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Properties and Structure of Naphthalimide Dyes Derived from Pyrazolones

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ABSTRACT

A series of monoazo dyes has been obtained using aminonaphthalenes, 3-, and 4-aminonaphthalimides and their N-methyl and sulpho derivatives as diazo compounds and derivatives of 1-phenyl-3-methylpyrazolone-5 as coupling components. UV-VIS data and determined calculations using the PPP-MO method indicate that the dyes exist in an equilibrium of azo-hydrazone of two hydrazone forms.

1 INTRODUCTION

It has been shown in recent investigations[1,2] that the use of diazo components such as 4-aminonaphthalimide has an advantageous effect on the dyeing properties of the derived azo dyes. The presence of the naphthalimide system also results in the dyes having a deep and intense colour. During investigations on methods of reducing 4-nitronaphthalimide using cheaper and more readily available reagents than those described in the literature, e.g. stannous chloride, 4-amino-3-sulphonaphthalimide and its *N*-methyl derivative were prepared.[3] The use of these sulpho derivatives of 1,8-naphthalimide in the synthesis of new acid dyes in which pyrazolone derivatives are used as diazo compounds instead of the previously used naphthol derivatives,[4,5] was with the objective of attaining yellow and orange hues.

The following pyrazolone derivatives were used as coupling components (X):

1-Phenyl-3-methylpyrazolone-5 (**A**), 1-(4′-sulpho)phenyl-3-methylpyrazolone-5 (**B**), 1-(4′-sulpho-2′,5′-dichloro)phenylpyrazolone-5 (**C**)

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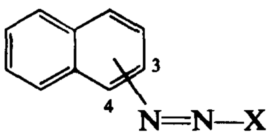
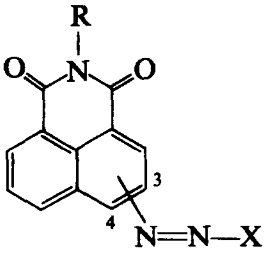
As diazo components the following were used:

1-Naphthylamine (**1**), 2-naphthylamine (**2**), 3-aminonaphthalimide (**3**), 3-amino-*N*-methylnaphthalimide (**4**), 4-aminonaphthalimide (**5**), 3-sulpho-4-aminonaphthalimide (**6**), 4-amino-*N*-methylnaphthalimide (**7**), 3-sulpho-4-amino-*N*-methylnaphthalimide (**8**).



1,2-A



3–8-A–C

Model dyes **1–5**, **7-A** not containing a sulpho group were synthesised in order to investigate the azo-hydrazone equilibrium of the dyes.

2 EXPERIMENTAL

2.1 Synthesis of model dyes 1–5, 7-A

The appropriate amine (0·01 mol) was diazotized with nitrosylsulphuric acid ($15\,cm^3$ 96% H_2SO_4 and 1·2 g $NaNO_2$) at 10°C during 2 h. The solution was poured into $15\,cm^3$ of acetic acid and the diazo liquor was slowly added to a solution of 0·012 mol of 1-phenyl-3-methyl-5-pyrazolone in $50\,cm^3$ of 2% sodium hydroxide at 5°C (pH 8–9, adjusted by $NaCO_3$). The dye was separated by acidifying and was purified from hot 2% HCl and 5% Na_2CO_3, and finally crystallised from acetic acid. Yields 85–97%; melting points (°C): **1A** 171–173, **2A** 133–135, **3A** 253–260, **4A** 152–156, **5A** 334–336, **7A** 231–234.

2.2 Synthesis of acid dyes 1,3-A–C

Acid dyes were synthesised by the method described earlier, i.e. by diazotizing the amines **5–7** by the direct method, and the sulpho-amines **6–8** by the reverse method.[6]

2.3 Electronic spectra

Diffuse reflectance on wool and polyamide fibres and electronic spectra of acid dyes **6,8-A**, **5–8-B,C** in buffer solution at pH 7 at a concentration of 2 ×

10^{-4}–2×10^{-5} m/dm^3 in DMF (for dyes insoluble in water), or at a concentration 2×10^{-5} m/dm^3, were recorded on a Specord M40 (Carl Zeiss-Jena). Dyes **5,6-A–C** were run in cyclohexane (Chx) solution, in methanol (Me), in *N*,*N*-dimethylformamide (DMF) and in water at pH 14.

2.4 Dyeing procedure

Wool and polyamide samples were dyed in a Roaches apparatus. The samples were dyed for 1 h at 98°C, in 95 cm^3 of water, 5 cm^3 of buffer solution at pH 5, using 2·5 g fabrics and 0·025 g of dye (100%).

3 RESULTS AND DISCUSSION

Dyes derived from naphthols can occur in either azo or hydrazone configurations.[6] The relative proportion of these depends on several factors; for example, the type of solvent used for investigations is particularly important. On the other hand, pyrazolone dyes occur, according to the data in the literature,[7–14] only in the hydrazone form (in normal circumstances). Few data are available with respect to the nature of the fibre on the azo-hydrazone equilibrium of the dyes and their spectra in solvents of different character.

