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AZOCOUPLING PRODUCTS. PART IV[+]. THE STRUCTURE OF DYES OBTAINED BY AZO-COUPLING REACTION OF 1-(4-HYDROXY-6-METHYLPYRIMIDIN-2-YL)-3-METHYLPYRAZOLIN-5-ONE WITH AROMATIC DIAZONIUM SALTS

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ABSTRACT*.* The number and positions of the absorption bands have been studied for the title dyes, in the range of 350-600 nm, as a function of solvent nature, acidity or basicity of the solutions as well as of the nature of the substituent X in para position on the benzene ring. The obtained results, including Hammett correlations, quantum calculation by using AM_1- SM_2 method and the mechanism of formation of the dyes ***5*** prove the existence of some tautomeric azo-hydrazono- and pyrazolin-5-one-5-hydroxy-pyrazole (***5a* ⇔ *5b* ⇔ *5c* ⇔ *5d***) equilibria, coupled with acid-base equilibria. The visible and (^{1}H-, ^{13}C-) NMR spectra support the hydrazonic structure ***5d*** of the only species detectable in the used aprotic solvents.

INTRODUCTION

Taking into account the formal analogy between 1-(3,4-dihydro-6-methylpyrimidin-4-one-2-yl)-3-methylpyrazolin-5-one ***1*** and 1-phenyl-3-methyl-pyrazolin-5-one ***2*** and the fact that the last is commonly employed in obtaining[1-4] of commercial dyes ***3*** we performed[5-7] the azo coupling of ***1*** with aromatic diazonium salts ***4***. The results were a series of coloured azocoupling products ***5*** of 1-pyrimidinyl 5-pyrazolone ***1***, exhibiting strong absorption bands in visible range. Beside this first argument for the real analogy between the two substituted pyrazolones ***1*** and ***2***, there exists[5-12] a similar tautomerism (***1a-c*, *2a-c***), although ^{1}H-NMR spectra in $CDCl_3$ indicated different structures: ketomethylenic ***2a*** in the case of 1-phenyl derivative[9,10] and hydroxypyrazolic ***1b*** or iminopyrazolonic ***1c*** in the case of 1-pyrimidinyl derivative[12], respectively.

Another proof for their analogy came from the kinetics of the azocoupling reaction[6, 8, 11]. Both compounds participate in the azocoupling process as mesomeric anions ***6*, *7*** and follow the same mechanism. All these arguments justify the supposition that the dyes ***3***, ***5*** are also structural analogues.

The structural study of dyes ***3*** obtained by azocoupling of 1-phenyl-3-methyl-pyrazolin-5-one ***2*** and of the analogue hetaryl-pyrazolin-5-ones has lead to many contradictory assessments[3, 4, ,7b, 9, 13-28]. For such dyes, four tautomeric forms ***3a***- ***3d*** were formulated[3, 9, 15, 20, 21, 25]; each of them can exists[20] as two E/Z diastereoizomers, and a series of conformers. It is worth mentioning that the majority of papers published within the last 30 years support the existence of hydrazonic

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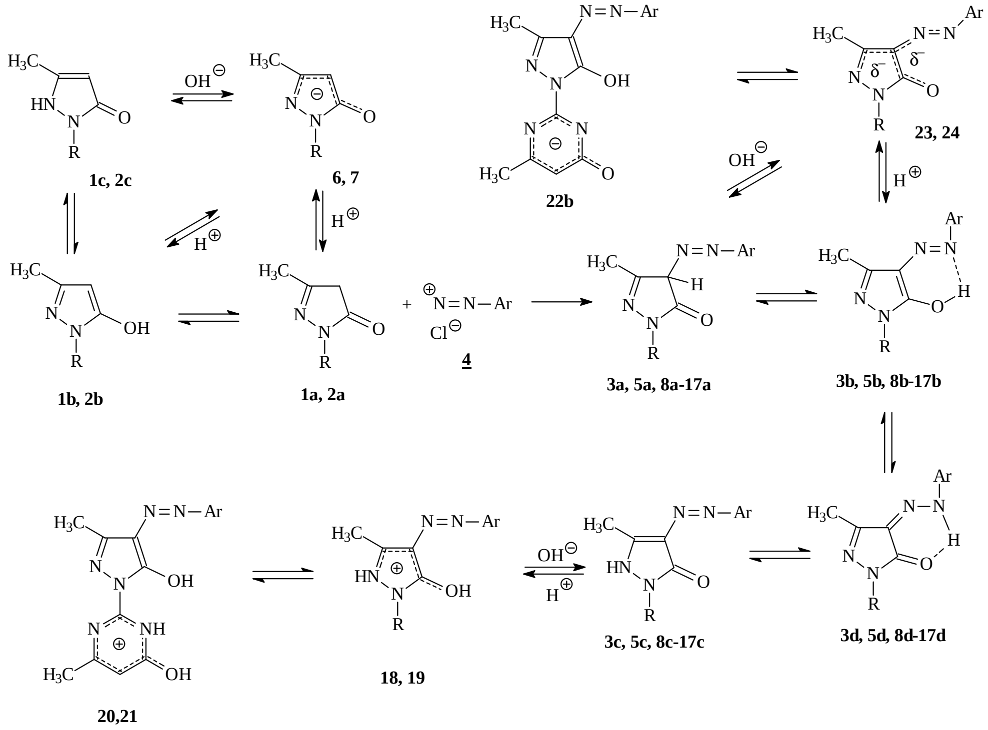
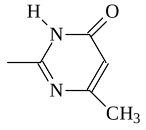
[+] Part III. Reference [7b]

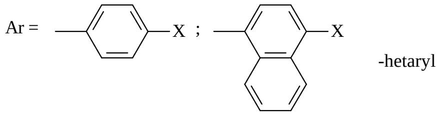
tautomer ***3d*** in a Z configuration, as a prevalent form[3, 7b, 9, 15, 17, 18, 21b] or as the only form[13, 14, 19, 20, 22, 23, 25] of the dyes ***3***. It must be underlined however, that the detection of a single tautomeric form does not rule out the tautomeric equilibria[14, 21b, 29].



in **1a, b, c**; **5a, b, c**; **6**; **8a, b, c-17a, b, c**; **18**; **19**; **23**; R =



in **2a, b, c**; **3a, b, c**; **7**; **24**: R = -C_6H_5 ; -hetaryl



X = H; alkyl-; halogen-; -OH; -O-alkyl; -COOH; -$COOCH_3$; -$N(CH_3)_2$; -NH-CO-CH_3;
-NO_2; -SO_3H; -SO_2-NH_2.

