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Colour and Constitution of Azo Dyes Derived from 2-Thioalkyl-4,6-diaminopyrimidines and 3-Cyano-1,4-dimethyl-6-hydroxy-2-pyridone as Coupling Components

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SUMMARY

Three series of dyes have been prepared by coupling diazonium salts to 2-thioethyl- and 2-thio-n-butyl-4,6-diaminopyrimidine and to 3-cyano-1,4-dimethyl-6-hydroxy-2-pyridone. Infrared spectra and visible absorption spectroscopic behaviour indicate that the arylazopyrimidines exist in the azo tautomeric form, whereas the pyridone dyes exist as hydrazones. The light absorption properties of the yellow to orange arylazopyrimidines are well accounted for by PPP-MO calculations, although when substituents are present in the aryl ring ortho to the azo group, steric effects cause poorer agreement between theoretical and experimental λ_{max} *values. The colour properties of the bright yellow pyridone dyes can also be predicted well by PPP-MO theory. These dyes have higher molar absorption coefficients than the arylazopyrimidines, but this is due to their narrower absorption bands rather than to intrinsically higher absorption intensities.*

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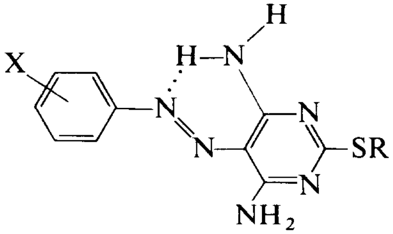
1. INTRODUCTION

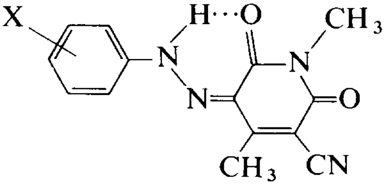
In recent years there has been considerable technical interest in dyes produced by coupling diazonium ions to 'enolisable' heterocyclic coupling components.[1] The so-called arylazopyrazolones are the oldest dyes of this type, and provide greenish-yellow to reddish-yellow shades in the acid and disperse classes. More recent developments have been dyes derived from hydroxypyridone coupling components, and since the mid-1960s more than 200 patents related to these have been published. It has been stated that the introduction of pyridone coupling components may be regarded as one of the most significant developments in dye chemistry over the last 20 years.[1]

Azo dyes of the pyrazolone and pyridone type are characterised by structures which can, at least in theory, exist in several different tautomeric forms. In the case of the pyrazolones, it is now accepted that under most conditions these exist predominantly in the hydrazone form.[2] This explains why the colours of these dyes are restricted to yellows and oranges. There is less unanimity of opinion about the azo pyridones, although their restricted colour range is also indicative of predominant hydrazone structures. When amino groups rather than hydroxyl groups are present in the heterocyclic coupler, useful yellow to orange dyes also result, as evidenced by arylazo derivatives of aminopyrazoles.[1] These may also exist as true aminoazo structures, or as iminohydrazones.

Aminopyridine and aminopyrimidine couplers have also been described for producing 'azo' dyes,[1] and recently the colour and constitution properties of some examples of such dyes have been examined.[3] We now report the synthesis and colour and constitution properties of a range of dyes derived from two aminopyrimidine couplers, series **1** and **2**, and a related series of dyes derived from a 6-hydroxy-2-pyridone



1 R = —C_2H_5
2 R = —$(CH_2)_3CH_3$



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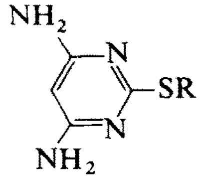
coupler, series **3**. The question of the most favoured tautomeric form in these series has also been considered.

2. RESULTS AND DISCUSSION

The coupling components required for synthesis of dye series **1** and **2** were prepared from 4,6-diamino-2-mercaptopyrimidine **4**. Thus alkylation of **4** with bromoethane and with 1-bromobutane gave **5** and **6** respectively. The properties of these intermediates are summarised in Table 1.



4 R = —H
5 R = —C_2H_5
6 R = —$(CH_2)_3CH_3$

A range of dyes was prepared by coupling various diazotised arylamines to **5** and **6** under aqueous acidic conditions. Characterisation data for the two series of pyrimidine dyes **1** and **2** are summarised in Tables 2 and 3 respectively.

The arylazopyridone dyes **3** were prepared by coupling a similar range of diazotised amines to 3-cyano-1,4-dimethyl-6-hydroxy-2-pyridone under aqueous alkaline conditions. Mass spectrometric, microanalytical and melting point data for the dyes are given in Table 4.

TABLE 1
Properties and Analytical Data for Aminopyrimidine Intermediates

Compound	*Recrystallisation solvent*	*Appearance*	*M.p. (°C)*	*Required (%)*				*Found (%)*			
				C	*H*	*N*	*S*	*C*	*H*	*N*	*S*
4	H_2O	Off-white needles	300	33·8	4·3	39·4	22·6	33·4	4·4	39·2	22·3
5	H_2O–EtOH	Off-white flakes	146–147	42·3	5·9	32·9	18·8	42·3	5·8	33·0	18·8
6	H_2O–EtOH	Off-white flakes	93–94	48·5	7·1	28·3	16·2	48·5	7·1	28·3	16·3

TABLE 2

Properties and Analytical Data for Dyes **1** Derived from 2-Thioethyl-4,6-diaminopyrimidine