On the basis of the author's investigations it was observed that the dyes **6,8-A** and **5–8-B,C** have different spectral characteristics in solution and on dyed fibre. This implies that the dyes occur in an equilibrium of azo and hydrazone forms, which absorb at different wavelengths. This phenomenon is particularly apparent on dyed fibres, such as wool and polyamide. In this case, in the reflectance spectra the appearance of an additional band, in the form of an inflexion point with rather high intensity, in the range above 500 nm, can be observed. These dyes in aqueous solutions at pH 7 absorb within the range 434–477 nm (Table 1). It seems probable that this phenomenon is caused by the occurrence of the dyes in the hydrazone form, involving the imide heterocyclic ring. The conjugation is longer in this case, thus resulting in a bathochromic effect. The dependence of the form in which the dyes occur in a particular environment has been previously observed for some acid dyes derived from 1- and 2-naphthol derivatives.[6]

Preliminary investigations were carried out on the acid dyes in aqueous solution and on dyed wool and polyamide (Table 1). The results led to general conclusions concerning the influence of the imido system in the naphthalimide derivatives on the properties of the dyes. It was found that the presence of an *N*-methyl group in the imido system (dyes **7** and **8**) results in an increase in the contribution of the hydrazone form H_{III}. The presence of

TABLE 1
Spectrophotometric Data for the Naphthalimide Acid Dyes **5–8-A–C** and Half-Widths of the Absorption Bands

	λ_{max} (*nm*)				$\Delta\nu_{1/2} \times 10^{-3}$ $(\Delta\lambda_{1/2})$ (cm^{-1} (*nm*))			
	5	***6***	***7***	***8***	***5***	***6***	***7***	***8***
A	—	448 (351, ~561)	—	448 (353)	3·0 (98)	w	3·0 (97)	w
B	437	444 (347)	441 (354, ~575)	434 (~541)	3·1 (80)	w	w	w
C	472	474	473	477	7·4 (160)	w	6·9 (150)	w

The spectra were run in water solution at pH 7. Side bands are given in parenthesis. w, Wide band with high absorption at the short wavelength range of the spectrum, higher than $1/2 \times A$ at $\Delta\lambda_{1/2}$.

TABLE 2
The Proportion of the Hydrazone Form H_{III} in Azo-Hydrazone Equilibrium of the Dye in Water Solution (H_2O) and on the Dyed Polyamide (PA) and Wool (W) Fibre in %

	5			*6*			*7*			*8*		
	H_2O	*PA*	*W*	H_2O	*PA*	*W*	H_2O	*PA*	*W*	H_2O	*PA*	*W*
A	—	—	—	26	43	41	—	—	—	20	36	33
B	6	39	38	—	10	17	5	32	25	—	25	24
C	—	44	47	—	21	25	—	41	46	17	41	40

a sulpho group in the diazo component ring (dyes **6A** and **8A**) results in these dyes occurring exclusively in the hydrazone form H_I.

The water-soluble pyrazolone derivatives **6,8-A** and **5–8-B,C** in the conditions of application occur mainly in the hydrazone forms H_I and H_{III}. In the above-mentioned sulpho derivatives of 1- and 2-naphthol, used as azo components, the influence of sulpho substituents on the spectrum of the compound can be observed.[6] In contrast, pyrazolone dyes containing sulpho groups in their coupling component, do not show any such dependence, because the three-dimensional configuration of the molecules is such that the additional steric hindrance between the sulpho group in the phenyl ring of pyrazolone and the hydroxyl group of enol form does not occur. The sulpho groups in the phenyl ring of pyrazolone can influence only the solubility of dyes and not their three-dimensional structure (**6,8-A**).

Other authors, who investigated pyrazolone derivatives of a different type, came to similar conclusions concerning the influence of the sulpho group on the colour.[15]

In an alkaline environment (pH 14), a bathochromic shift of the absorption bands in relation to the bands ascribed to the azo form takes place. This is a result of ionisation of the hydroxyl group.

The dyes derived from pyrazolones occur, in solution and on fibre, in one of the hydrazone forms; form H_{III} increases significantly on dyed fabrics in relation to solution (Table 2).

4 SPECTRAL ANALYSIS OF MODEL DYES

For the **1–5,7-A** dyes the spectra were run in cyclohexane, in aqueous solution at pH 14 and in methanol and DMF (Table 3, Fig. 1).