Scheme 1

The purpose of this work is to determine the structure of azocoupling dyes ***5*** and, on the basis of the analogy between ***5*** and ***3***, to contribute to the elucidation of the controversial structure of commercial dyes ***3***. For the sake of simplicity we will use in general the denomination of the azoic pyrazolin-*5*-one tautomers ***5a, 5c*** and for the substituent in position *1*-(pyrimidinic), that corresponding to the lactimic form. To indicate the compounds, in general, we will use figures without letters, e.g. ***5***.

RESULTS AND DISCUSSION

Electronic spectra; general presentation

The electronic absorption spectra at wavelegngth over *35*0 nm for azocoupling products ***5*** of *1*-(*4*-hydroxy-6-methyl-pyrimidin-*2*-yl)-*3*-methyl-Δ^3-pyrazolin-5-one ***1*** exhibit one, two or three intense and relatively narrow bands, as a function of (i) the nature of the substituent on the benzene ring in the azocoupling products ***5***, (ii) the nature of the solvent (protic or aprotic), and (iii) the acidity or basicity of the medium. These spectra are presented in Figure *1-4* and Table *1*. It should be mentioned that within this wavelength range and under similar conditions there are also two absorption bands, one of them observed at least as a shoulder near the main one, for various aryl-***3*** or hetaryl-pyrazolin-*5*-one azodyes. This behaviour has been attributed to the tautomerism[7b, 21] or to the simultaneous presence of the corresponding anion[20, 30, 31]. Such a second band may be distinguished too on the published spectra[17, 23, 25] of some *1*-phenyl-*3*-methyl-pyrazolin-*5*-one azodyes ***3***.

Electronic spectra recorded in absolute ethanol and methanol

Among the recorded electronic spectra of the studied compounds ***5***, the most illustrative concerning the tautomerism are those obtained in absolute ethanol or methanol (Fig. *1*A, B; *2*, *3*). For example, the absorption spectrum of *1*-(*4*-hydroxy-6-methyl-pyrimidin-*2*-yl)-*3*-methyl-*4*-(*4*-N-dimethylaminophenylazo)-pyrazolin-*5*-one [***5***: Ar = *4*-$(CH_3)_2N-C_6H_4$-] **8** exhibits three bands above *35*0 nm, quite well outlined (Fig.*1*.A, B) with molar absorptivities of the order of magnitude of 10^4. On the other hand, *4*-(phenylazo)- [***5***: Ar = C_6H_5-] ***9***, *4*-(*4*-methylphenylazo)- [***5***: Ar = *4*-$CH_3-C_6H_4$-] ***10***, *4*-(*4*-hydroxyphenylazo)- [***5***: Ar = *4*- HO- C_6H_4-] ***11***, *4*-(*4*-methoxyphenylazo)- [***5***: Ar = *4*-$CH_3O-C_6H_4$-] ***12***, *4*-(*4*-ethoxyphenyl-azo)- [***5***: Ar = *4*-$C_2H_5O-C_6H_4$-] ***13*** and *4*-(*4*-chlorophenylazo)- [***5***: Ar = *4*-$Cl-C_6H_4$-] ***14***, -*1*-(*4*-hydroxy-6-methyl-pyrimidin-*2*-yl)-*3*-methyl-pyrazolin-*5*-one respectively, exhibit in absolute methanol two bands over *35*0 nm. There are also compounds ***5*** such as *4*-(*4*-acetylaminophenylazo)- [***5***: Ar = *4*-$H_3CCONH-C_6H_4$-] ***15***, *4*-(*4*-sulphonamidophenylazo)- [***5***: Ar = *4*-$H_2N-SO_2-C_6H_4$-] ***16*** and *4*-(*4*-nitrophenylazo)- [***5***; Ar = *4*-$O_2N-C_6H_4$-] ***17***, -*1*-(*4*-hydroxy-6-methylpyrimidin-*2*-yl)-*3*-methylpyrazolin-*5*-one, respectively, presenting only one band. These data could indicate the detection of three species in the first case ***8***, two species in the second case (***9*** – ***11***) and apparently only one species in the third case (***15***-***17***). Within all these molecular species should exist the most extended delocalisation of π electrons because their absorption bands are in the visible range with molar absorptivities of 10^4 $mol^{-1c}m^{-1}$.

Spectra recorded in aprotic solvents

On the contrary, by using aprotic solvents (benzene, CCl_4, $CHCl_3$, dioxane, dimethyl-sulfoxide, anhydrous pyridine), the absorption spectra of all the dyes ***8*** – ***17*** exihibit only one band over *35*0 nm, corresponding to the longest wavelength of those in absolute ethanol or methanol for each dye (Fig. *1*, *2*, *4*; Table *1*). This behaviour can be explained by the presence of some tautomeric equilibria ***5a⇔5b⇔5c⇔5d***, the position of which depends on the nature of the substituent X as well as on the nature of the solvent. When only a band was recorded in absolute methanol (***15*** –***17***), or when aprotic solvents were used (***8*** –***17***), the equilibrium seems to be completely shifted towards one of the tautomers, namely that exhibiting the absorption band at the longest wavelength in absolute alcohol.

Table 1

UV-Vis-spectral data of some dyes ***5*** obtained by azocoupling of *1*-(*4*-hydroxy- 6-methyl-pyrimidin-*2*-yl)-*3*-methyl-pyrazolin-*5*-one ***1*** with *4*-substituted benzenediazonium salts (4-X-C_6H_4-N=N^+Cl^-)

X-; (dye)	λ_{max} [nm] (ε), in $CHCl_3$	λ_{max} [nm] (ε), in CH_3OH	$\lambda_{1\,max}$ [nm] $\overline{\nu}_1$ [cm^{-1}] in CH_3OH; HCl 0.1 M	$\lambda_2^{*}{}_{max}$ [nm] $\overline{\nu}_2$ [cm^{-1}] in CH_3OH; KOH 0.1 M	$\Delta\overline{\nu} = \overline{\nu}_1 - \overline{\nu}_2$ [cm^{-1}]	σ_p (ref. 32) for X
$(CH_3)_2N$-(**8**)	530 (30000)	530 (24800) 450 (18630) sh 400 (10350) sh	527 (19000) [**][HCl] = 2.6×10^{-4} mol	435 397 (25150)sh	-6150	-0.83
OH- (***11***)		440 (16300) 390 (13850)	450 (22200)	437 383 (26150)sh	-3950	-0.36
H_3CO- (***12***)	455 (22000)	435 (23150) 380 (20250)	448 (22300)	410 sh 382 (26200)	-3900	-0.27
H_5C_2O- (***13***)		450 (22830) 385 (20000)	452 (22150)	410 sh 385 (26000)	-3850	-0.24
H_3C- (**10**)		423 (28600) 383 sh (23175)	430 (23200)	410 sh 384 (26100)	-2900	-0.16
H_3C-CO-NH (***15***)		445 (25000)	444 (22500)	420 sh 395 (25300)	-2800	-0.09
H- (**9**)	420 (23000)	410 (19930) 380 (23900)	417 (24000)	410 sh 379 (26400)	-2400	0
Cl- (***14***)		415 sh 394 (23250)	420 (23800)	415 sh 390 (25650)	-1850	+0.23
H_2N-SO_2- (**16**)		397 (20600)	408 (24640)	418 sh (23900) 408	+740	+0.62
O_2N- (**17**)	414 (22000)	420 (41765)	416 (24000)	474 (21050)	+2950	+1.24[***]

