New Azo Compounds Derived from 1*H*-5-amino-4-ethoxycarbonyl-3-methyl-pyrazole and 3-mono- or 1,3-disubstituted pyrazol-5-ones

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The coupling reaction between 1H-4-ethoxycarbonyl-3-methyl-pyrazol-5-yl-diazonium chloride and 3-mono- and 1,3-disubstituted pyrazol-5-ones leads to the corresponding pyrazol-5-yl-azo-pyrazol-5-ones, characterized through MS, IR, UV-VIS, ^{1}H-NMR and ^{13}C-NMR spectroscopy.

Keywords: azo compounds, 1H-4-ethoxycarbonyl-3-methyl-pyrazol-5-yl-diazonium chloride, 1H-4-(4-ethoxycarbonyl-3-methyl-pyrazol-5-yl)-azo-pyrazol-5-ones

The literature presents a large number of azo dyes derived from pyrazoles or pyrazolones, but the number of azo dyes derived from 3(5)-amino-pyrazoles and pyrazoles or pyrazolones is low, probably due, in part, to the lower availability of the starting materials.

They are used as ingredients of inks and toners [1-6], while some possess antimicrobial and antifungal activity [7,8]. Their synthesis is achieved by the diazotation of 3(5)-amino-pyrazoles, followed by coupling [1-6,9,10] or by other synthetic methods [11].

The aim of our work is the synthesis of some novel 1*H*-4-(4-ethoxycarbonyl-3-methyl-pyrazol-5-yl)-azo-pyrazol-5-ones (**4**), besides those previously obtained [12], by coupling 1*H*-4-ethoxycarbonyl-3-methyl-pyrazol-5-yl-diazonium chloride (**2**) with 3-mono- and , 3-disubstituted pyrazol-5-ones (**3**), azo dyes with cation complexing potential or intermediates in the synthesis of new polycondensed heterocyles, being a continuation of our previous works [13,14].

Experimental part

Materials and methods

The employed reagents were commercial products (Merck, Fluka) used as received, and the pyrazole derivatives were prepared according to the literature: 1*H*-5-amino-4-ethoxycarbonyl-3-methyl-pyrazole (**1**) [15],1,2-dihydro-5-methyl-pyrazolin-3-one (**3a**) [16], 1,2-dihydro-5-phenyl-pyrazolin-3-one (**3b**) [17], ethyl ester of 1*H*-2,5-dihydro-5-oxo-pyrazol-3-carboxylic acid (**3c**) [18], 1,2-dihydro-5-methyl-2-phenyl-pyrazol-3-one (**3d**) [19], 1,2-dihydro-2,5-diphenyl-pyrazol-3-one (**3e**) [20], 5-anilino-1,2-dihydro-2-phenyl-pyrazol-3-one (**3f**) [21], 1*H*-2,5-dihydro-5-oxo-1-(4-sulphophenyl)-pyrazol-3-carboxylic acid (**3g**) [22].

The melting points were determined on a Böetius PHMK (Veb Analytik Dresden) instrument, and thin-layer chromatography was performed on silica plates $60F_{254}$ Merck using benzene:methanol 7:3 (vol) as eluant.

Mass spectra ESI-MS were recorded on a Varian 320-MS TQ Mass Spectrometer, using as mobile phase water/acetonitrile/acetic acid 10/90/0,1.

The IR spectra were recorded in KBr pellet on a Jasco FT/IR-410 spectrophotometer, and the electronic spectra in the visible domain were recorded in methanolic solutions on a Jasco V-530 UV/VIS spectrophotometer. The ^{1}H- and ^{13}C-NMR spectra were recorded on a Bruker Avance AC200 spectrometer and a Brucker Avance3 spectrometer, respectively, at 25°C in DMSO-d_6, using TMS as reference, the chemical shifts being reported in ppm, and the coupling constants in Hz.

*Preparation of 1H-4-ethoxycarbonyl-3-methyl-pyrazol-5-yl-diazonium chloride (**2**)*

A mixture of 0.85g (5 mmol) 1*H*-5-amino-4-ethoxycarbonyl-3-methyl-pyrazole (**1**), 1,1 mL water and 1.5 mL concd. HCl is heated to about 40°C, filtered on charcoal and the solution thus obtained is cooled to 0-5°C. To the fine suspension formed is added dropwise, over approximately 15 min, a solution containing 0.36g (6 mmol) $NaNO_2$ in 1.4 mL water. The solution of diazonium salt (**2**) thus obtained is discolored with charcoal and filtered cold, and immediately used in the coupling step.