In cyclohexane, the dyes are not solvated with the solvent. Dyes **1A** and **2A** absorb within the range 416–426 nm (Fig. 1), and in the spectrum of dye **2A**, these occur at *c.* 370 nm, a clear inflexion point, which confirms the

TABLE 3

Spectrophotometrical Data of 1-Phenyl-3-methylpyrazolon-5 Derivatives

Dye	*—N=N—*	*R*	*Cyclohexane*		*DMF*		*Methanol*		*Water (pH 14)*	
			λ_{max} (ε_{max}) (*nm*) (*mol*$^{-1}$ *cm*$^{-1}$ *dm*^{3})	$\Delta\nu_{1/2}$ (*cm*$^{-1}$)	λ_{max} (ε_{max}) (*nm*) (*mol*$^{-1}$ *cm*$^{-1}$ *dm*^{3})	$\Delta\nu_{1/2}$ (*cm*$^{-1}$)	λ_{max} (ε_{max}) (*nm*) (*mol*$^{-1}$ *cm*$^{-1}$ *dm*^{3})	$\Delta\nu_{1/2}$ (*cm*$^{-1}$)	λ_{max} (ε_{max}) (*nm*) (*mol*$^{-1}$ *cm*$^{-1}$ *dm*^{3})	$\Delta\nu_{1/2}$ (*cm*$^{-1}$)
2A	2-	—	416 (21 900)	6 800	429 (24 000)	8 600	416 (22 800)	7 600	395 (13 500)	11 000
									418 (13 300)	
3A	3-	N—H	[344][a]	—	332 (15 800)	—	343 (16 400)	—	348 (12 000)	
					557 (3 800)	—	~417	—	~445	
4A	3-	N—CH_3	[355][a]	—	332 (9 400)	—	345 (8 400)	—	352 (6 200)	
					557 (1 800)	—	~472	—	~458	
1A	1-	—	426 (19 600)	5 700	452 (17 600)	6 800	309 (15 600)			
							429 (27 000)	6 100	412 (5 800)	7 800
5A	4-	N—H	421[a]	—	424 (12 300)	—	443[a]	—	345 (10 000)	
					583 (24 700)	2 900	[340, ~535][a]	—	494 (20 000)	6 000
7A	4-	N—CH_3	437[a]	5 800	334 (27 500)	—	441[a]	5 100	360	
					386 (15 700)	—	~525	—	458[a]	
					586 (36 900)	3 100				

[a] The spectra were run for saturated solutions; [...], bands of low intensity; ~, inflexion point. Concentration of the solutions c_0 [$\times 10^{-5}$ mol/dm^3]: (Cyclohexane) [**1A**, **2A**] 11·9; (DMF, methanol, water pH 14) [**2A**] 8, [**1A**, **3A**, **4A**] 10; (DMF) [**7A**] 0·822, [**5A**] 10; (water pH 14) [**5A**] 10.

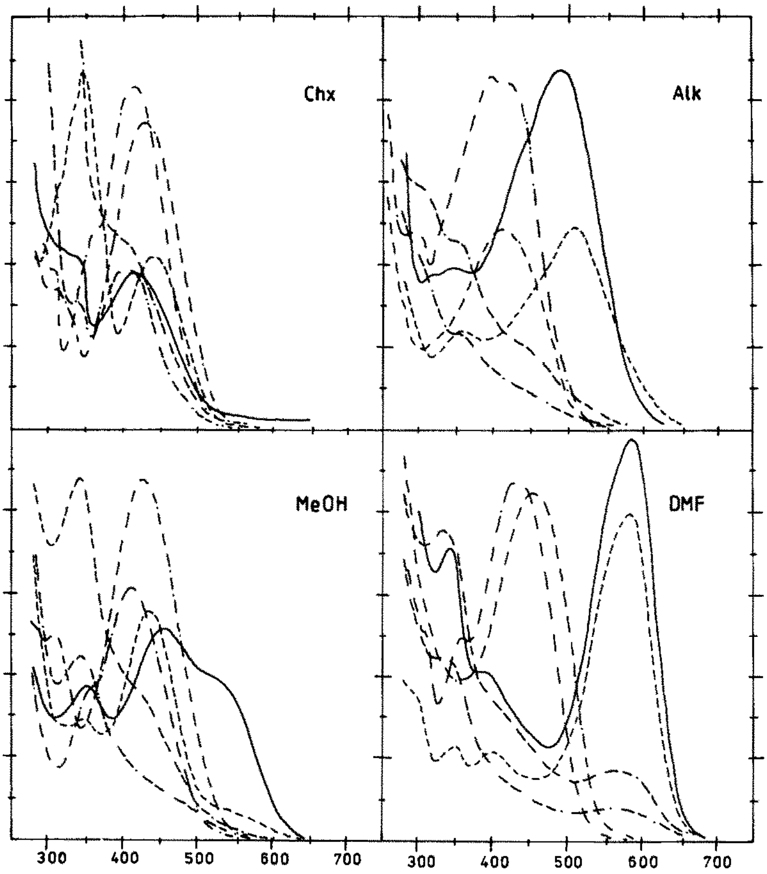


Fig. 1. Relationship A = $f(\lambda)$ for dyes **1A** (—·—), **2A** (— —), **3A** (—— ——), **4A** (—— ——), **5A** (———) and **7A** (— — —) in different solvents at range of absorbances: [Chx] **1,2-A** 0–3·0; **3,4,7-A** 0–0·8; **5A** 0–0·2; [Alk] **1,2-A** 0–2·0; **3–5,7-A** 0–2·5; [MeOH] **1,2-A** 0–3·0; **3–5,7-A** 0–1·8; [DMF] **1–4-A** 0–2·0; **5,7-A** 0–3·0.