sh = shoulder

[*] The values λ_2 and ν_2 used to calculate the $\Delta\nu$ are those underlined; they correspond to the azohydroxy tautomeric form, as such and/or as anions (see discussion). The λ_1 values correspond to hydrazonic tautomers ***5d***.

[**] For this dye was used a lower HCl concentration because at 0.1 mol the protonation of ***8*** occured and the presence of hydrazonic tautomer became negligible.

[***] Here was used the σ_p^- value[32] since the NO_2 group is through-conjugated with the chromophore system containing the deprotonated pyrazolic HO group of azohydroxy tautomer ***17b***.

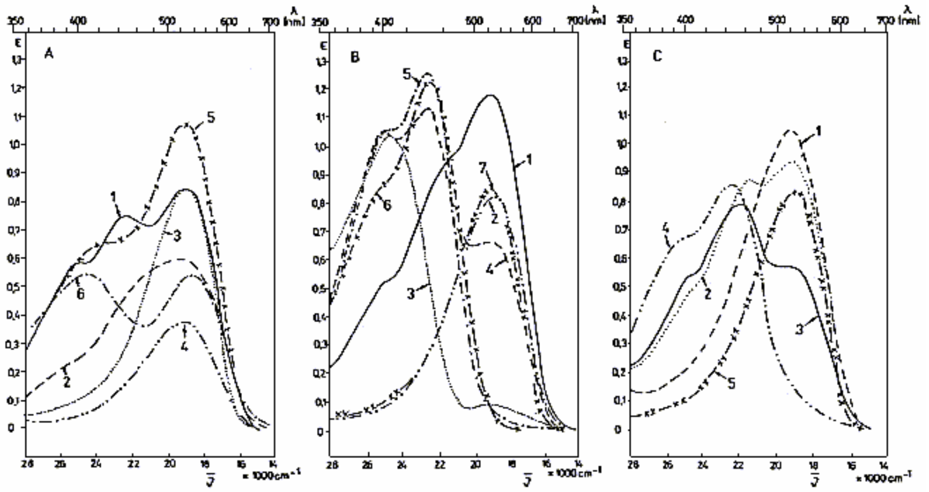
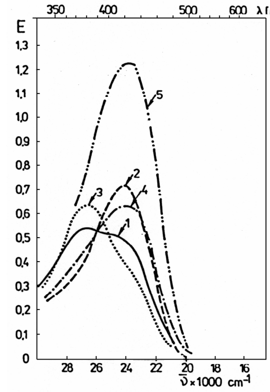


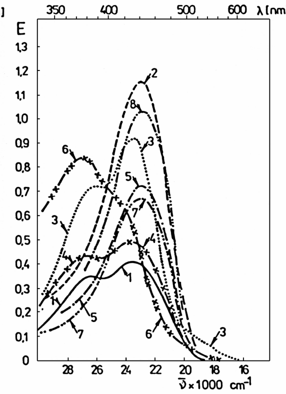
Figure 1. *The UV-VIS absorption spectra of 4-[4-(N-dimethyl)-aminophenylazo)]-1-(4-hydroxy-6-methyl-pyrimidin-2-yl)-3-methyl-pyrazolin-5-one (**8**) in the range 350-600 nm:*

A. in various solvents or solvent mixtures, *1*). Absolute ethanol; *2*). Ethanol:water (*1*:*1*); *3*). Chloroform; *4*).dimethylsulfoxide; *5*). Acetic acid *1*00%; 6). Acetic acid 96% (*4*% water);

B. in absolute methanol, methanol with hydrochloric acid or potassium hydroxide addition, and in chloroform: *1*). Absolute methanol ([***8***] = 4.36×10^{-5} mol); *2*). Methanol + HCl ([***8***] = 2.14×10^{-5} mol; [HCl] = 2.58×10^{-4} mol); *3*). Methanol + HCl ([**8**] 4.59×10^{-5} mol; [HCl] = 10^{-1} mol); *4*). Methanol + KOH ([***8***] = 4.29×10^{-5} mol; [KOH] = 6.62×10^{-5} mol); *5*). Methanol + KOH ([8] = 4.59×10^{-5} mol; [KOH] = 10^{-1} mol); 6). Methanol + KOH ([***8***] = 4.3×10^{-5} mol); [KOH] = *1*.8 mol); 7). Chloroform ([***8***] = 2.82×10^{-5} mol);

C. in anhydrous pyridine; pyridine with water addition and chloroform: *1*). Anhydrous pyridine; *2*). Pyridine: water (99.*5*:0.*5*); *3*). Pyridine: water (98.*5*:*1*.*5*) *4*). Pyridine: water (*1*:99); *5*). Chloroform.





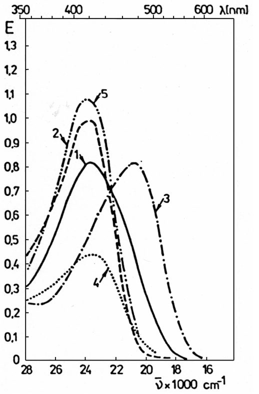


Figure *2*. Visible spectra of dye ***9*** in: *1*). Absolute methanol; *2*). Methanol + HCl ([HCl] = 0.*1* mol); *3*). Methanol + KOH ([KOH] = 0.*1* mol); *4*). Dimethylsulfoxide; *5*). Chloroform.

Figure 3. Visible spectra of dyes ***11***, ***12***: *1*). ***11*** in absolute methanol; *2*). ***11*** in methanol + HCl ([HCl] = 0.*1* mol); *3*). ***11*** in methanol + KOH ([KOH] = 0.*1* mol); *4*). ***12*** in methanol; *5*). ***12*** in methanol + HCl ([HCl] = 0.*1* mol); 6). ***12*** in methanol + KOH ([KOH] = 0.*1* mol); 7). ***11*** in glacial acetic acid; 8). ***12*** in glacial acetic acid.

