-substituted azocoupling products (*para*>*ortho*) is supported also by the fact that the acidity of the corresponding nitro-anilines is reversed (*para*<*ortho* [12]). Indeed, if the acidity of the *para*- and *ortho*-nitro-substituted azocoupling products **5** and **10**, respectively, would be determined only by the hydrazonic tautomers **5a** and **10a**, respectively, which have the hydrazonic N-H group bond to the nitro-substituted benzenic ring as in the corresponding anilines, the acidity of **5** and **10** (*para*>*ortho*) should vary as the one for the nitroanilines (*para*<*ortho* [12]), which is not the case.

A strong bathochromic shift (~60 nm) has been observed also in the case of the addition of alkali to the methanolic solution of the azocoupling product substituted in the benzenic ring in *para* with nitro and in *meta* with methyl (**12**, Figure 1a). In exchange, the addition of alkali to the methanolic solution of the *ortho*-nitro-*para*-methyl-substituted azocoupling product (**15**) caused no bathochromic shift. Consequently, the differentiation of the effect of alkali addition as a function of the nitro group position in the benzenic ring of azocoupling products **4** manifests itself similarly both in mono- and di-substituted derivatives. Therefore, the discussed effect of alkali addition may be used to establish the position of the nitro-group in benzenic ring of the azocoupling products **4** in the case when this group may be situated either in *ortho* or in *para*-position.

B. ^{1}H-NMR Study

The ^{1}H-NMR data of the new azocoupling products (**12**-**14**) together with those of the examined pairs of *ortho*- and *para*- substituted isomers (**5**, **10**; **6**, **8**; **7**, **9**) and of the azocoupling product (**15**) between **11** and the diazonium salt obtained from 4-methyl-2-nitro-aniline are presented in Table 2.

The ^{1}H-NMR spectra of the azocoupling products **5**-**10**, **12**-**15** recorded in $CDCl_3$ solution show the formal existence of a single species and the presence of a mobile hydrogen atom by a very low field signal (δ between 13 and 15 ppm). Such a deshielded proton signal in the ^{1}H-NMR spectra of other azocoupling products of

1-(pyrimidin-2-yl)-3-methyl-pyrazolin-5-ones (**1**, **11**) or of 1-phenyl-3-methyl-pyrazolin-5-one (**2**) has been assigned [8-10] to the strongly chelated hydrazonic N-H (e.g. **4a**). Therefore, it is very probable that in $CDCl_3$ the examined azocoupling products (**5**-**10**, **12**-**15**) are detectable by ^{1}H-NMR practically only as hydrazonic tautomers **5a**-**10a**, **12a**-**15a**. The greater chemical shift of the lowest field ^{1}H-NMR signal in the case of each azocoupling product monosubstituted in benzenic ring in *ortho*-position (**8**-**10**), comparative to the corresponding *para*-monosubstituted product (**5**-**7**) proves a close steric proximity effect (compare [14]) of *ortho* substituent on the mobile hydrogen that determines such a signal. This is a manifestation of the *ortho*-effect and it is compatible with the hydrazonic structure (**5a**-**10a**) of examined pairs of isomeric azocoupling products in chloroformic solutions. As is known [15] the difference between the behaviour of *ortho*- and *para*-substituted isomeric derivatives has been defined as the simplest quantitative measure of the *ortho*-effect. In NMR study the examined difference is that of the chemical shifts (see [16]). The chemical shift difference of the lowest field ^{1}H-NMR signal between the *ortho*- and *para*- isomer ($\Delta\delta_{o\text{-}p}$) of the azocoupling products bearing in the benzenic ring a methyl- (**8**, **6**) or chloro- (**9**, **7**) substituent ($\Delta\delta_{o\text{-}p}$~0.26 ppm) is due, very probably, to the intramolecular van der Waals shift (see [14]) or, in other words, to the steric effect contribution (see [17]) to the *ortho* effect. This steric effect is expected to be a function of the bulk or size of the substituent.

As is known, the apparent sizes [18] and the van der Waals radii[3] [19a], respectively, of the methyl group and of the chlorine atom are relatively similar [19b]. However, although the apparent size of the nitro group is smaller than the one of the methyl group and of the chlorine atom [18], the chemical shift difference of the lowest field ^{1}H-NMR signal between *ortho*- (**10**) and *para*- (**5**) isomers of the azocoupling products mono-nitro-substituted in benzenic ring is unusually great ($\Delta\delta_{o\text{-}p}$~1.5 ppm).

This is due to the fact that the *ortho*-effect of nitro group includes, beside the steric effect, the contribution of the intramolecular hydrogen bonding formation (compare [17, 20]) between nitro and the hydrazonic NH group of the hydrazonic tautomer **10a**. This interpretation is supported by the similar explanation of the effect on electronic absorption spectra of acid or alkali addition to the methanolic solution of **10**.