possibility of occurrence of this compound also in the azo form. The bathochromic shift of the **2A** isomer in relation to the **1A** isomer results from the different character of the 1- and 2-positions in the naphthalene molecule. The relative reactivity constant in the 1-position is 0·00, and in the 2-position it is −3·4 (for benzene, this constant is −7·8).[16,17]

The naphthalene ring is an acceptor substituent, on the whole stronger than a benzene ring, e.g. benzene-azo-pyrazolone dyes absorb in the range of 250 (azo form) to 390 nm (hydrazo form).[18] In addition to this, the character of the naphthalene ring undergoes a change as a result of the introduction of two carbonyl groups in the 1,8-positions. In the 4-isomers (**5A**, **7A**) (Fig. 1) they are in a position of conjugation with the azo system, but in the 3-isomers (**3A**, **4A**) (Fig. 1) they only lower the electron density of the naphthalene ring by an inductive effect. This phenomenon had been previously investigated and described using model compounds, simple derivatives of aminonaphthalimides.[19]

The possibility of electron rearrangement and internal polarisation of the lactam system O=C—N plays an important part in the pyrazolone dyes. As a result, we obtain a polar structure $^{-}$O—C=N^{+} with negative charge on the oxygen atom, and with large dipole moment and high electron polarisation,[18] (see Fig. 2, showing the electron density changes for dyes **2A** and **5A**). Polar forms contribute only a small part to the ground state, but they make a large contribution to the excited state. In connection with this, the long wavelength band can be a result of co-operation of the different forms, viz. hydrazone forms of the lactam system and of one polar system. For example, in ethanol λ_{max} undergoes a bathochromic shift in relation to the band in non-polar solvents because the energy of excitation is lowered by

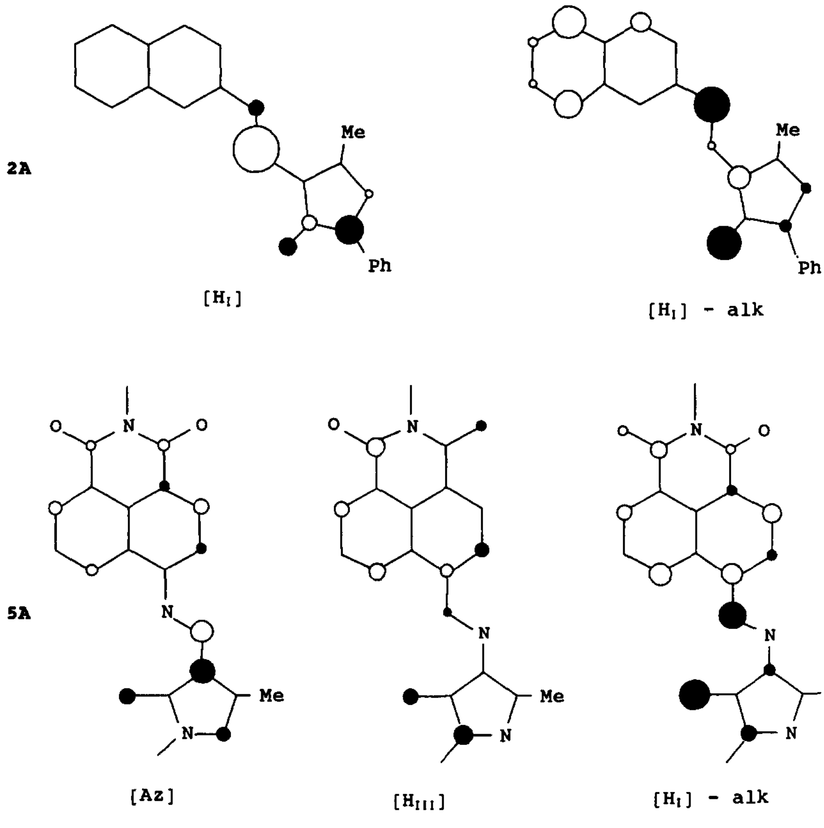
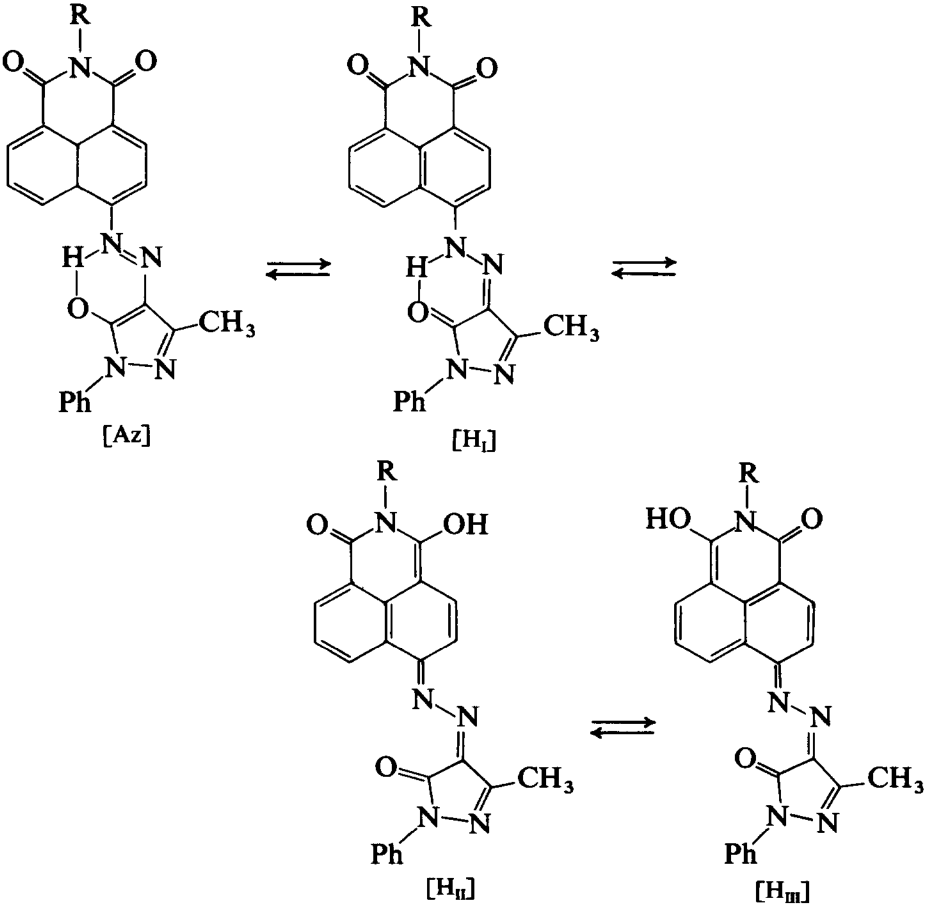