Figure 4. Visible spectra of dye ***17*** in: *1*). Absolute methanol; *2*). Methanol + HCl ([HCl] = 0.*1* mol); *3*). Methanol + KOH ([KOH] = 0.*1*molM); *4*). Dimethylsulfoxide; *5*). Chloroform.

Effect of the acidification on the electronic spectra and the assignement of the longest wavelength band

The additional proofs for the existence of such equilibria comes from the effect of the addition of HCl or KOH on the spectrum of each dye ***8 –17*** in absolute methanol. Thus, the solution of ***8*** (2.1×10^{-5} mol), exhibiting three bands in absolute methanol, changes the shape of the spectrum (Fig.*1*.B) after acidification with HCl up to 2.6×10^{-4} mol. It presents now only one more intense band in the visible range with the maximum located at *53*0 nm, corresponding to the one at the longest wavelength in absolute methanol; it is similar to the absorption spectrum recorded in aprotic solvents. This behaviour is compatible with the presence of three tautomeric forms in comparable concentration in absolute methanol; by adding a small amount of HCl, the equilibria are shifted towards the form favoured in weak acidic medium.

A similar change occurs in the case of those dyes ***9*** –***14*** exhibiting two absorption bands over *35*0 nm in absolute methanol. Upon acidification with HCl (~0.*1* mol) only one band appears located at the longest wavelength as compared to the neutral solution. This band corresponds also to the visible band in aprotic solvents or in glacial acetic acid. (Fig. 2, 3). Therefore, the dyes ***9*** –***14*** behave similarly to ***8***, although only two tautomeric forms are present in significant concentration in absolute methanol. In the acidic solution the tautomeric equilibrium is shifted again towards the form favoured in acidic media.

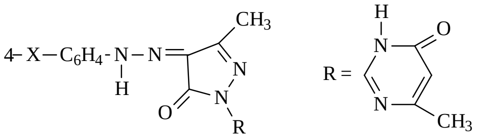
In the case of other hydroxyazoic dyes, including *4*-arylazo-*1*-phenyl-*3*-methyl-pyrazolin-*5*-ones ***3*** it is known[7b, 21b, 31, 33-40] that the favoured form in acidic media is the hydrazonic one ***3d***. Thus, we appreciate that the band located at the longest wavelength in the spectra of dyes ***8 –17*** recorded in absolute ethanol or methanol, is caused by the hydrazonic tautomeric form ***5d***. It was detected in the solutions with aprotic solvents as the only form, all equilibria being shifted towards it. This assesment is also in accord with the detection[9, 13, 14, 20, 22, 25, 27, 31] of only the hydrazonic form ***3d*** in aprotic solvents, especially in $CHCl_3$, for the analogue dyes ***3***.

NMR-proofs for hydrazonic structure 5d of the only form detected in aprotic solvents

The hydrazonic structure ***5d*** in aprotic solvents is also supported by ^{1}H- and ^{13}C-NMR spectra recorded in $CDCl_3$ and $(CD_3)_2SO$. The ^{1}H-NMR spectra of ***5*** exhibit a singlet corresponding to a mobile hydrogen atom at *13*-*14* ppm (Table *2*). In the case of the analogues ***3*** this signal is considered[9, 13, 14, 23] as being characteristic for the hydrazonic (N-H) proton.

Table *2*

^{1}H-Chemical shift of N-H group in hydrazono tautomer ***5d*** of the dyes ***5*** in $CDCl_3$[*].



X	$(CH_3)_2N$	OC_2H_5	OCH_3	CH_3 or H	Br	NO_2 or Cl	$COOCH_3$
δ (ppm)	*13.5*0	*13.35*	*13.31*	*13.21*	*13.18*	*13.17*	*13.15*

A NOESY experiment with the dyes ***10*** and ***12*** (Fig.*5*) is showing a spatial close proximity of the hydrogen atom causing the signal at *13-14* ppm with the hydrogen atoms of benzene ring in *ortho* position with respect to the two nitrogen atoms bridge between the rings. Such a disposition takes place only with tautomeric forms ***5b*** and ***5d*** where the mobile hydrogen atom may be involved in an intramolecular hydrogen bonding.

Since for the hydroxyazoic tautomers ***3b*** of the dyes ***3***, there have not been provided[39, 41, 42] any intense absorption bands above *4*00 nm, the same is to be expected for the analogues ***5***. Therefore, for the dyes ***5*** in aprotic solvents, presenting an intense absorption band over *4*00 nm, the only compatible structure should be the hydrazonic one ***5d***. This structure can form the above mentioned intramolecular hydrogen bonding. It is worth mentioning that for the dyes having hydroxyazo-ketohydrazonic tautomeric equilibrium, the ketohydrazonic form exhibits intense absorption bands at the longest wavelength[7b, 21b, 28, 33-39, 41, 43]. The hydrazonic structure ***5d*** for the only form detected in aprotic solvents is also compatible with ^{13}C-NMR spectra. The ^{13}C- chemical shifts of similar carbon atoms from the coresponding hydrazonic tautomers ***5d***, studied here, and ***3d*** of the analogue[13, 14, 22] dyes ***3*** are practically the same, as presented in Table *3*.

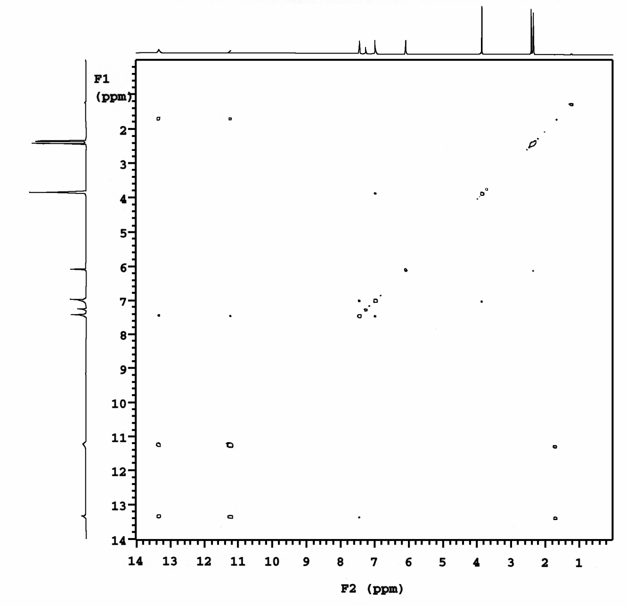


Figure 5. NOESY Spectrum of dye ***12***.

