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Azoic Dyes Derived from 1-Aryl-5-methyl-3-hydroxypyrazoles

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SUMMARY

The potentialities for 1-aryl-5-methyl-3-hydroxypyrazoles as intermediates in the field of dyes have been analysed. Some azoic derivatives have been synthesized and both electronic spectra and tinctorial properties on various substrates (wool, nylon, polyester, plasticized PVC) examined. The effect of substituents on the position of the long wavelength absorption maxima is discussed in terms of Hammett σ constants and interesting relationships are obtained. For each application the most important technical properties are assessed and significant fastness to various agents is evaluated.

Finally a comparison with properties of similar pyrazol-5-one derivatives is made.

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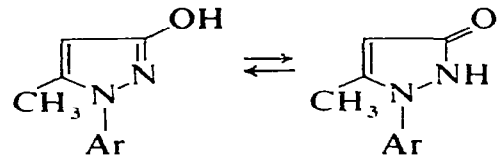
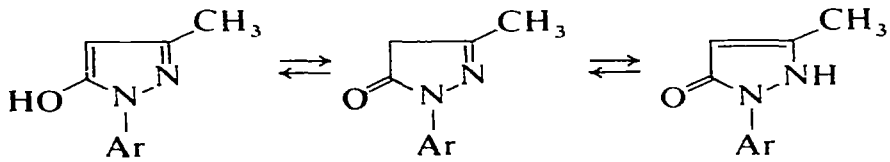
1. INTRODUCTION

1-Aryl-5-methyl-3-hydroxypyrazole (or 'pyrazol-3-one'), **I**, is an isomer of a very popular coupling agent in the chemistry of azo-compounds: 1-aryl-3-methyl-5-hydroxypyrazole or 'pyrazol-5-one', **II**.[1,2]



(I)

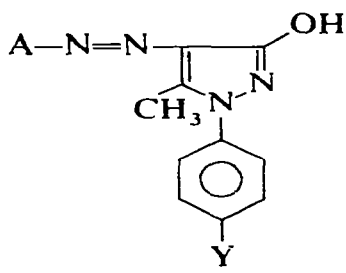


(II)

Pyrazol-3-one itself is considered an interesting intermediate in various fields, such as dyes and pharmaceuticals.

Aspects related to syntheses, properties and molecular structures (with respect to tautomeric forms) have been described.[3-7] Studies have also been made of the physico-chemical properties of azo-derivatives.[8,9] Oddly, very few data on utilization of azopyrazol-3-ones exist: only a very old patent on azo–metal complex dyes prepared from 4-aminopyrazol-3-one is available.[10]

We report here a series of data related to some azopyrazol-3-ones, **III**. Electronic spectra are examined and the influence of some substituents on the long wavelength absorption band is considered.



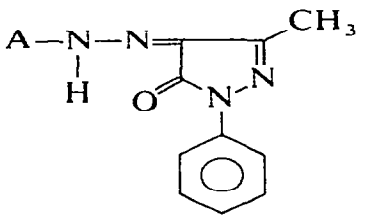
(III)

A = aryl, (arylazo)aryl, anthraquinonyl

Some important technical properties on various substrates have been measured. Wool was considered to be the most significant among natural fibres, nylon-6.6 and polyester among synthetic ones. Some metal–azo 1:2 complexes (metal chromium) have been prepared also and tested on wool.

A non-textile utilization of azopyrazol-3-ones is also considered. A few derivatives having some pigmentary properties are used as colouring matters for plastics (polyvinyl chloride, PVC).

A parallel study on some similar azoic derivatives of pyrazol-5-one, **IV**, has been carried out for comparative purposes.



A = aryl, (arylazo)aryl, anthraquinonyl

(IV)

2. EXPERIMENTAL

Pyrazol-3-ones are not commercial products. They were synthesized by a new method, studied in our laboratories, utilizing biacetyl and primary aromatic amines as starting materials.[11]

All dyes **III** and **IV** were obtained by conventional diazotization methods and coupling techniques. Pyrazol-3-ones were less reactive than pyrazol-5-ones in coupling reactions.[12] In general longer reaction times (2–3 h instead of 30 min) and higher pH values (7–8 instead of 2–3) were needed, and lower yields (75–80% instead of 95% or higher) were obtained.

Products were purified by repeated washings and crystallization from solvents (ethanol for dyes 1–17, chlorobenzene for dyes 18–22 and 32–34, ethanol–water mixtures for dyes 23–28; metal–azo complex dyes 29–31 were purified only by repeated washing with sodium chloride solutions and elementary analyses were chosen as a criterion of purity) until only one spot was present on TLC. Ionic derivatives still contained variable amounts of sodium chloride (used for precipitations). In Table 1 all the synthesized azopyrazol-3-ones are listed, with melting points and elementary analyses.