Fig. 2. Pictorial representation of the electron density changes for dyes **2A** and **5A**. The open circle signifies increase in electron density and their areas indicate the magnitude of the changes.

ionic forms. The extent of the bathochromic shift, following from the presence of substituents, is similar for the hydrazone and the azo tautomer.[7]

DMSO and pyridine are, according to literature data, solvents which stabilise the azo tautomers.[8] The dyes derived from 3-aminonaphthalimide (**3A**, **4A**) absorb in the range 344–355 nm (Fig. 1, Table 3). The most intense bands are at the range *c*. 210–240 nm. This hypsochromic effect is caused by the presence of two electron-acceptor substituents, i.e. the carbonyl groups in the napthalene ring. These lower the electron density of the naphthalene ring and, indirectly, of the β-atom nitrogen atom. This makes the formation of the hydrazone form of the dye difficult, so the prevailing form, in cyclohexane, is the azo form. This is also stabilised by the intramolecular hydrogen bond.[1,8,20]

The 4-isomers (**5A**, **7A**) can occur in one of the four proposed forms, i.e. one azo form Az, and three hydrazone ones H_I–H_{III}, depending on the environment of the dye.



The tautomeric equilibrium depends strongly on the solvent molecules which surround the dye molecules. Polar solvents favour, in general, the hydrazone tautomer (H_I, H_{II} or H_{III}) over the azo (Az) tautomer.

The effect of the solvents on the position of the equilibrium does not correlate with the dielectric constant of the solvent, but depends on the solvent structure and the microscopic environment of the dye in the solvent matrix.[4]

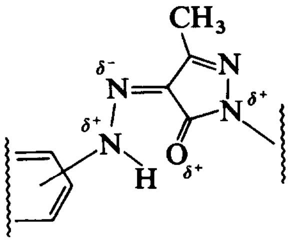
DMF is a polar solvent and a proton acceptor, and solvates only cations,[20,21] while methanol solvates cation and anions. Comparing the spectrum in cyclohexane, the dyes in methanol and DMF show a bathochromic effect, as is typical of many solvated organic compounds[22] (Fig. 1, Table 3).

5 CALCULATION OF MODEL DYES BY PPP-MO METHOD

In order to investigate the azo-hydrazone equilibrium of the pyrazolone dyes, six water-insoluble model dyes were prepared, in which 1-phenyl-3-methylpyrazolone-5 (**A**) was the coupling component, and 1- (**1**) and 2-aminonaphthalene (**2**) and derivatives of 3- (**3**, **4**) and 4-aminonaphthalimides (**5**, **7**) were diazo components. These dyes are good models for spectral investigations and quantum-chemical calculations by the PPP-MO method. Standardised and corrected input data for atoms of the molecule were used;[23–25] in the remaining cases, suitable input data were used.