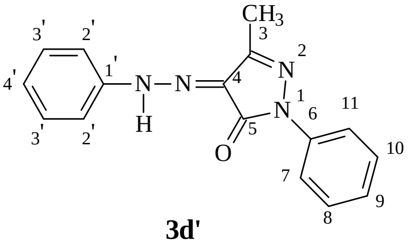
Tautomeric equilibria coupled with protonation equilibria

An additional support for the hydrazonic structure ***8d***, which displays an absorption band at the longest wavelength (*53*0 nm) and for the hydroxyazo structure ***8b***, exhibiting an absorption band at the shortest wavelength above *35*0 nm, comes from the spectra recorded in methanolic solution containing more concentrated acid (up to 0.*1* mol HCl).

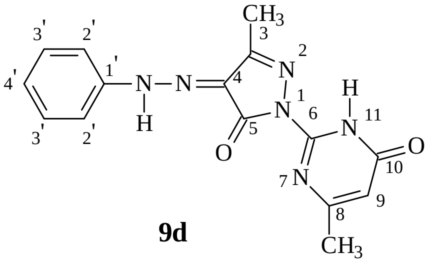
Upon acidification (up to 0.1 mol HCl) of methanolic solution of ***8*** carring a dimethylamino group on benzene ring (5.0 × 10^{-5} mol) another change of the spectrum occurs. The initial spectrum in absolute methanol exhibiting three bands in the visible, changes into one with a single intense band (see Fig.1B, curves 1, 3) located at about 400 nm. It corresponds to the shortest wavelength visible band in neutral methanolic solution. Under the acidic conditions, the protonation of the dye molecule is likely to occur[4, 25]. The protonation causes a large hypsochromic shift of the longest wavelength band (around 130 nm). This is in agreement with a major change of chromophore system of ***8***, from the hydrazono ***8d*** to the hydroxyazo ***8b*** structure. Because the protonation of nitrogen atoms in azo group causes a bathochromic shift of the absorption maximum[4], the protonation should take place either at the pyridinic nitrogen atoms of the heterocycles[25] [***18***; Ar = $(CH_3)_2N$-C_6H_4-] **19**, [***20***; Ar = $(CH_3)_2N$-C_6H_4-] ***21*** or at the $(CH_3)_2N$- group.

Table 3

^{13}C-Chemical shifts-δ_C (ppm) of 3-methyl-1-phenyl-4-phenylhydrazono-pyrazolin-5-one ***3d'***, its 1-(4-hydroxy-6-methyl-pyrimidin-2-yl)-ic ***9d*** analogue, and the 4'-CH_3 derivative of latter ***10d*** in $CDCl_3$. The underlined values are for similar positions and therefore compared.



3d'



9d

Position of ^{13}C	Compound			
	3d (ref. 13, 22)	***9d***	***10d***	***10d***$^+$
3	148.4	146.6	146.8	
4	128.4	125.8	125.5	
5	157.7	159.0	159.4	
6	138.0	161.3	161.4	
7	118.4	-	-	
8	128.8	152.5	152.5	
9	125.0	109.5	109.7	
10	128.8	165.8	165.9	
11	118.4	-	-	
1'	141.1	140.4	138.1	137.5
2'	115.7	116.7	116.8	116.6
3'	129.6	129.9	130.7	130.6
4'	125.7	127.5	138.2	136.8
CH_3 of 3-position	11.7	12.1	12.2	
CH_3 of 8-position	-	24.6	24.7	
CH_3 of 4'-position	-	-	21.4	

$^+$ *Calculated from values of **9d** with increments of the CH_3-substituent in the 4'-position[49].*

These protonated groups of azo form ***8b*** cannot be involved in the conjugation with the azoic chromophore. Therefore, the longest wavelength absorption band of ***8b*** and its protonated form, recorded around 400 nm respectively, should be close together. Consequently, the absorption band located at 400 nm should be attributed to the hydroxyazoic form ***8b***.

On the other hand, the protonated form of ***8*** should be in equilibrium with the most stable not protonated species of ***8*** present in neutral or weak acidic media. As we have show above, the stable unprotonated species of ***8*** is the hydrazonic tautomer ***8d***, with the absorption maximum at 530 nm. A weak band at 530 nm still exists, in the spectra of ***8*** in acidic (0.1 mol HCl) methanol (Fig.1B curve 3) along with the main band located at 400 nm and attributed to protonated form. It proves the involvement of the assumed equilibrium and, therefore, supports the assignement of the maximum at 530 nm to the hydrazonic tautomer ***8d***. The same equilibrium between protonated azoform (***19, 21***) and hydrazonic tautomer ***8d*** is also evident in the spectra in acetic acid (Fig.1A, curves 5, 6).

Effect of KOH or water addition on the electronic spectra of the dyes 8-10, 12-14

For the dyes ***8-10, 12-14***, having a substituent X without mobile hydrogen, either electron-donating or weak electron-withdrawing, the hydrazonic structure, ***8d-10d, 12d-14d*** of the tautomer corresponding to the longest wavelength band in the visible spectra, is supported by the effect caused by addition of potassium hydroxide to their methanolic solutions. A small addition of potasium hydroxide diminishes and a consistent addition suppresses completely the absorption band at the longest wavelength, accompanied by an increasing of the intensity of the other two (Fig. 1B) or the other one (Fig. 2, 3) at shorter wavelength. Such an effect could be expected in the case of azo-hydrazono tautomeric equilibrium ***5b⇔5d*** because the alkaline medium favours the azo tautomer and diminishes the concentration of hydrazono tautomer[21b, 30, 36a, 37, 38, 40]. The above presented effect of alkalis addition proves at the same time the azoic structure ***8b-14b*** of the tautomer exhibiting the shortest wavelength absorption band on the spectra above 350 nm of the dyes ***8-14*** in absolute methanol. This effect is very illustrative with the dye ***8***. The addition of KOH up to a concentration of 6.6×10^{-5} mol to the solution in absolute methanol of ***8*** (4.3×10^{-5} mol) brings about an increase of the intensity of the two absorption bands under 500 nm and diminishes the intensity of the absorption band, located at the longest wavelength. The addition of KOH up to 0.1 mol had the result of suppressing the band located at 530 nm in absolute methanol. A similar effect on the shape of the spectra is caused by the addition of twice distilled water to the solution of ***8*** in anhydrous pyridine. The visible spectrum in anhydrous pyridine exhibits only one absorbtion band at 530 nm, given by the hydrazonic tautomer ***8d***. When the water concentration of the pyridine solution reaches 1.5% a spectrum containing three absorption bands was recorded. Higher concentration of water brought about the suppression of the 530 nm band (Fig. 1C). Similar changes of the spectra were observed by water addition to absolute ethanol, glacial acetic acid (Fig. 1A), dimethylsulfoxide or dioxane solution of ***8***, but the modifications were not so significant as compared to those observed in pyridine solution. This behaviour evidentiates however the involvement of hydrogen bonding in determining the stability of various tautomeric forms (see[20, 34, 38]). The effects caused by KOH or water addition to solutions of ***8*** are in agreement with the assumed equilibria ***8b⇔8c⇔ 8d***. The addition shifted the equilibrium towards the azohydroxy form ***8b*** and/or azoiminic form ***8c***. Such equilibria have been ascertained in the case of other azohydroxy dyes[7b, 21b, 15, 38, 40, 44], including the ones of *4*-arylazo-*5*-hydroxypyrazole dyes ***3b***.