TABLE I

Characterization Data of Azopyrazol-3-one Dyes of General Formula **III**

Dye no.	*A*	*Y*	*Melting point (°C)*	*Empirical formula*	*C(%)*		*H(%)*		*N(%)*		*Cr(%)*	
					Calcd	*Found*	*Calcd*	*Found*	*Calcd*	*Found*	*Calcd*	*Found*
1	Phenyl	H	94-96 (96)[a]	$C_{16}H_{14}N_4O$	69·05	68·95	5·07	5·04	20·12	20·01		
2	2-Chlorophenyl	H	146-48 (154-55)[a]	$C_{16}H_{13}ClN_4O$	61·45	61·74	4·19	4·13	17·91	17·84		
3	3-Chlorophenyl	H	115-16 (118-20)[a]	$C_{16}H_{13}ClN_4O$	61·45	61·05	4·19	4·21	17·91	17·61		
4	4-Chlorophenyl	H	158-60 (158-60)[a]	$C_{16}H_{13}ClN_4O$	61·45	61·82	4·19	4·25	17·91	17·85		
5	2-Nitrophenyl	H	140-42 (141-42)[a]	$C_{16}H_{13}N_5O_3$	59·44	59·49	4·05	3·95	21·66	21·51		
6	3-Nitrophenyl	H	160-62 (161-63)[b]	$C_{16}H_{13}N_5O_3$	59·44	59·51	4·05	3·86	21·66	21·40		
7	4-Nitrophenyl	H	210-12 (206-09)[a]	$C_{16}H_{13}N_5O_3$	59·44	59·66	4·05	3·93	21·66	21·43		
8	2-Methoxyphenyl	H	138-40 (137-38)[a]	$C_{17}H_{16}N_4O_2$	66·22	66·13	5·23	5·21	18·18	18·17		
9	3-Methoxyphenyl	H	112-14 (109-10)[a]	$C_{17}H_{16}N_4O_2$	66·22	66·60	5·23	5·20	18·18	18·18		
10	4-Methoxyphenyl	H	127-28 (122-24)[a]	$C_{17}H_{16}N_4O_2$	66·22	66·15	5·23	5·11	18·18	18·02		
11	3-Trifluoromethylphenyl	H	125-26	$C_{17}H_{13}F_3N_4O$	58·96	58·83	3·78	3·83	16·18	15·98		
12	4-Carbomethoxyphenyl	H	169-71	$C_{18}H_{16}N_4O_3$	64·28	64·42	4·79	4·71	16·65	16·54		
13	4-Bromophenyl	H	161-62 (160-62)[a]	$C_{16}H_{13}BrN_4O$	53·80	53·66	3·67	3·69	15·68	15·53		
14	2-Chloro-4-nitrophenyl	H	201-03	$C_{16}H_{12}ClN_5O_3$	53·72	53·70	3·38	3·40	19·54	19·10		
15	3-Chloro-4-methoxyphenyl	H	217-18	$C_{17}H_{15}ClN_4O_2$	59·57	59·38	4·41	4·42	16·35	16·10		
16	4-(Phenylazo)phenyl	H	165-67	$C_{22}H_{18}N_6O$	69·10	68·96	4·74	4·91	21·97	21·53		
17	3-Methyl-4-(2′-methylphenylazo)phenyl	H	144-46	$C_{24}H_{22}N_6O$	70·22	70·07	5·40	5·17	20·47	20·32		
18	Phenyl	NO_2	218-19	$C_{16}H_{13}N_5O_3$	59·44	59·36	4·05	4·02	21·66	21·51		
19	4-Nitrophenyl	NO_2	217-19	$C_{16}H_{12}N_6O_5$	53·18	53·00	3·29	3·27	22·82	22·80		
20	4-Nitrophenyl	CH_3	208-10	$C_{17}H_{15}N_5O_3$	60·53	60·36	4·48	4·45	20·76	20·40		
21	4-Nitrophenyl	Cl	205-06	$C_{16}H_{12}ClN_5O_3$	53·72	53·98	3·38	3·40	19·58	19·29		
22	2-Chloro-4-nitrophenyl	Cl	194-96	$C_{16}H_{11}Cl_2N_5O_3$	49·00	48·81	2·83	2·75	17·86	17·67		
23	2-Sulphophenyl	H	>300	$C_{16}H_{13}N_4NaO_4S$	50·53	50·12	3·44	3·61	14·73	14·26		
24	3-Sulphophenyl	H	>300	$C_{16}H_{13}N_4NaO_4S$	50·53	50·17	3·44	3·55	14·73	14·34		
25	4-Sulphophenyl	H	>300	$C_{16}H_{13}N_4NaO_4S$	50·53	50·26	3·44	3·62	14·73	14·57		
26	2,5-Dichloro-4-sulphophenyl	H	>300	$C_{16}H_{11}Cl_2N_4NaO_4S$	42·78	42·93	2·47	2·53	12·47	12·25		
27	Phenyl	SO_3H	>300	$C_{16}H_{13}N_4NaO_4S$	50·53	50·77	3·44	3·50	14·73	14·21		
28	2-Methyl-5-(*N*-phenylsulphonamide)phenyl	SO_3H	>300	$C_{23}H_{20}N_5NaO_6S_2$	50·27	50·58	3·67	3·89	12·74	12·55		
29	2-Carboxyphenyl Azo–chromium 2:1 complex	H	>300	$C_{34}H_{24}CrN_8NaO_6$	57·06	58·01	3·38	3·34	15·65	15·23	7·26	7·23
30	2-Carboxy-4-nitrophenyl Azo–chromium 2:1 complex	H	>300	$C_{34}H_{22}CrN_{10}NaO_{10}$	50·69	51·35	2·75	2·83	17·38	18·48	6·45	6·45
31	2-Carboxy-4-sulphophenyl Azo–chromium 2:1 complex	H	>300	$C_{34}H_{22}CrN_8Na_3O_{12}S_2$	44·74	45·04	2·41	2·50	12·18	12·00	5·65	5·50
32	Anthraquinonyl	H	210-12	$C_{24}H_{16}N_4O_3$	70·59	70·56	3·95	4·01	13·71	13·49		
33	Anthraquinonyl	NO_2	212-14	$C_{24}H_{15}N_5O_5$	63·60	63·54	3·33	3·43	15·40	15·24		
34	Anthraquinonyl	Cl	225-27	$C_{24}H_{15}N_4O_3$	65·10	65·15	3·41	3·40	12·60	12·36		