*Coupling of 1H-4-ethoxycarbonyl-3-methyl-pyrazol-5-yl-diazonium chloride (**2**) with 3-mono- and -1,3-disubstituted 1H-5-pyrazolones (**3**)*

To a solution obtained by mixing a solution of 0.02 moles 5-pyrazolone (**3**) in 40 mL ethanol with a solution obtained

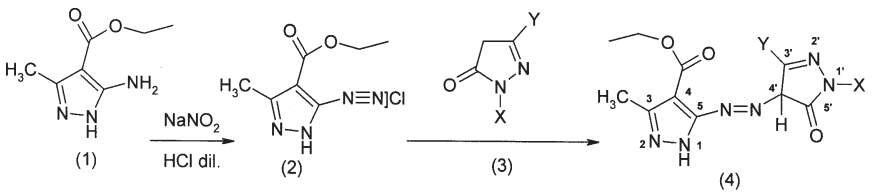

Fig. 1. Coupling of 1*H*-4-ethoxycarbonyl-3-methyl-pyrazol-5-yl-diazonium chloride (**2**) with 3-mono- and 1,3-disubstituted pyrazol-5-ones (**3**)

X=H, Y= -CH_3 (a)[12]; X= H, Y= -C_6H_5 (b); X=H, Y= -$COOC_2H_5$ (c)[12]; X= -C_6H_5 ,X= -CH_3 (d)

X=Y= -C_6H_5 (e); X= -C_6H_5 , Y= -NH-C_6H_5 (f); X=4-HO_3S-C_6H_4- , Y= -COOH (g)[12]

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from 0.0062 moles NaOH and 0,02 moles CH_3COONa in 40 mL water is added dropwise, under stirring, at 0-5°C, the solution of diazonium salt (**2**) freshly prepared from 0.02 moles 1*H*-5-amino-4-ethoxycarbonyl-3-methyl-pyrazole hydrochloride (**1**) and is perfected for half an hour. The colored suspension is diluted with water and acidified with HCl to *p*H 1-1.5. After filtration and drying, the products are recrystallized from absolute ethyl alcohol.

*1H-4-(1H-4-ethoxycarbonyl-3-methyl-pyrazol-5-yl)-azo-3-methyl-5-pyrazolone (**4a**)* [12]

Yellow powder, m.p. 294-298°C; yield 79%.

ESI-MS (M/z): 279 (M+1) (1.5 torr), 278 (M) (1,6 torr)

UV-VIS λ max [nm] (ε x 10^{-4}): 216 (1,01), 350 (11,3), 401 (1,08)

IR (KBr): 442s, 546s, 587m, 605s, 687m, 709m, 759i, 779m, 832m, 862m, 885m, 973m, 1019m, 1042m, 1103i, 1153i, 1205i, 1280i, 1370m, 1438m, 1544i, 1588m, 1671i, 1714i, 1932s, 1963s, 2904m, 2935m, 2986m, 3080m, 3187m.

^{1}H-NMR δ_H (DMSO-d_6, 200 MHz): 4.30 (q, 2H, J = 7.0Hz, -O-CH_2CH_3), 2,43 (s, 3H, 3-C- CH_3), 2,14 (s, 3H, 5-C-CH_3), 1.35 (t, 3H, J = 7,0Hz, -O-CH_2CH_3)

^{13}C-NMR δ_C (DMSO-d_6, 50 MHz): 162.7 (C=O), 159.9 (2'-C), 149.8 (5-C), 146.7 (3-C), 145.1 (1'-C), 130.0 (1'-C), 97.6 (4-C), 59.6 (-O-CH_2CH_3), 14.2 (-O-CH_2CH_3), 11.7 (-O-CH_2CH_3), 11.4 (5'-C-CH_3)

*1H-4-(1H-4-ethoxycarbonyl-3-methyl-pyrazol-5-yl)-azo-3-phenyl-5-pyrazolone (**4b**)*

Orange powder, m.p. 230-240°C (transition to needles), 291-293°C; yield 80%.