Assignement of the shortest wavelength band at the dyes 8-14

On the basis of previously described phenomena when either HCl, KOH or water was added to the dye solutions, as well as taking in account that hydroxyazoic tautomers absorb light at shorter wavelength[33, 34, 36-38, 43] as compared to hydrazonic ***3d*** or azoketoiminic ***3c*** tautomers[++], we consider that the absorption band at the shortest wavelength in the range *35*0-600 nm of alcoholic or pyridine-aqueous solutions of *1*-(pyrimidinyl)-*5*-pyrazolone dyes ***8**-**16*** (Fig.*1*-*3*) is due to the hydroxyazoic tautomer ***8b**-**16b***. An additional support for this assignement is the fact that when the basicity of the solution is quite high (*2* mol KOH), the intensity of the absorption band of ***8*** located around *4*00 nm is decreased and the one located at *45*0 nm is increased in intensity. Because among the tautomeric forms of *4*-arylazo-*5*-pyrazolone dyes ***3***, the form ***3b*** is the strongest acid[44], we expect the same to be true with *4*-arylazo-*1*-pyrimidinyl-*5*-pyrazolone dyes ***5***. Therefore the moreover addition of KOH will neutralize more azohydroxy form ***5b***. The effect can be interpreted more comprehensibly on the basis of tautomeric and coupled acid-base equilibria (Scheme *1*). Indeed, Scheme *1*, clearly points out to the connection between the tautomeric and acid-base equilibria.

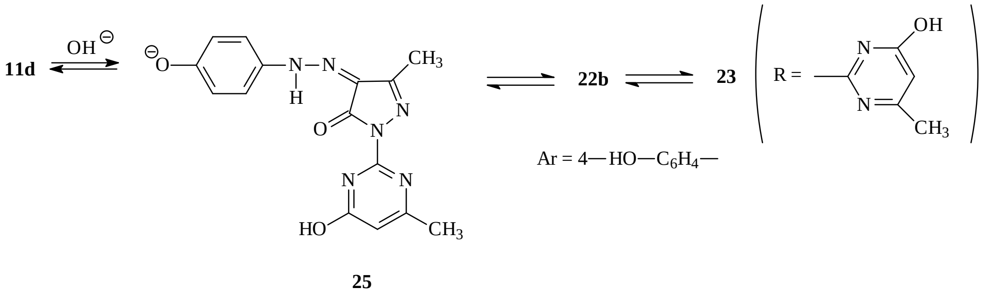
Tautomeric equilibria coupled with deprotonation equilibria

Since the measurements of pKa in the case of *1*-(*4*-hydroxy-6-methyl-pyrimidin-*2*-yl)-*3*-methyl-pyrazolin-*5*-one ***1*** have shown that the first step acid dissociation corresponds to *4*-hydroxy-6-methylpyrimidinic moiety[11], it seems likely that in alkaline media deprotonation of the dyes ***8**-**14*** should involve also the pyrimidine moiety of azohydroxylic forms ***8b**-**14b*** with the formation of ***22b*** species. Because the substituent in position *1* of pyrazolonic moiety does not exert any influence within the chromophore system[17, 28], the absorption band of hydroxyazoic tautomer ***8b**-**14b*** should not be modified by the first deprotonation of pyrimidinic moiety ***22b***. Therefore the absorption band located at the shortest wavelength in the range *35*0-600 nm in alcoholic, alkaline-alcoholic or pyridine-aqueous solutions, can be attributed to the azohydroxy tautomer ***8b**-**14b*** and for the anion ***22b***. A large excess of KOH can bring about a two-fold deprotonation, both in the pyrazole and in the pyrimidine moieties. The absorption band of ***8*** located at *45*0 nm, which is rising in intensity upon addition of more KOH (up to *2* mol) (Fig. *1*B) could correspond to a doubly deprotonated species of **8**. The less evident modification of the absorption band of ***8*** around *45*0 nm upon addition of large amount of KOH solution could be explain by the fact that this maximum may also correspond to the absorption of the azoketoiminic isomer ***8c***. This last assignement is compatible with the intermediary position of the absorption band of the azoiminic tautomer between those of the corresponding hydroxyazo- and hydrazono- form[43].

[++] only as a supposition[21, 39, 41] in the case of 4-arylazo-1-phenyl-5-pyrazolones ***3***.

On the other hand in the case of dyes ***5*** having strong electron-withdrawing substituent X, especially for X = $-NO_2$ (***17***) or with substituent possessing mobile hydrogen (X = -OH) (***11***), the addition of KOH causes other effects than those discussed with dyes ***8-10, 12-14***, having electron-donating or weak electron-withdrawing substituents. Thus, a concentration of 0.*1* mol KOH in a methanol solution of ***17*** brings about a bathochromic shift of about 60 nm (Fig. *4*). This quite large shift can be explained by the strong acidifiying effect of the nitro group[30, 31]. Because of this effect the first dissociated proton comes from the pyrazolic hydroxyl group (***23***; Ar = $4-O_2N-C_6H_4-$, R = *4*-hydroxy-6-methyl-pyrimid-*2*-yl) of the hydroxy- azo tautomer ***17b***, and not from pyrimidine moiety (***22b***; Ar = $4-O_2N-C_6H_4-$). Consequently in this particular case (***17***) in alkaline media the azochromophore system has a strong donor ($-O^-$) and acceptor (O_2N-) of electrons at the ends (***23***; Ar = $4-O_2N-C_6H_4-$). Within this system the conjugation is much more intense as compared with the starting one (***17b***). As it is known[45], the intensification of conjugation within azodyes leads to a bathochromic shift. A similar effect, by increasing the KOH concentration, up to 0.*1* mol has been observed[17] with the analogous *3*-methyl-*1*-phenylpyrazolin-*5*-one dye (***3b***; Ar = $4-O_2N-C_6H_4-$) when the acid dissociation may involve only the proton of pyrazolic –OH (***24***; Ar = $4-O_2N-C_6H_4-$).