The above discussed *ortho*-effects of methyl and nitro groups, respectively, on the lowest field ^{1}H-NMR signal of the *ortho*-mono-methyl-, and mono-nitro-substituted azocoupling products, respectively, (**8**, **10**) manifest themselves also in practical identical way with the disubstituted azocoupling products, provided that only one of the *ortho* positions is substituted with a methyl (**13**) or nitro (**15**) group, respectively (Table 2).

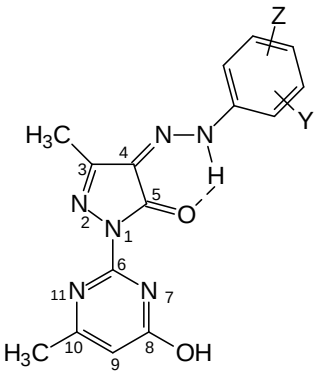
It is worth noting that: (i) the *ortho*-effect of the nitro group on the chemical shift of mobile hydrogen generating the lowest field signal in the azocoupling products **10**, **15** ($\Delta\delta_{o\text{-}p}$~1.5 ppm) is much stronger than in *ortho*-nitro-aniline ($\Delta\delta_{o\text{-}p}$~0.7 ppm [21]) although in the hydrazonic structure assigned for these (**10a**, **15a**) the mentioned mobile hydrogen belongs to a NH group directly linked to the nitro-substituted benzenic ring as in *ortho*-nitro-aniline; (ii) the chemical shift of hydrazonic NH hydrogen in all studied azocoupling products **4**-**10**, **12**-**15** is much greater (about 7-9 ppm) than

[3] The van der Waals radius is considered the best steric parameter [17]

that of the aminic hydrogen in corresponding anilines (compare Table 2 with [21]); (iii) the variation of the chemical shift of the mobile hydrogen, that gives the herewith discussed lowest field signal in the azocoupling products **4**, as a function of the substituent nature in *para* position of benzenic ring of these (**4**), is inverted [9] comparative to that of the aminic hydrogen in corresponding anilines [21]. All these observations relating to the lowest field ^{1}H-NMR signal in the azocoupling products **4**-**10**, **12**-**15** may be understood on the basis of chelated intramolecular hydrogen bonding formation between the hydrazonic NH group and the pyrazolin-5-onic C=O group, respectively the nitro group - when this group is present in the *ortho*-position of the benzenic ring - of the hydrazono tautomer **4a**-**10a**, **12a**-**15a**.

Table 2

The ^{1}H-NMR data (chemical shift δ [ppm], multiplicity,* number of hydrogen atoms and coupling constant J [Hz]) of azocoupling products **5**-**10**, **12**-**15** recorded in $CDCl_3$



5-**10**; **12**-**15**

Substituents Y, Z; Compound no.	***Hydrogens of the groups***						
	C_3-CH_3 s, 3H	C_{10}-CH_3 s, 3H	C_9-H s, 1H	Benzenic ring	*Pyrimidinic NH or OH* s, 1H	*Hydrazonic NH* s, 1H	Other
Y=H, Z=4-NO_2 **5**	2.48	2.39	6.15	7.62, d, 2H, 7.50 8.32, d, 2H, 7.50	10.93	13.17	-
Y=H, Z=4-H_3C **6**	2.41	2.34	6.07	7.24 d, 2H, 8.00 7.37 d, 2H, 8.00	11.21	13.20	benzylic 4-CH_3 2.37 s, 3H
Y=H, Z=4-Cl **7**	2.44	2.37	6.11	7.44 m, 4H	11.15	13.17	-
Y=H, Z=2-H_3C **8**	2.44	2.36	6.10	7.15-7.40 m, 3H 7.78 d, 1H, 8.10	11.23	13.45	benzylic 2-CH_3 2.42 s, 3H

Substituents Y, Z; Compound no.	***Hydrogens of the groups***						
	C_3-CH_3 s, 3H	C_{10}-CH_3 s, 3H	C_9-H s, 1H	Benzenic ring	*Pyrimidinic NH or OH* s, 1H	*Hydrazonic NH* s, 1H	Other
Y=H, Z=2-Cl **9**	2.43	2.35	6.09	7.21 t, 1H, 7.50 7.38 t, 1H, 7.45 d, 1H, 7.84 d, 1H, 8.00	11.18	13.44	-
Y=H, Z=2-NO_2 **10**	2.49	2.38	6.14	7.40 t, 1H, 7,60 7.80 t, 1H, 8.20 d, 1H, 8.50 8.35 d, 1H, 8.30	11.15	14.63	-
Y=3-CH_3, Z=4-NO_2 **12**	2.48	2.39	6.15	7.40 s, 1H 7.44 d, 1H, 8.19 d, 1H, 9.00	10.95	13.10	benzylic 3-CH_3 2.73 s, 3H
Y=2-H_3C, Z=4-H_3C **13**	2.44	2.34	6.09	7.06 s, 1H 7.12 d, 1H, 8.20 7.66 d, 1H, 8.20	11.29	13.48	benzylic 2-CH_3 2.39 s, 3H benzylic 4-CH_3 2.36 s, 3H
Y=3-O_2N, Z=4-H_5C_2 **14**	2.44	2.36	6.10	7.46 d, 1H, 7.50 7.66 d, 1H, 7.50 8.13 s, 1H	11.23	13.12	*CH_3*-CH_2- 1.32 t, 3H, 7.3; CH_3-*CH_2*- 2.93 q, 2H, 7.3;
Y=2-NO_2, Z=4-H_3C **15**	2.47	2.36	6.15	7.58 s, 1H, 8.30 8.06 d, 1H, 8.30 8.13 s, 1H	11.13	14.57	benzylic CH_3 2.47 s, 3H