TABLE 2
Spectroscopic Data of Dyes of General Formula **III** and **IV**

Structure		*Pyrazol-3-one derivative*		*Pyrazol-5-one derivative*	
A	*Y*	λ_{max} (*nm*)	*log ε*	λ_{max} (*nm*)	*log ε*
Phenyl	H	376	4·05	401	4·23
2-Chlorophenyl	H	384	4·16	400	4·24
3-Chlorophenyl	H	376	4·16	396	4·23
4-Chlorophenyl	H	373	4·11	402	4·27
2-Nitrophenyl	H	387	4·15	412	4·23
3-Nitrophenyl	H	376	4·15	388	4·21
4-Nitrophenyl	H	394	4·31	404	4·41
2-Methoxyphenyl	H	391	4·19	421	4·29
3-Methoxyphenyl	H	376	4·16	403	4·24
4-Methoxyphenyl	H	380	4·25	424	4·30
3-Trifluoromethylphenyl	H	375	4·07	395	4·23
4-Carbomethoxyphenyl	H	382	4·27	401	4·37
4-Bromophenyl	H	375	4·21	403	4·30
2-Chloro-4-nitrophenyl	H	407	4·34	—	—
3-Chloro-4-methoxyphenyl	H	379	4·30	—	—
4-(Phenylazo)phenyl	H	408	4·35	434	4·43
3-Methyl-4-(2′-methylphenylazo)phenyl	H	417	4·38	437	4·43
Phenyl	NO_2	381	4·27	—	—
4-Nitrophenyl	NO_2	399	4·24	—	—
4-Nitrophenyl	CH_3	393	3·82	—	—
4-Nitrophenyl	Cl	395	4·29	—	—
2-Chloro-4-nitrophenyl	Cl	404	4·28	—	—
2-Sulphophenyl	H	376	4·20	395	4·25
3-Sulphophenyl	H	367	4·15	398	4·27
4-Sulphophenyl	H	372	4·23	402	4·30
2,5-Dichloro-4-sulphophenyl	H	391	4·32	398	4·34
Phenyl	SO_3H	372	4·18	398	4·31
2-Methyl-5-(*N*-phenylsulphonamide)phenyl	SO_3H	375	4·26	400	4·30
Anthraquinonyl	H	409	4·15	396	4·15
Anthraquinonyl	NO_2	398	4·12	—	—
Anthraquinonyl	Cl	409	4·17	—	—

Electronic spectra were determined in 95% ethanolic solutions (10^{-5}–10^{-6}M) on a Pye–Unicam SP 1800 spectrophotometer. Characterization data of the long wavelength absorption band, for dyes **III** and **IV**, are reported in Table 2: metal-azopyrazol-3-one complex dyes, however, showed two partially superimposed maxima in the range 399–446 nm and related data could not be exactly evaluated.

Dyeings were carried out on fabrics by standard procedures. Depths were 1·2% for wool and for nylon, 0·5% for polyester; pH values of baths were 4·5–5·0 for azoic dyes on nylon, 6·5–7·0 for metal–azo dyes on wool; polyester was dyed at 130 °C. Sheets of coloured plasticized PVC (0·2 mm thick) were obtained by extrusion at 150 °C of mixtures containing azo-compound (0·3 g), polyvinyl chloride (70 g) and dioctylphthalate (as plasticizer, 30 g).

Substantivities were evaluated qualitatively by exhaustion dyeings.

Fastness to the various agents was determined by standard methods (ISO).[13] Lightfastness was evaluated after a 300 h exposure to a xenon lamp. Fastness to washing (for wool and for nylon) and to sublimation (for polyester) were described by three values in a 1–5 scale. The first one refers to the change of colour, the second to the staining of the same kind of fabric as the specimen and the third value refers to the staining of cotton (washing of wool at 40 °C and dry-heating of polyester at 210 °C) and of wool (washing of nylon at 60 °C and dry-heating of polyester at 180 °C).

Resistance to migration in coloured PVC was measured using sheets placed in contact, for 24 h at 80 °C in a ventilated stove, with an identical sheet pigmented with titanium dioxide. Staining was evaluated by Grey Scales.

The properties of the azopyrazol-3-one dyes and of some similar pyrazol-5-one derivatives are listed in Tables 3 and 4, respectively.

3. DISCUSSION

3.1. Visible absorption maxima

From the study of the colorimetric properties of arylazopyrazol-3-ones in ethanolic solutions the first observation relates to the range of the long-wavelength absorption band maxima. 1-Phenyl-4-(phenylazo)-5-methyl-pyrazol-3-one (**IIIa**, X = H, Y = H) is greenish yellow and absorbs