	VSIP	A_Y	β_{XY}	*Z*
=N—N—C	17·00	9·80	−2·62	2
—NH—N=	15·00	0·97	−2·90	1
C—O⁻	21·50	5·20	−2·60	1
⁻N—N=	16·50	4·00	−2·42	1

The isomeric dyes **1A** and **2A**, 1- (**1**) and 2-naphthylamine (**2**) derivatives absorb at 416 and 426 nm, respectively. According to previously published data,[7–9,11–13] similar phenylazopyrazolone dyes occur in the hydrazone form. Calculations with the PPP-MO method for this structure gave values of 410 and 430 nm, respectively, which are in accord with those determined in Chx (Table 4). The phenyl ring also affects the electron density of the lactam pyrazolone ring, acting as a weak electron-acceptor substituent. In the excited state, the molecule occurs in the H_I form with delocalised electron density, quantitive changes of which are presented in Table 5.



Dye **2A** in Chx has an additional band, in the form of an inflexion within the range corresponding to the calculated absorption of the azo form (Table 4, Fig. 1). The author did not observe such a phenomenon for **1A**. The calculations suggest an equilibrium of the azo and hydrazone forms, with a prevailing hydrazone tautomer (Table 4). Calculations of the spectra of dyes in the ionised form, corresponding to the absorption in water at pH 14, provide additional evidence. They are hypsochromically shifted in relation to the spectra in Chx; good correlation of the calculated and determined λ_{max} for different solvent indicates that in alkaline solution the dyes occur in the ionised hydrazone form, derived from H_I (Fig. 1).

According to the calculations, the dyes derived from naphthalimide should have an absorption maxima for the azo form at 335 and 370 nm (**3**, **4-A**) and at 432 nm (**5**, **7-A**), and for the hydrazone form at 450 and 484 nm, respectively. The concurrence of the calculated and determined λ_{max} values leads to the assumption that these dyes occur in the azo form in Chx. This is affected by the carbonyl groups, which lower the basicity of the azo nitrogen atom, thus making difficult the formation and stabilisation of the hydrazone form (similar to that occurring in **1A** and **2A**). In dyes **3A** and **4A**, the presence of the hydrazone form appears as a band of low intensity in Chx,

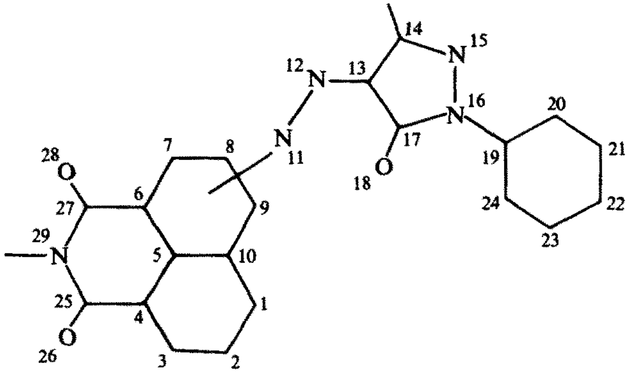
TABLE 4
Calculated λ_{max} (in nm) Values of Azo and Hydrazone Forms of the Dyes 1–5,7-A in Non-ionised and Ionised Forms

Dye	*Chx*				*Alk*			
	A	H_I	H_{II}	H_{III}	*A*	H_I	H_{II}	H_{III}
2A	370	410	—	—	397	397	—	—
3A	370	449	—	—	377	369	—	—
4A	377	450	—	—	376	370	—	—
1A	389	430	—	—	416	418	—	—
5A	432	468	499	568	508	491	531	555
7A	430	466	500	568	505	490	533	555

A, Azo form, H_I, H_{II}, H_{III}, appropriate hydrazone forms (see text).

TABLE 5

Differences of the Electron Density in the Ground and Excited State of Dyes **1A**, **2A**, **3A**, **5A**



Atom	*1A*		*2A*		*3A*		*5A*		
	H_I	*Alk*	H_I	*Alk*	*A*	*Alk*	*A*	H_{III}	*Alk*
1	—	0·16	—	0·08	0·11	0·13	0·06	0·10	0·13
2	—	0·05	—	—	—	—	—	—	−0·02
3	—	0·05	—	0·03	0·09	0·11	0·06	0·09	0·12
4	—	0·18	—	0·05	0·04	0·05	—	—	—
5	—	—	—	—	−0·02	−0·02	—	—	—
6	—	0·11	−0·02	0·05	0·03	0·02	−0·05	−0·04	−0·08
7	—	—	—	0·04	0·06	0·11	0·07	0·03	0·10
8	0·02	0·04	−0·02	−0·11	−0·02	—	−0·05	−0·04	−0·10
9	—	—	—	0·07	0·07	—	0·04	0·07	0·11
10	—	—	—	−0·03	—	—	—	—	−0·02
11	−0·08	−0·20	−0·11	−0·19	−0·09	−0·19	−0·04	−0·05	−0·16
12	0·25	—	0·24	0·18	0·03	−0·03	0·13	—	0·02
13	0·03	−0·12	0·02	−0·06	−0·21	−0·12	−0·16	0·03	−0·06
14	0·02	0·02	0·04	0·07	—	—	0·02	−0·03	—
15	0·04	−0·05	0·04	—	−0·12	−0·07	−0·07	—	−0·04
16	−0·15	−0·06	−0·09	−0·04	—	−0·08	—	−0·10	−0·07
17	0·08	—	0·07	0·05	−0·11	—	−0·04	0·02	—
18	−0·09	−0·20	−0·08	−0·08	−0·12	−0·24	−0·07	−0·09	−0·16
19	−0·02	—	—	—	—	−0·02	—	—	—
20	−0·04	—	−0·02	—	—	—	—	−0·02	—
22	−0·04	—	−0·02	—	—	−0·02	—	−0·02	—
24	−0·04	—	−0·02	—	—	−0·02	—	−0·02	—
25	—	—	—	—	0·08	0·13	0·05	0·10	0·10
26	—	—	—	—	0·06	0·08	0·02	—	0·05
27	—	—	—	—	0·08	0·19	0·06	—	0·07
28	—	—	—	—	0·05	0·07	—	−0·04	0·02
29	—	—	—	—	—	—	—	0·02	—