In exchange, when KOH is brought up to 0.*1* mol in the methanolic solution of ***11***, it causes the appearance of a supplimentary absorption band, not well defined, but as a shoulder, located at *52*0 nm, and a spectrum with three bands is apparent (Fig. *3*). It is very similar to the spectrum of ***8*** in neutral or weak alkaline alcoholic solutions (Fig. *1*B, curve *4*), as well as to the one in pyridine-aqueous (*1.5*% water) solution (Fig. *1*C, curve *3*). The resemblance of these spectra indicates the similitude of the most extended π-delocalized electron systems. The weak absorption at *52*0 nm of the dye ***11*** in alkaline alcoholic solution coresponds to that at *53*0 nm attributed to the hydrazonic tautomer ***8d***. A delocalized π electron system chromophore very similar to that of ***8d*** appears in the anion ***25***, formed from phenolic hydroxyl group of hydrazonic tautomer ***11d***. That is why we suppose that the weak absorption at *52*0 nm in 0.*1* mol KOH alcoholic solution of ***11*** is due to its anion ***25***. The involvement of tautomeric and acid-base equilibria shown in Scheme *1* and *2* requires the presence of the anion ***25*** in a small concentration along with other more favoured anions formed by ionisation of pyrimidinic moiety ***22b*** or pyrazolic moiety ***23***.



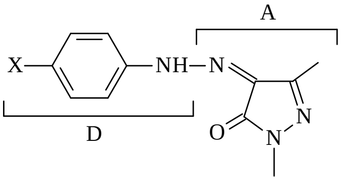
Scheme *2*

On the other hand the analogy between the chromophore system of ***11*** and that of ***12*** should determine similar electronic spectra. This was confirmed with methanol, acidic methanol and glacial acetic acid solution (Fig. *3*). However when alkaline methanol solutions were used (0.*1* mol KOH) the absorption spectra were quite different. This difference can be explained only by the acid dissociation of ***11*** at phenolic hydroxyl, a phenomenon which is not possible with ***12***, and demonstrates the involvement of the anion ***25***.

Hammett correlations

An attempt has been made to test some Hammett correlations by using the position of the bands over *35*0 nm (in cm^{-1}) for hydrazonic or the hydroxyazoic tautomers. Each category gave linear relationships[6] with different slopes, depending on the electron-donating or electron-withdrawing nature of the X substituent on the arylic moiety. Moreover, the position of the absorption bands remained independent on the substituent constant σ_p for the electron-withdrawing substituents in the case of the hydrazonic tautomers ***8d-17d***, or for the electron-donating substituents in the case of hydroxyazoic tautomers ***8d-17d*** or their anions, respectively (Table *1*).

Such a behaviour has been described previously[46] as being characteristic for the absorption bands due to charge-transfer or donor-acceptor chromophores. This behaviour has been recommended[20] as a criterion to differentiate between hydrazonic and hydroxyazoic nature of the chromophore. According to this criterion in the hydrazono derivatives ***8d-17d***, which have charge-transfer chromophore ***26***, the electron-withdrawing substituents X should determine a relatively constant position of the absorption band in the visible range. The electron-donating substituents should determine a shift of the absorption band towards the longer wavelength as the negative value of Hammett substituent constant σ_p is increased. On the contrary, for azoderivatives ***8d-17b*** (as such or as anions ***22b***) the charge-transfer chromophore ***27*** should involve an invariant position of absorption bands in visible for the electron-donating substituents, and a bathochromic shift directly proportional to the σ_p value for the electron-withdrawing substituents.



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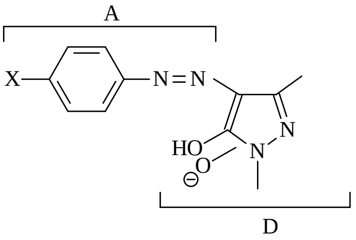


27

The experimental data (Table *1*) confirm also, on the basis of this criterion, the hydrazonic nature of the tautomer, which corresponds to the longest wavelength band in absolute alcohol or weak acid alcoholic solution, as well as in aprotic solvents. Alike was confirmed the hydroxyazostructure (as it is ***8d-17b*** or as the anion ***22b***, ***23***) for the species presenting the absorption band at the shortest wavelength over *35*0 nm, for the dyes ***8***-***15***, or of the longest wavelength for the dyes ***16, 17***, in basic solutions (Table *1*).

For species involved in equilibria, as attributed to dyes ***5***, better Hammett correlation were obtained[17, 37, 46] by using the difference $\Delta\bar{\nu}$ between the wavenumber of the absorption maxima as compared to the correlations given by the maxima position themselves. Such a correlation was also found with the difference $\Delta\bar{\nu}$ for hydrazonic tautomers ***8d-17d*** and hydroxyazoic (as ***8d-17b*** and/or their anions ***22b***, ***23***) ones (Fig. 6).

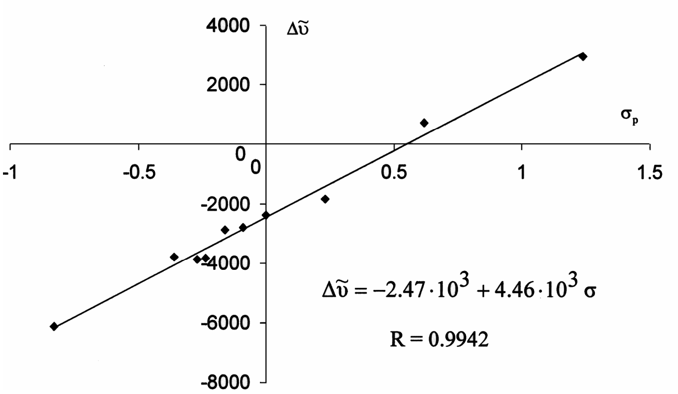


Figure 6 Hammett plot of $\Delta\bar{\nu}$ *versus* substituent constant σ_p.