TABLE 3

Technical Properties of Pyrazol-3-one Dyes of General Formula **III**

Dye no.	*Substrate*	*Colour of dyeing*	*Lightfastness*	*Fastness to sublimation*						*Fastness to washing*						*Resistance to migration*
				180°C			*210°C*			*60°C*			*40°C*			
1	Polyester	Greenish yellow	4–5	3	3	3–4	2–3	2	3–4							
2	Polyester	Greenish yellow	5	4	3–4	4	3	2–3	4							
3	Polyester	Greenish yellow	6	3–4	3	4	3	2–3	4							
4	Polyester	Greenish yellow	5–6	4	3–4	4	2–3	2–3	4							
5	Polyester	Yellow	4–5	4	3–4	4–5	3	2–3	4							
6	Polyester	Greenish yellow	5	4	4	4–5	3–4	3	4							
7	Polyester	Yellow	6	4–5	3–4	4–5	3–4	2–3	3–4							
8	Polyester	Brownish yellow	4	4	3	3–4	3	2–3	3–4							
9	Polyester	Greenish yellow	5	4	3–4	3–4	3–4	3	4							
10	Polyester	Greenish yellow	5–6	4	3	3–4	3–4	2–3	3–4							
11	Polyester	Greenish yellow	6	4	3	4	3	2–3	4							
12	Polyester	Greenish yellow	4–5	3–4	3–4	4	3	2	3–4							
13	Polyester	Greenish yellow	5–6	4	3–4	4–5	3	2–3	4							
14	Polyester	Orange	5	4	3–4	4–5	4	2–3	3–4							
15	Polyester	Greenish yellow	6	4	3–4	4–5	3–4	3	4							
16	Polyester	Reddish yellow	6–7	4	3–4	4	3–4	2–3	3–4							
17	Polyester	Orange	6	4	4	4	3–4	3	3–4							
18	Polyester	Greenish yellow	6	4	3	4	3–4	2–3	4							
19	Polyester	Yellow	6	4–5	4	4–5	4	3	4–5							
20	Polyester	Yellow	5	4	3–4	4–5	4	2–3	3–4							
21	Polyester	Yellow	6	4	3	4	4	2–3	3–4							
22	Polyester	Yellow	5	4–5	4	4	4	3	4							
23	Nylon-6.6	Greenish yellow	5–6							3–4	4–5	4–5				
24	Nylon-6.6	Greenish yellow	5–6							3–4	4–5	4–5				
25	Nylon-6.6	Greenish yellow	5–6							3–4	4–5	4–5				
26	Nylon-6.6	Reddish yellow	4							3	4–5	4–5				
27	Nylon-6.6	Greenish yellow	5							3–4	4–5	4				
28	Nylon-6.6	Yellow	5							3	4–5	4				
23	Wool	Brownish yellow	5										2–3	4	3	
24	Wool	Brownish yellow	4–5										2–3	3–4	3	
25	Wool	Brownish yellow	4–5										2–3	3–4	3	
26	Wool	Reddish yellow	4										3	3	3	
27	Wool	Brownish yellow	4–5										2–3	3–4	3	
28	Wool	Brownish yellow	4–5										2–3	3–4	2–3	
29	Wool	Brownish orange	7										4	3	3–4	
30	Wool	Brownish orange	6–7										3–4	3–4	4	
31	Wool	Brownish	6–7										3	3–4	3	
32	PVC	Reddish yellow	2–3													2
33	PVC	Orange	2–3													2
34	PVC	Reddish yellow	2–3													2

TABLE 4

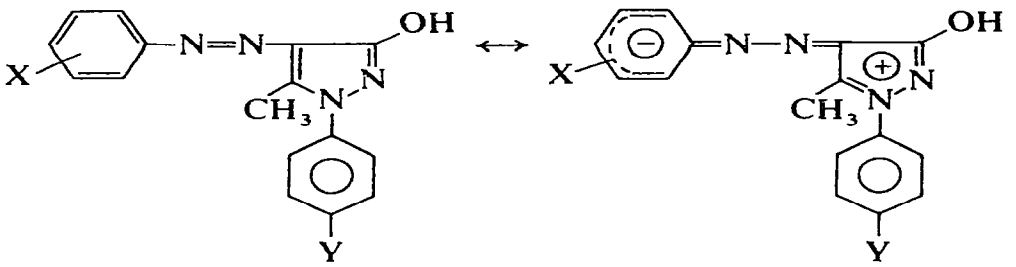
Technical Properties of Pyrazol-5-one Dyes of General Formula **IV**

Similar to dye no.	*Substrate*	*Colour of dyeing*	*Lightfastness*	*Fastness to sublimation*						*Fastness to washing*						*Resistance to migration*
				180°C			*210°C*			*60°C*			*40°C*			
1	Polyester	Yellow	4–5	3–4	2	3–4	2–3	1–2	3							
2	Polyester	Yellow	5–6	3–4	2–3	3–4	2–3	2	4							
3	Polyester	Yellow	6	4	3	3–4	3	2	4							
4	Polyester	Greenish yellow	5–6	4	2–3	3–4	2–3	2	4							
5	Polyester	Reddish yellow	6–7	4	3–4	4–5	3	2–3	4							
6	Polyester	Yellow	5–6	4	4	4–5	3–4	3	4							
7	Polyester	Reddish yellow	6–7	4	3–4	4–5	3–4	2–3	3–4							
8	Polyester	Reddish yellow	4	4	3	3–4	3	1–2	3							
9	Polyester	Yellow	5	4	3	3–4	3–4	1–2	3–4							
10	Polyester	Orange	4	4	2–3	3	3–4	1–2	3							
11	Polyester	Yellow	6	3–4	2–3	4	2–3	2	4							
12	Polyester	Greenish yellow	6	3–4	3	4	3	2	3–4							
13	Polyester	Yellow	5–6	3–4	3	4	3	2	4							
16	Polyester	Reddish yellow	6	4	3–4	4	3–4	2–3	4							
17	Polyester	Reddish yellow	5–6	4	4	4–5	3	3	4							
23	Nylon-6.6	Yellow	5–6							4	4–5	4–5				
24	Nylon-6.6	Yellow	5							3–4	4–5	4–5				
25	Nylon-6.6	Yellow	5–6							3–4	4–5	4–5				
26	Nylon-6.6	Reddish yellow	6–7							3–4	4	4				
27	Nylon-6.6	Yellow	5							4	4–5	4				
28	Nylon-6.6	Yellow	5							3–4	4–5	4				
23	Wool	Yellow	5–6										2	3	3	
24	Wool	Yellow	5										2–3	3–4	3	
25	Wool	Yellow	5										2–3	3–4	3	
26	Wool	Reddish yellow	6										3–4	3	3	
27	Wool	Yellow	4–5										2–3	3–4	3	
28	Wool	Yellow	5										2–3	3–4	2–3	
29	Wool	Brownish yellow	7										4	4	4–5	
30	Wool	Brownish yellow	6–7										4	4	4–5	
31	Wool	Brownish yellow	6–7										3–4	3–4	3	
32	PVC	Reddish yellow	6–7													2