UV-VIS λ max [nm] (ε x 10^{-4}): 209 (1,91), 222 (1,88), 377 (1,59)

IR (KBr): 492s, 621s, 657s, 691s, 755m, 887s, 947m, 1027s, 1060s, 1075s, 1102m, 1143m, 1164s, 1216i, 1277i, 1371s, 1449s, 1493m, 1537i, 1591s, 1667i, 1690m, 1725m, 3068s, 3190s, 3430s.

*1H-3-ethoxycarbonyl-4-(1H-4-ethoxycarbonyl-3-methyl-pyrazol-5-yl)-azo-5-pyrazolone (**4c**)* [12]

Yellow powder, m.p. 221-224°C; yield 95%.

UV-VIS λ max [nm] (ε x 10^{-4}): 210 (1,37), 241 (0,62), 422 (1,56)

IR (KBr): 472s, 635s, 691s, 741m, 771m, 834s, 863s, 886s, 998m, 1036s, 1105m, 1163m, 1216m, 1289m, 1388s, 1441m, 1501m, 1547i, 1684i, 1717i, 2794m, 2842m, 2871m, 2932m, 2981s, 3067m, 3133m, 3195m, 3340s, 3554s.

^{1}H-NMR δ_H (DMSO-d_6, 400 MHz): 14.08 (s, 1H, 1-NH), 12.66 (s, 1H, 4'-NH), 4.34-4.29 (m, 4H, 4-C-$COOCH_2CH_3$, 5'-C-$COOCH_2CH_3$), 2.46 (s, 3C-CH_3), 1.37-1.30 (m, 6H, 4C-$COOCH_2CH_3$, 5'-C-$COOCH_2CH_3$)

^{13}C-NMR δ_C (DMSO-d_6, 100 MHz): 162.6 (5-C-C=O), 159.3 (5'-C-C=O), 149.4 (5-C), 144.9 (3-C), 138.3 (5'-C), 126.8 (2'-C), 98.6 (4-C), 98.5 (1'-C), 60.8 (-O-CH_2CH_3), 60.1 (-O-CH_2CH_3), 14.2 (-O-CH_2CH_3), 14.0 (-O-CH_2CH_3), 11.2 (-CH_3).

*1H-4-(1H-4-ethoxycarbonyl-3-methyl-pyrazol-5-yl)-azo-3-methyl-1-phenyl-5-pyrazolone (**4d**)*

Yellow powder, m.p. 245°C (transition to needles), 288-289°C; yield 87%.

ESI-MS (M/z): 354 (M)

UV-VIS λ max [nm] (ε x 10^{-4}): 209 (2.27), 246 (2.82), 379 (2,3)

IR (KBr): 472s, 635s, 691s, 740m, 771m, 834m, 864s, 886s, 999m, 1036m, 1105m, 1163m, 1216i, 1289i, 1388m, 1441m, 1547i, 1684i, 1717i, 1957s, 2842m, 2871m, 2935m, 2981m, 3059m, 3133m, 3195m, 3340m, 3554s.

*1H-1,3-diphenyl-4-(1H-4-ethoxycarbonyl-3-methyl-pyrazol-5-yl)-azo-5-pyrazolone (**4e**)*

Orange powder, m.p. 233-237°C (transition to needles), 260-263°C; yield 96%.

ESI-MS (M/z): 417 (M+1)

UV-VIS λ max [nm] (ε x 10^{-4}): 209 (2,99), 271 (2,23), 401 (1,7)

IR (KBr): 489s, 578s, 631s, 651s, 666m, 686m, 714s, 761m, 786m, 914s, 958i, 1002s, 1053m, 1112m, 1141i, 1172i, 1243m, 1281m, 1339i, 1361s, 1387m, 1415s, 1449m, 1494i, 1522m, 154i, 1598m, 1661i, 1714s, 1945s, 2835s, 2903s, 29412s, 2979s, 3063s, 3137s, 3253m.

*1H-4-(1H-4-ethoxycarbonyl-3-methyl-pyrazol-5-yl)-azo-1-phenyl-3-phenylamino-5-pyrazolone (**4f**)*

Red-brown powder, m.p. 290-294°C; yield 79%.