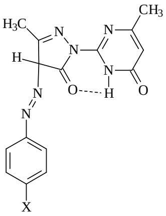
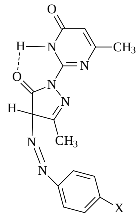
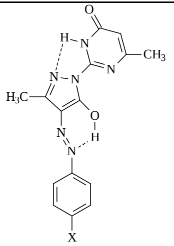
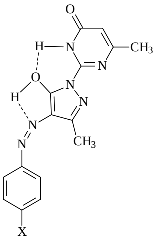
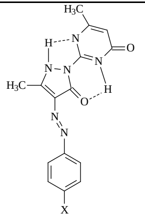
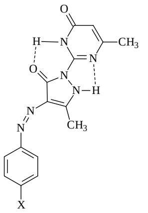
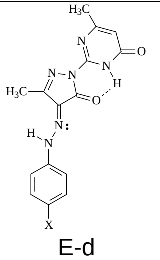
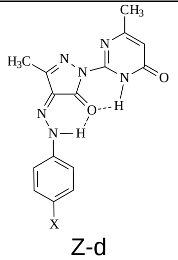
The good correlation coefficient (r = 0.995) sustained the involvement of the equilibrium between the mentioned species.

Quanto-mechanical calculation of the relative stability of the possible tautomers

Our measurements did not detect the azoketomethylenic form ***5a***. However, this form should be involved, at least as an intermediate ("σ" complex at electrophilic aromatic substitution[4]) according to the mechanism of dyes ***5*** formation, by azocoupling of diazonium salts ***4*** with mesomeric anion ***6*** of *1*-pyrimidinyl-pyrazolin-*5*-ones[6, 8, 11]. The intermediate can undergo changes to other tautomeric forms ***5b, 5c, 5d*** by deprotonation yielding the mesomeric anion ***23***, which can be reprotonated (see[47]). These changes involve otherwise *1*,*3*-shifts forbidden by symmetry as suprafacial concerted processes (see Part II of this series) and they depend upon the stability of the involved species. The latter can be estimated by the enthalpy of formation. As shown by calculations carried out by means of AM_1-SM_2 method[48] the azoketomethylenic intermediates ***8a, 10a, 12a*** rank in the third place as far as the stability is concerned (see Table *4*). However, their involvement cannot be detected by electronic spectroscopy as it has been done with the other three (***8b, 8c, 8d***), or two (***9b, 9d-13b, 1 3d***) type of tautomers in absolute alcohol, because the azoketomethylenic tautomers ***8a-13a*** should have weak absorptions in visible range[41] and they are expected to be masked by the overlapping with stronger absorptions of other tautomers. On the other hand, the stability estimated by the formation enthalpy for the tautomers of ***8***, detected in absolute alcohol, correlates itself qualitatively with the intensity of the absorption bands attributed to each of the tautomers (***8b***<***8c***< ***8d***) (Fig. *1*A, curve *1*). Thus the quanto-mechanic calculations agree with the tautomeric forms considered here.

Table *4*

The lowest formation enthalpies (kcal/mol) for conformations of E- and Z- configurations of possible tautomers in the case of dyes **8**, ***10*** and ***12*** calculated by AM_1-SM_2 method.

Tautomers of the E-isomers	X; compound: $(CH_3)_2N$; CH_3; CH_3-O **8** ***10*** ***12***	Tautomers of the Z-isomers	X; compound: $(CH_3)_2N$; CH_3; CH_3-O **8** ***10*** ***12***
 E-a	92.67 81.16 48.54	 Z-a	92.30• 78.79 46.79
 E-b	98.76 85.38 53.22	 Z-b	96.72 83.39 51.27
 E-c	94.47 81.1 48.93	 Z-c	91.09 77.65 45.77
 E-d	95.79 81.39 50.20	 Z-d	90.87 76.96 45.26

• It is interesting that always the lowest values of formation enthalpies correspond to Z-configurations. Consequently the tautomers should exist in these configurations. Therefore, the values to be compared for the estimation of tautomer stabilities of dye ***8*** are those underlined.

CONCLUSION

The spectrophotometrical measurements in visible range, (^{1}H, ^{13}C)-NMR spectroscopy, Hammett correlation of $\overline{\nu}$ or $\Delta\overline{\nu}$ as a function of σ_p, the quantic calculations as well as the mechanistic considerations for the formation of the dyes ***5*** proved the involvement of various tautomers. The tautomeric equilibria are coupled with acid-base equilibria. Such assumptions provide coherent explanations of all experimental data. Our data clearly show the similitude between commercial dyes ***3*** and those investigated by us ***5***. Thus, some dyes ***3*** also exhibit two absorption bands in visible that are influenced by the addition of acid or base in the same manner as the one observed for ***5***.

For the two types of dyes ***3*** and ***5*** there are also other similarities concerning:

- ^{1}H, ^{13}C-NMR data for common moieties
- Hammett correlations
- The stability order of tautomers ascertained by quantic calculations.

All these analogies of dyes ***3*** and ***5*** support the existence of tautomeric equilibria also in the case of ***3***. Therefore, to define the appropriate structure of dyes ***3*** or ***5***, one should take into consideration all the tautomeric forms. Their concentrations depend upon the actual conditions (solid state or solution, protic or aprotic solvents, pH, metal complexes, the substrate for the dyes). Sometimes the dyes can exist (solid state) or are detected (solution in $CHCl_3$) in only one form.

EXPERIMENTAL

The synthesis and purification of the dyes ***5*** were accomplished as previously described[5-7, 21b]. Analytical grade reagents and solvents, provided by Reactivul (Bucharest, Romania), Merck (Darmstadt, Germany), UCB (Bruxelles, Belgium) and Fluka (Buchs, Switzerland), were used without further purification. Each solution was prepared in the corresponding solvent and diluted to the requested concentration, or directly to the concentration needed for spectral measurements (10^{-5} M). An UV-VIS Spectrophotometer (Zeiss-Jena) was employed.

NMR (^{1}H- and ^{13}C-) spectra were obtained in $CDCl_3$ and CD_3-$SOCD_3$ at room temperature by means of a Varian Gemini 300 (300 MHz) and INOVA 500 (500 MHz) spectrometer. The assignments of chemical shifts for ^{13}C-NMR- spectrum of ***9*** were verified by means of the substituent increments[49] calculations for ***8***, ***10*** and ***12***. The calculated ^{13}C- chemical shifts for dyes ***9*** substituted in 4'-position with CH_3-, CH_3O- or $(CH_3)_2N$- were practically identical to the experimental values (Table 3).

Full geometry optimisation for all conformations of E- and Z- configurations of tautomers ***5a***-***5d*** of dyes ***8***, ***10***, ***12*** have been carried out by means of the semiempirical AM_1-SM_2 method[48] as implemented in PC-Spartan 1.0 package of program[50].

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