maximally at 276 nm and monosubstituted derivatives (**III**, X = OCH_3, Cl, NO_2, Br, CF_3, $COOCH_3$, SO_3^-, Y = H) absorb in the range 267–294 nm. For similar monosubstituted arylazopyrazol-5-ones (**IVa**) the range of λ_{max} is 388–424 nm and the unsubstituted derivative is yellow with λ_{max} at 401 nm.

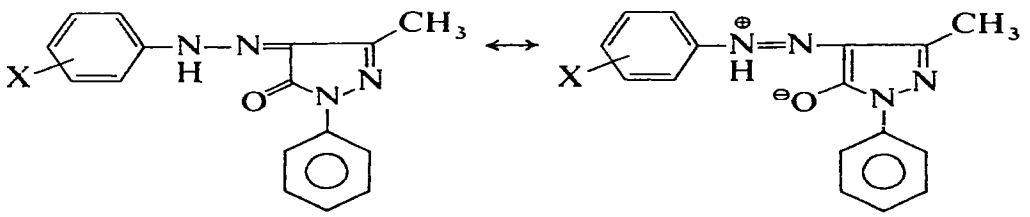
Comparison of the two sets of isomers shows a general hypsochromic effect (21–30 nm) with the azopyrazol-3-ones. Resonance theory appears to fail to predict the substituent effects on position of λ_{max}.

Arylazopyrazol-3-ones can be regarded as hybrids of structures **IIIa** and **IIIb**. The high-energy dipolar structure **IIIb** is stabilized when X is an electron-withdrawing substituent. Among monosubstituted structures



(IIIa) (IIIb)

the most bathochromic one is really the *p*-nitro derivative but the most hypsochromic one is not a methoxy derivative, as expected. Resonance approach does not appear to hold for arylazopyrazol-5-ones either. Considerations based on the most stable excited tautomeric form **IVb**



(IVa) (IVb)

would suggest it is to be stabilized when X is an electron-donating substituent. Table 2 shows that the *p*-methoxy group is indeed the most effective one in promoting a red shift but the *p*-nitro group also has a bathochromic influence.

A different empirical approach to substituent effects is based on polar characteristics expressed in terms of Hammet σ constants. Many attempts have been made to correlate the colour of dyes with the Hammet σ constants of substituents, sometimes with good results.[14-20] Analyses have been generally limited to monosubstituted derivatives for which values of σ constants, accurately evaluated, are readily available.[21]

The values of λ_{max} for the arylazopyrazol-3-ones (**IIIa**, X = H, *m*- and *p*-Cl, *m*- and *p*-NO_2, *m*- and *p*-OCH_3, *m*-CF_3, *p*-Br, *p*-$COOCH_3$, Y = H) show very poor correlation with values of σ constants. The calculated correlation coefficient $r = 0{\cdot}382$ corresponds to a probability that the *r*-value occurred by chance ($P > 0{\cdot}1$).[22,23] Exclusion from the computations of data relative to *p*-OCH_3 gives a higher correlation coefficient ($r = 0{\cdot}595$) but the relation between λ_{max} and σ remains still uncertain ($P \simeq 0{\cdot}1$).

Absorption maxima values relative to similar arylazopyrazol-5-ones correlate better with σ constants. Here *p*-OCH_3 fits well and the correlation coefficient is $r = -0{\cdot}72$, with $P \geq 0{\cdot}02$ (the negative value of *r* means an inverse dependence between λ_{max} and σ).

The best straight lines through the points, determined by the least squares method, are

$$\lambda_{max} = 14{\cdot}50\sigma + 372{\cdot}76 \text{ (nm)} \quad (1)$$

and

$$\lambda_{max} = -20{\cdot}92\sigma + 408{\cdot}06 \text{ (nm)} \quad (2)$$

for arylazopyrazol-3-ones and for arylazopyrazol-5-ones, respectively (Fig. 1). Clearly predictive power of these relationships is very poor. However, an opposite influence of polar characteristics of substituents on λ_{max} in the two series of derivatives, as already suggested by resonance theory, can be observed.

Very interesting indications result for both dye sets from a separate examination for *m*- and for *p*-substituted derivatives. For *m*-substituted arylazopyrazol-3-ones (**IIIa**, X = *m*-Cl, *m*-OCH_3, *m*-NO_2, *m*-CF_3, Y = H) a very low correlation coefficient is determined, $r = -0{\cdot}10$, indicating an evident lack of linear dependence between λ_{max} and σ. Least-squares analysis of the data gives in fact the relationship