For clarification the values of electron density changes in excited and ground state <0·02 were omitted.

A, Neutral form (azo); H_I, H_{III}, corresponding hydrazone forms (see text), Alk, alkaline form.

and also in Me and DMF. These are placed at the range characteristic of the λ_{max} calculated for the hydrazone form.

In dyes **5A** and **7A**, additional hydrazone forms can occur resulting from the conjugation of the azo-pyrazolone residue with the naphthalimide ring.[16,26]

According to the calculations, the long wavelength band at 583–586 nm in DMF (Fig. 1) originated from the hydrazone form H_{III}, for which the calculated long wavelength λ_{max} was 568 nm. This is stabilised by solvation with the molecules of an aprotic solvent such as DMF. This phenomenon will be the subject of further investigations. Calculations were also carried out for the ionised structures, which often differ considerably from those run in Chx; calculations were for both azo and hydrazone forms. It was found that good correlation of calculated and determined λ_{max} values were obtained for the hydrazone derivatives (Fig. 3), which confirms the occurrence of these dyes in alkaline solution in this tautomeric form and also for the naphthalimide derivatives **5,7-A**. The influence of the carbonyl groups which lower the electron density on the β-azo nitrogen atom,[19] also relates to this.

In dyes **1A** and **2A** (naphthalene derivatives) in the hydrazone form, the nitrogen atom N(12) is a donor and the atom N(16) and O(18) of the lactam pyrazolone ring are acceptors. In the isomer **1A**, there is a stronger shift of electrons from the N(16) atom towards N(11), and the electron-acceptor character of the oxygen atom O(18) decreases. It is interesting to note that the naphthalene residue plays only a small part in the transfer of the electron density. The values on individual atoms are $<0{\cdot}02$.

In an alkaline environment, the influence of the naphthalene ring on the electron density of the molecule can be observed. The naphthalene ring is a donor centre, while the nitrogen atom N(11) is an acceptor. In the isomer **2A**, this phenomenon is of a very significant character. ‘Fragmentation’ of the molecule caused by the isolating influence of the nitrogen atom N(12) takes place at the same time, so polarisation of the lactam ring has no effect on the naphthalene residue. Dye **1A**, in which, like in other phenyl-azo-naphthalene dyes,[27] the naphthalene and lactam rings affect the changes of electron density in the excited state only to a small degree, behaves differently. The largest changes in the nitrogen atoms of the azo bond, which is also reflected in the changes of the calculated value and that determined by the spectrophotometric method dipole moment of the molecule.[28]

The naphthalimide dyes, however, behave differently. The acceptor substituents, i.e. the carbonyl groups in the 1,8-positions play an important role. They increase the acceptor character of the aromatic naphthalene ring, lowering its electron density. These differences follow from the fact that the dyes probably occur in the azo form (see Section 4). In **3A** the naphthalimide ring is an electron donor, isolated from the lactam ring, which has