ESI-MS (M/z): 431 (M)

UV-VIS λmax [nm] (ε x 10^{-4}): 210 (1.44), 242 (1.3), 271 (1.56), 382 (1.44)

IR (KBr): 472s, 635s, 691s, 740m, 771m, 834m, 864s, 886s, 999m, 1036m, 1105m, 1163m, 1216i, 1289i, 1388m, 1441m, 1547i, 1684i, 1717i, 1957s, 2842m, 2871m, 2935m, 2981m, 3059m, 3133m, 3195m, 3340m, 3554s.

*1H-4-(1H-4-ethoxycarbonyl-3-methyl-pyrazol-5-yl)-azo-1-(4-sulphophenyl)-3-carboxy-5-pyrazolone (**4g**)* [12]

Red powder, m.p. >340°C; yield 93%.

UV-VIS λ max [nm] (ε x 10^{-4}): 210 (0.74), 262 (0.96), 406 (0.78)

IR (KBr): 568m, 634m, 685m, 739i, 778i, 838m, 921m, 1006i, 1038i, 1063m, 1130i, 1197i, 1275m, 1309m, 1348i, 1386m, 1410m, 1444m, 1500i, 1548i, 1625i, 1692i, 1913s, 2835s, 2901m, 2987m, 3065m, 3110m, 3196i, 3440.

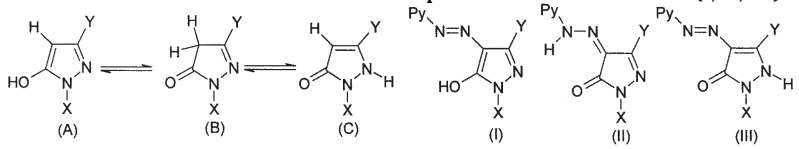
^{1}H-NMR δ_H (DMSO-d_6, 200MHz): 7.97 (d, 2H, J = 7.6 Hz, 2"-H, 6"-H), 7.72 (d, 2H, J = 7.6 Hz, 3"-H, 5"-H), 4.28 (q, 2H, J = 6.5 Hz, -CH_2CH_3), 2.42 (s, 3H, -CH_3), 1.29 (t, 3H, J = 6.5 Hz, -CH_2CH_3)

Results and discussions

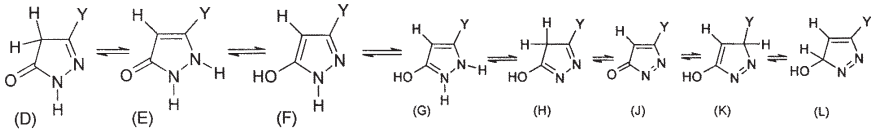
The coupling of 1*H*-4-ethoxycarbonyl-3-methyl-pyrazol-5-yl-diazonium chloride (**2**) with 3-mono- and 1,3-disubstituted pyrazol-5-ones (**3**) occurs in aqueous solution at a weakly alkaline *p*H with yields between 79-96%, the products of the coupling reaction being the corresponding azo dyes or the tautomeric hydrazones. The IR spectra display the characteristic vibrations of the functional groups in the molecule: ν_{NH}~3400m, ν_{CH2}~ 2900m, $\nu_{C=O}$~1700i (ester), $\nu_{C=O}$~1650i (amide), $\nu_{C=N}$~1640s and $\nu_{C=N}$~1550s (pyrazole ring).

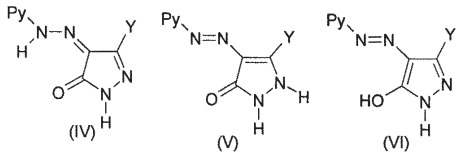
In the UV-VIS spectra the absorption maxima of the pyrazole rings are present between 209-216 nm; for the other absorption bands the attribution is difficult because of the tautomeric forms presented by pyrazole rings.

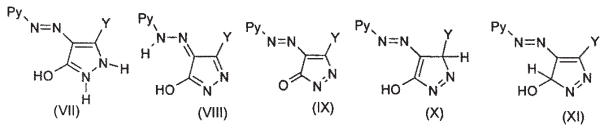
Thus, for 1,3-disubstituted 5-pyrazolones three tautomeric forms (A, B, C) are possible, from which three tautomeric forms for the pyrazolyl-azo-pyrazol-5-one compounds can be derived (I, II, III):



while for 3-substituted 1*H*-5-pyrazolones there are 8 possible tautomeric forms (D-L), from which eight tautomeric forms for the pyrazolyl-azo-pyrazol-5-one compounds can be derived (IV-XI):