$$\lambda_{max} = -0{\cdot}20\sigma + 375{\cdot}8 \text{ (nm)} \quad (3)$$

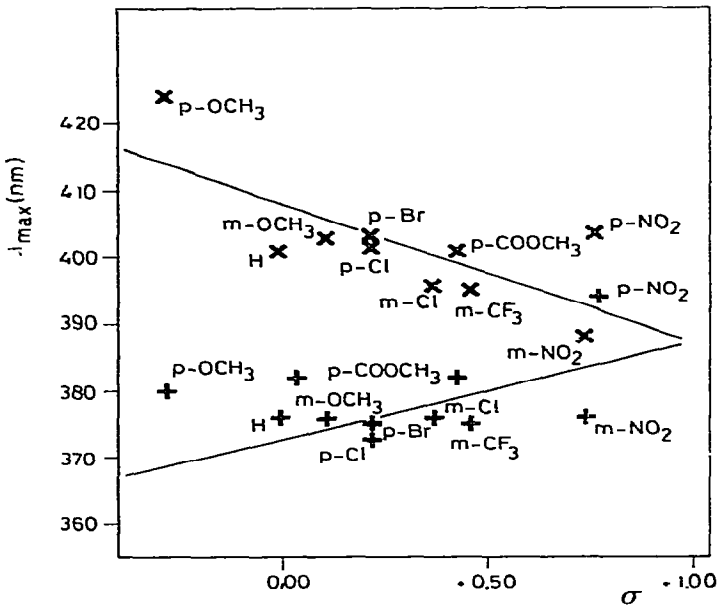


Fig. 1. Correlations between Hammett substituent constants (σ) and λ_{max} of derivatives of pyrazol-3-one (+) and of pyrazol-5-one (×).

which defines a line almost parallel to the abscissa (Fig. 2). So all *m*-substituents appear to have the same, virtually zero, effect on colour.

For *p*-substituted derivatives (**IIIa**, X = *p*-Cl, *p*-OCH_3, *p*-NO_2, *p*-$COOCH_3$. Y = H) a correlation coefficient $r = 0{\cdot}996$ is obtained corresponding to a very high probability that the variables are related ($P < 0{\cdot}01$). The following relationship is determined:

$$\lambda_{max} = 36{\cdot}40\sigma + 366{\cdot}07 \text{ (nm)} \quad (4)$$

Inspection of plot of the data (Fig. 2) shows that the spectral value for the (*p*-OCH_3)-substituted derivative is exceptional, so it was excluded from computations.

A clear influence on colour of substituents in the *p*-position is observed, with a hypsochromic effect for σ constant values lower than 0·27 and a bathochromic effect for higher values. A parallel analysis conducted on arylazopyrazol-5-ones gives the following relationships:

m-*Derivatives:* $\lambda_{max} = -23{\cdot}54\sigma + 405{\cdot}4$ (nm) (5)

p-*Derivatives:* $\lambda_{max} = 2{\cdot}56\sigma + 401{\cdot}5$ (nm) (6)

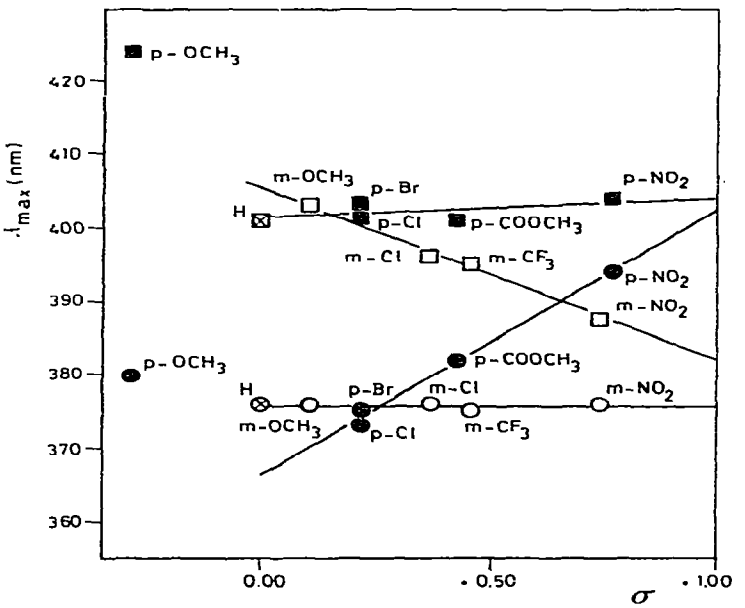


Fig. 2. Correlations between Hammett substituent constants (σ) and λ_{max} of arylazopyrazol-3-ones (*meta-* ○, *para-* ●) and of arylazopyrazol-5-ones (*meta-* □, *para-* ■).

Correlation coefficients are $r = -0{\cdot}997$ ($P < 0{\cdot}01$) and $r = 0{\cdot}51$ (λ_{max} and σ unrelated) for relationships 5 and 6 respectively. The data are shown in Fig. 2. Again the (p-OCH_3)-substituted derivative behaves irregularly and was not included in computations. In contrast to the 3-isomers, p-substituents in this case have very little influence on colour, while m-substituents cause a definite shift. A limiting value for bathochromic or hypsochromic effects is found to be $\sigma = 0{\cdot}20$.

Where the relationship between σ and λ_{max} has been shown to exist, the relationship gives good predictions for both sets of dyes (Table 5). Analysis of differences of λ_{max} values between arylazopyrazol-5-ones and arylazopyrazol-3-ones is not really justified. However, a regular trend may be noted, with a higher value for p-methoxy derivatives and a lower one for p-nitro structures. Relationship 7 (Fig. 3) was obtained

$$\Delta\lambda_{max} = -28{\cdot}37\sigma + 32{\cdot}03 \text{ (nm)} \qquad (7)$$

Curiously the complete set of data correlated well with Hammett σ constants ($r = 0{\cdot}974$, with a surprisingly low probability of a dependence

TABLE 5
Absorption Maxima of Dyes of General Formula **III** and **IV**, Calculated from Equations 3, 4, 5, 6 and 8