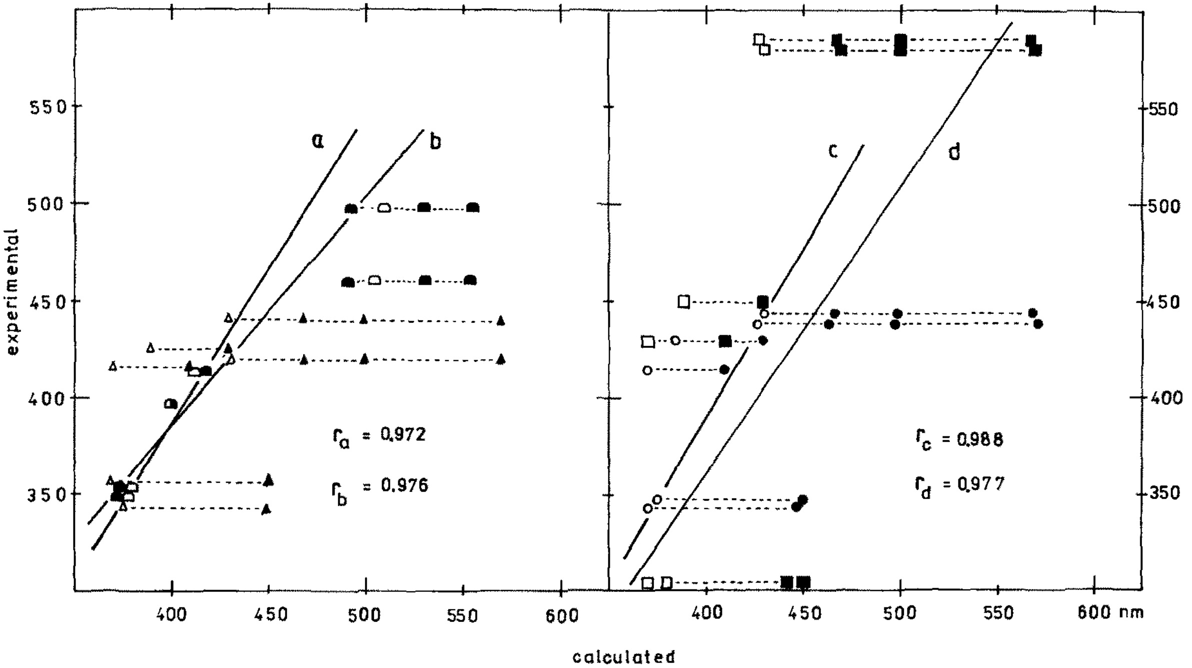


Fig. 3. $\lambda_{max}^{exp} = f(\lambda_{max}^{calc})$ relationship for dyes **1–5,7-A** in cyclohexane (a) (△, azo form; ▲, hydrazone form), in alkaline solutions (b) (⌓, azo form; ◖, hydrazone form), in methanol (c) (○, azo form; ●, hydrazone form) and in *N*,*N*-dimethylformamide (d) solutions (□, azo form; ■, hydrazone form). *r*, Correlation coefficient.

donor–acceptor properties with considerable excess of electrons in the excited state on the carbon atom (C(13) (donor). In the isomer **5A** (4-derivatives) the naphthalimide ring has donor–acceptor properties, with partial electron deficiency on the carbon atoms C(6) and C(18), i.e. in the positions of conjugation with the nitrogen atom N(11) (Fig. 2). The lactam ring acts as the acceptor for the atom N(12) of the azo bond. In the hydrazone form H_{III}, the donor–acceptor properties of the naphthalimide ring considerably increase the acceptor properties on the atoms C(9), C(1), C(3) and C(25). The lactam ring, however, has very little effect on the spectrum.

In an alkaline environment, in which these compounds occur in the hydrazone form (Section 3), the effects discussed here are increased and the observed changes are illustrated in Table 5.

It follows from the results presented that the bathochromic effect of the dyes **1A** and **5A** in relation to **2A** and **3A** is caused by the mixed donor–acceptor character of the naphthalene ring.

6 CONCLUSION

The 3- and 4-aminonaphthalimide acid azo dyes are oranges of different hues. Their colour depends to a large extent on the proportion of the azo or hydrazone form in which they can occur in normal circumstances. Simple phenyl derivatives of the pyrazolone dyes usually occur in the hydrazone form. On the basis of the investigations, it has been comfirmed that the naphthalimide dyes have, in the diffuse reflectance spectra of dyed fabric samples, an additional, strongly bathochromically shifted absorption band of considerable intensity, usually in the form of an inflexion point.

Investigations of model compounds confirmed that this band originates from stabilisation, on the fibre, of one of the additional hydrazone forms, in the creation of which the carbonyl group of the imido system takes part. This phenomenon has already been referred to in previous papers,[1,26] but without interpretation or theoretical confirmation. The bathochromically shifted absorption bands in the spectra of the dyes in solution in organic solvents suggested the presence of the hydrazone forms.

The placement of the bands ascribed to the azo and hydrazone forms was calculated by the PPP-MO method (Fig. 3, Table 4) and their compatibility with values determined in DMF (a solvent solvating one of the hydrazone forms (H_{III})) was demonstrated. Probably, both wool and polyamide perform a similar function to the strongly polar aprotic solvent. This phenomenon leads to a dulling of the shades of the dyes and to a widening of their absorption band. The calculations also indicate the possibility of the occurrence of the naphthalimide derivatives **3–5,7-A** in the azo form, while the naphthalene derivatives **1,2-A** occur, like most dyes of this type, exclusively in the form of hydrazone tautomers. In an alkaline environment (pH 14) all dyes occur in the ionised hydrazone form. These suppositions and determinations are confirmed by the relationship of the calculated and determined λ_{max} values for the dye solutes in cyclohexane and in alkaline solution (Table 4).

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