* s: singlet; d: doublet; t: triplet; q: quartet; m: complex multiplet.

CONCLUSIONS

The different number of absorption bands in the range 350-600 nm of the electronic spectrum of each azocoupling products (**12**-**14**) as a function of (i) the substituent located in benzenic ring, (ii) the solvent and (iii) the acid or alkali addition to the methanolic solutions, supports the tautomerism of these dyes. However, in aprotic solvents and in acidic conditions has been detected only one species. The ^{1}H-NMR spectra prove the hydrazonic structure **12a**-**14a** of this species.

The comparative spectroscopic study of the pairs of isomeric azocoupling products, *ortho*- (**8**-**10**) and *para*- (**5**-**7**) substituted, respectively, shows the manifestation of the *ortho*-effect of the substituent on the acidity and the chemical shift of the mobile hydrogen, that causes the lowest field ^{1}H-NMR signal of the examined dyes. This proves the steric proximity of the *ortho*-substituent and the mobile hydrogen in the azocoupling products **8**-**10**, a situation compatible with chelated hydrazonic structure **8a**-**10a** of these. However, the different visible spectrum of the *ortho*-isomer (**8**; **10**) with respect to *para*-isomer (**6, 5**) in methanol, respectively by addition of alkali, in

the case of several examined azocoupling products, may be explained only by the assumption of the involvement of both hydrazono- and azohydroxy-tautomer in these circumstances.

The very strong *ortho*-effect of the nitro-group in azocoupling products **10**, **15** may be determined by the formation of intramolecular hydrogen bonding between this group and the discussed mobile hydrogen of the dyes **10**, **15**.

EXPERIMENTAL

The procedure for the preparation of 1-(4-hydroxy-6-methylpyrimidin-2-yl)-3-methyl-pyrazolin-5-one (**11**) was previously described [22]. Aromatic amines used for the preparation of diazonium salts **3** were commercial products; their diazotization was achieved by standard methods [6, 23a]. The coupling reaction between diazonium salts **3** and 1-(4-hydroxy-6-methylpyrimidin-2-yl)-3-methyl-pyrazolin-5-one (**11**) was performed [7] in similar conditions to those used [6,23b] for the azoic coupling of 1-phenyl-3-methyl-pyrazolin-5-one (**2**).

Elemental analysis were carried out at the Chemistry and Pharmaceutical Research Institute Cluj-Napoca.

Melting points were taken with an Electrothermal IA 6304 apparatus and are uncorrected. UV-VIS spectra were recorded on a Zeiss-Jena Specord UV-VIS spectrophotometer; the analytical grade reagents and solvents were provided by Reactivul (Bucharest), Merck (Darmstadt) and Fluka (Buchs); they were used without further purification. Each solution was prepared in corresponding solvent and diluted to the requested concentration or directly to the nedeed concentration ($\sim 10^{-5}$ mol/dm^3) for electronic absorption spectroscopy measurement. The ^{1}H-NMR spectra were recorded in $CDCl_3$ at room temperature with a Varian Gemini 300 (300MHz) spectrophotometer.

General procedure for the azoic coupling: 0.01 mol 1-(4-hydroxy-6-methyl-pyrimidin-2-yl)-3-methyl-pyrazolin-5-one (**11**) was treated with a warm solution prepared from 0.01-0.02 mol sodium hydroxide, 0.05 mol sodium carbonate and 20 cm^3 water (pH~10). This mixture was cooled to 0-5℃ and into it was pourred, under stirring and keeping the temperature below 10℃, one of the diazonium salts **3**, freshly prepared from 0.01 mol of the corresponding aromatic amine. Usually the coupling reaction was rapid, the reaction mixture became coloured immediately; however, the mixture was stirred for 0.5-12 hours at 15℃. After that the pH of the mixture was corrected to 6-7 with acetic acid. The suspension was filtered off, washed with water on the filter, dried and crystallized from methanol. The newly synthesized dyes **12**-**14**, the yields and some characteristics of these are presented in Table 1.

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