Structure		*Azopyrazol-3-ones*		*Azopyrazol-5-ones*	
X	*Y*	λ_{calc} (*eqn*) (*nm*)	λ_{obs} (*nm*)	λ_{calc} (*eqn*) (*nm*)	λ_{obs} (*nm*)
m-OCH_3	H	375·8(3)	376	402·8(5)	403
m-Cl	H	375·7(3)	376	396·7(5)	396
m-CF_3	H	375·7(3)	375	394·6(5)	395
m-NO_2	H	375·6(3)	376	388·0(5)	388
p-Cl	H	374·1(4)	373	402·0(6)	402
p-Br	H	374·1(4)	375	402·0(6)	403
p-$COOCH_3$	H	381·7(4)	382	402·5(6)	401
p-NO_2	H	394·1(4)	394	403·4(6)	404
p-NO_2	CH_3	392·8(8)	393	—	—
p-NO_2	H	393·9(8)	394	—	—
p-NO_2	Cl	395·3(8)	395	—	—
p-NO_2	NO_2	398·8(8)	399	—	—

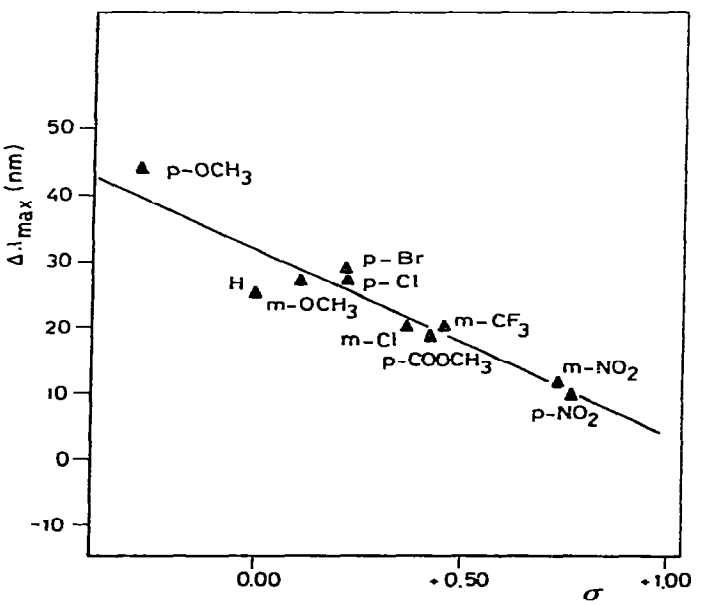


Fig. 3. Differences of λ_{max} between derivatives of pyrazol-5-one and of pyrazol-3-one versus Hammett substituent constants.

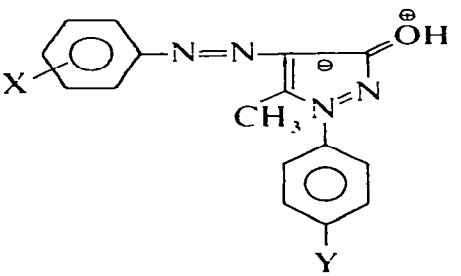
by chance, $P < 0{\cdot}001$). In the study of azopyrazol-3-ones the influence on colour was briefly examined also for a few substituents in the phenyl ring directly bonded to the pyrazole nucleus (**IIIa**, X = NO_2, Y = H, CH_3, Cl, NO_2). Within the range of substituents tested in the present work the colour extended over a very small interval (393–399 nm). Considerations based on resonance theory would suggest a destabilization of **IIIb** by electron-withdrawing groups with hypsochromic effects but, on the contrary, a red shift is observed for the nitro-substituted derivative.

A rather good linear dependence of λ_{max} on σ is observed ($r = 0{\cdot}996$, $P < 0{\cdot}01$) and least-squares analysis of the data gives the relationship

$$\lambda_{max} = 6{\cdot}40\sigma + 393{\cdot}9 \text{ (nm)} \qquad (8)$$

with a good predictive value (Table 5, Fig. 4).

So it appears necessary to consider a second high-energy dipolar structure (e.g. **IIIc**) as important in tautomeric equilibria of arylazopyrazol-3-ones.



(IIIc)

3.2. Dyeing properties on wool

The appearance of the dyeings clearly shows that sulphonic azoderivatives of pyrazol-3-one are not suitable for the coloration of wool. An altered colour results, with low saturation and very dull. Instead of a greenish-yellow (or yellow) hue, as expected from spectrophotometric data, a dull brownish-yellow appears. This marked 'bathochromic' effect is general. Appropriate substituents can improve some colour properties. Chlorine atoms, for example, increase saturation, but they cause lightfastness to fall considerably.

In general, substantivity (qualitatively evaluated by exhaustion dyeings) and lightfastness for acidic pyrazol-3-one dyes are slightly lower than for similar pyrazol-5-one derivatives. Fastness to washing is comparable.

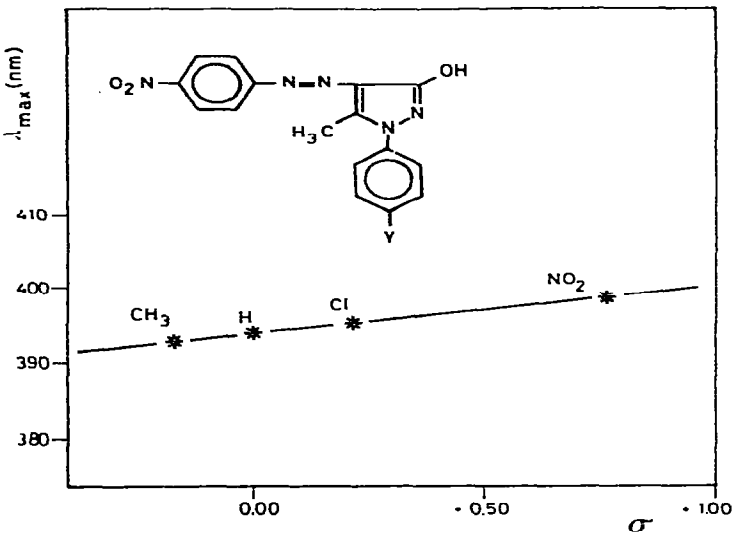


Fig. 4. Correlation between Hammett substituent constants (σ) and λ_{max} of derivatives of 1-arylpyrazol-3-ones.