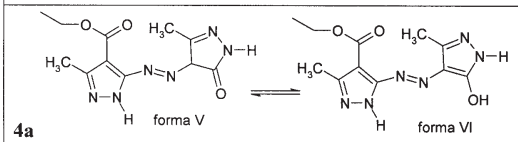
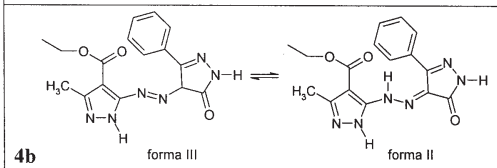
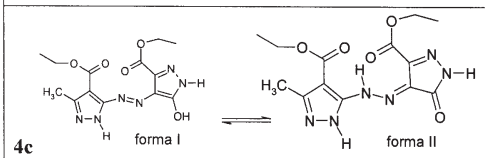
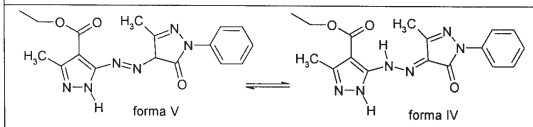
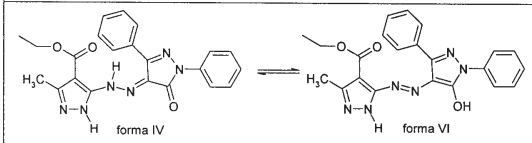
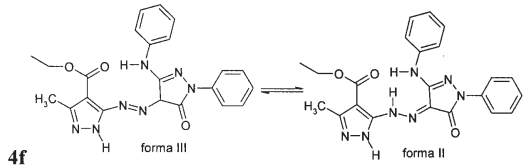
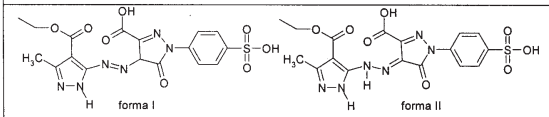
Tautomeric form	Pyrazole ring	hidrazo II	hidrazo IV	azo III, V	azo I, VI
 **4a**	216 (1,01)			350 (1.13)	401 (1.08)
 **4b**	209 (1.91)	250		377 (1.59)	
 **4c**	210 (1,37)	241 (0.62)			422 (1,56)
 **4d**	209 (2.27)		246 (2.82)	379 (2,3)	
 **4e**	209 (2.99)		271 (2.23)		401 (1.7)
 **4f**	210 (1.44)	242 (1,3)	271 (1,56)	382 (1.44)	
 **4g**	210 (0,74)	262 (0.96)			406 (0.78)

Table 1
TAUTOMERIC FORMS AND UV-VIS ABSORPTION MAXIMA [λ_{max} (εx 10^{-4})] OF 1*H*-4-ETHOXYCARBONYL-3-METHYL-PYRAZOL-5-YL-AZO-PYRAZOL-5-ONE DYES (**4a-g**)

Experimental studies [23] and calculations by semiempirical methods of theoretical chemistry [24,25] indicate that the "one" form (B, D) predominates in the solid state and in non-polar solvents, while the enamine (C, E) and the enolic form (A, F) predominate in aqueous solution and in polar solvents.

For the hydrazo form the literature [26] reports a specific absorption maximum between 247-278 nm; therefore, the absorption band at 240-271 nm could be ascribed to the hydrazo tautomeric form in structures II, IV, VIII. The absorption maximum at 358-380 nm of the investigated compounds lies between the specific absorption maximum of the azo group in aliphatic compounds (347 nm) and in the aromatic compounds (440 nm) [26].

In accordance with these data it can be stated that in methanolic solution the azo compounds **4a-g** exist as a mixture of tautomeric forms (table 1).

Conclusions

1*H*-4-(4-Ethoxycarbonyl-3-methyl-pyrazol-5-yl)-azo-pyrazol-5-ones (**4a-g**) are novel azo dyes, intermediates in the synthesis of new polycondensed heterocyles. Due to their particular structure they possess cation complexing properties that will be investigated.

As reported recently [10] the disazo-pyrazole dyes can display multiple tautomeric forms, a fact also confirmed in the case of 1*H*-4-(4-ethoxycarbonyl-3-methyl-pyrazol-5-yl)-azo-pyrazol-5-ones (**4a-g**), which can display in methanolic solution one, two or three tautomeric forms.

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