The properties of complex azo-metal dyes (2:1, chromium) are good. Again a bathochromic effect is observed on wool, and the colour of dyeings are redder for pyrazol-3-one dyes as compared with similar pyrazol-5-one derivatives. Here, however, good saturation and fair lightness produce interesting brownish-orange colours on fibre. Other technical properties (substantivity, lightfastness and fastness to washing) are good, too. A serious limitation of this ciass of pyrazol-3-one derivatives results from difficulties in their synthesis. It is known that pyrazol-3-ones are not very reactive in diazo-coupling reactions. In the synthesis of azo–metal complexes the most commonly used diazonium salts derive from *o*-aminophenols. In the reaction with pyrazol-3-ones they gave, however, no product at all under normal conditions (75–80 % yields for pyrazol-5-one azo-derivatives). More reactive diazonium salts derived from anthranilic acids reacted well, and they were used in this work to obtain metal complexes from azopyrazol-3-one structures.

3.3. Dyeing properties on nylon-6.6

Colours on nylon have a greenish-yellow hue, with a very low degree of saturation, as expected from spectrophotometric data. Chlorine atoms

are suitable substituents which greatly improve saturation but they cause, at the same time, a dramatic decrease of lightfastness level (cf. wool dyeing). Some dullness is also observed. Levels of substantivity, lightfastness and fastness to washing are a little lower than for similar pyrazol-5-one derivatives.

3.4. Dyeing properties on polyester

Many different substitution patterns were considered for disperse azopyrazol-3-one dyes.

The unsubstituted monoazoic structure has very poor colour and substantivity. All monosubstituted derivatives, except for *o*- and *p*-nitro (**IIIa**, X = *o*-, *p*-NO_2, Y = H), have greenish-yellow hues with a low degree of saturation.

Substituents have in general a good influence on technical properties. On the whole substantivity and sublimation fastness have comparable levels for the pyrazol-3-one and pyrazol-5-one derivatives. With regard to lightfastness it is interesting to note that the highest differences in values are for some strong electron-withdrawing groups (*o*-NO_2, *p*-$COOCH_3$) in favour of pyrazol-5-one dyes, and for a strong electron-donating group (*p*-OCH_3) in favour of pyrazol-3-one dyes. Substituents in 1-arylpyrazol-3-ones appear to have a positive effect only on properties of unsubstituted dye (**IIIa**, X = H, Y = H).

Introduction of methyl, chloro or nitro groups in 4(4'-nitrophenylazo)-pyrazol-3-one (**IIIa**, X = *p*-NO_2, Y = H, CH_3, Cl, NO_2) causes a slight improvement of substantivity but the colour becomes duller (for Y = CH_3 or NO_2) and the lightfastness decreases (for Y = CH_3). Sublimation fastness remains approximately unaltered.

A few bisazo-derivatives were also examined. Pyrazol-3-one derivatives show a 'bathochromic' effect on the fibre, and dark orange hues are obtained. Substantivity and lightfastness levels are higher for pyrazol-3-one derivatives than for similar pyrazol-5-one ones; sublimation fastness is comparable.

3.5. Coloration of plasticized polyvinyl chloride (PVC)

Only a limited study of mono-azo pyrazol-5-one derivatives as pigments was carried out. A serious limitation is the good solubility of these

structures in a number of organic solvents. This defect was minimized by using a diazonium salt derived from a high molecular weight primary aromatic amine (1-aminoanthraquinone).

Dispersions in PVC gave brownish-orange hues with low lightness. Lightfastness and resistance to migration were also very poor.

4. CONCLUSIONS

Monosubstituted arylazopyrazol-3-ones in ethanolic solution give a colour range limited to the greenish-yellow region of the electromagnetic spectrum.

Substituents in the *meta*-position (relative to the azo-group) appear to have no effect on colour; substituents in *ortho*- or *para*-positions, on the other hand, considerably influence the position of absorption maxima.

Substituents in the 1-aryl ring of the pyrazol-3-one nucleus affect the colour of azo-derivatives but the effect is very small, and the upper limit for λ_{max} is less than 400 nm irrespective of the polar characteristics of substituent.

Diazo structures absorb in the visible region, with simpler derivatives absorbing at more than 405 nm.

Examination of the technical properties of some pyrazol-3-one azoic derivatives on various substrates provides data regarding the general utility of the intermediate in the dyes field. Colour constitutes a general strongly limiting factor for this class of derivatives: greenish-yellow hues with low levels of saturation and with reduced lightness appear to be common features for most of monosubstituted structures. Azo-derivatives are clearly unsuitable for wool and nylon dyeing (curiously such fibres constitute the most common substrates for azopyrazol-5-one dyes[24]). Utilization as colouring matters for plastics is not promising.

Disperse structures having convenient substitution patterns possess fairly good properties on polyester fibres. The best results are obtained with azo–metal complexes in wool dyeing, all-round properties indicating potential for further research in that field. Difficulties in dye syntheses, however, could limit such possibilities seriously.

On the whole comparison between the isomeric pyrazolones is largely favourable to pyrazol-5-one for which colour and technical properties always have good levels.

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