Dye	*Substituents*	*Solvent*	*Appearance*	*M.p.* (*°C*)	*Required* (%)			*Found* (%)		
					C	*H*	*N*	*C*	*H*	*N*
1a	H	Toluene	Yellow flakes	188–189	46·67	4·24	27·21	46·60	4·20	27·20
1f	4′-NO_2	Toluene	Orange crystals	285–286	45·13	4·10	30·70	45·58	4·30	30·14
1n	2′-NO_2	Toluene	Orange crystals	264–265	45·13	4·10	30·70	45·09	4·17	30·62
1j	3′-NO_2	Toluene	Pale yellow needles	249–250	45·13	4·10	30·70	45·30	4·00	30·53
1c	4′-Cl	Toluene	Green–yellow needles	211–212	46·75	4·22	27·27	47·05	4·41	26·95
1l	2′-Cl	Toluene	Gold–yellow flakes	237–238	46·75	4·22	27·27	46·84	4·28	27·34
1h	3′-Cl	Toluene	Gold–yellow flakes	228–229	46·75	4·22	27·27	47·00	4·34	27·38
1b	4′-CH_3	Toluene	Yellow needles	198–199	54·14	5·59	29·14	54·48	5·31	29·35
1k	2′-CH_3	Toluene	Gold–yellow flakes	230–231	54·14	5·59	29·14	54·32	5·49	29·27
1g	3′-CH_3	Toluene	Orange–yellow needles	194–195	54·14	5·59	29·14	54·15	5·45	29·24
1d	4′-Br	Toluene	Yellow needles	224–225	40·80	3·71	23·79	41·06	3·60	23·92
1o	4′-NO_2, 2′-CH_3	Toluene	Orange–yellow crystals	384–385	46·83	4·54	29·41	47·15	4·40	29·12
1q	4′-NO_2, 2′-OCH_3	Dioxan	Red needles	385–386	44·69	4·33	28·07	45·21	4·06	28·31
1p	4′-NO_2, 2′-Cl	Dioxan	Red crystals	378–379	40·73	3·42	27·71	40·55	3·98	27·73
1r	2′,4′-di-NO_2	Dioxan	Red needles	375–376	39·56	3·30	30·77	39·62	3·32	30·60
1s	4′-NO_2, 2′-CN	Dioxan	Red needles	348–349	45·35	3·49	32·56	45·13	3·95	32·40
1u	2′,4′-di-NO_2, 6′-Br	Dioxan	Red needles	360–361	32·58	2·49	25·34	32·60	2·39	25·34
1t	4′-NO_2, 2′,6′-di-Cl	Dioxan	Red crystals	359–360	37·21	2·84	25·32	37·48	2·64	25·28
1e	4′-CN	Toluene	Orange–yellow flakes	238–239	52·17	4·35	32·78	52·22	4·47	32·76
1m	2′-CN	Toluene	Orange–yellow crystals	248–249	52·17	4·35	32·78	52·17	4·39	32·77
1i	3′CN	Toluene	Yellow needles	237–238	52·17	4·35	32·78	51·64	4·52	32·83

TABLE 3

Properties and Analytical Data for Dyes **2** Derived from 2-Thio-*n*-butyl-4,6-diaminopyrimidine

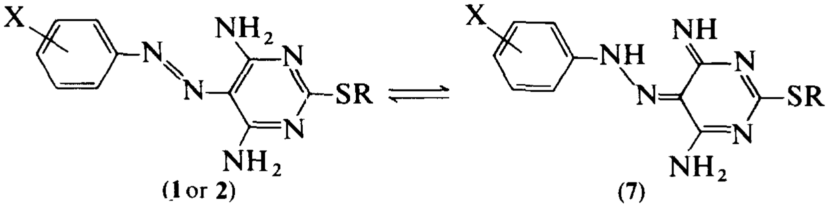
Dye	*Substituents*	*Solvent*	*Appearance*	*M.p.* (°*C*)	*Required* (%)			*Found* (%)		
					C	*H*	*N*	*C*	*H*	*N*
2a	H	Toluene	Yellow crystals	172–173	55·63	5·96	27·81	55·76	5·80	27·74
2f	4′-NO_2	Toluene	Orange crystals	192–193	48·42	4·90	28·24	48·51	4·89	28·36
2n	2′-NO_2	Toluene	Orange crystals	178–179	48·42	4·90	28·24	48·63	4·95	28·31
2j	3′-NO_2	Toluene	Pale yellow flakes	204–205	48·42	4·90	28·24	48·38	4·90	28·08
2c	4′-Cl	Toluene	Gold–yellow flakes	204–205	50·00	5·06	25·00	49·96	5·15	24·93
2l	2′-Cl	Toluene	Orange–yellow flakes	213–214	50·00	5·06	25·00	50·32	5·11	25·07
2h	3′-Cl	Toluene	Gold–yellow flakes	203–204	50·00	5·06	25·00	50·02	4·99	25·16
2b	4′-CH_3	Toluene	Yellow needles	179–180	56·96	6·33	26·58	57·00	6·32	26·69
2k	2′-CH_3	Toluene	Gold–yellow flakes	203–204	56·96	6·33	26·58	57·05	6·26	26·51
2g	3′-CH_3	Toluene	Yellow flakes	169–170	56·96	6·33	26·58	56·42	6·19	26·67
2d	4′-Br	Toluene	Gold–yellow flakes	209–210	44·21	4·47	22·21	43·89	4·51	21·73
2o	4′-NO_2, 2′-CH_3	Toluene	Yellow crystals	242–243	49·86	5·26	27·15	49·68	5·27	26·82
2q	4′-NO_2, 2′-OCH_3	Toluene	Red needles	243–244	47·75	5·04	25·99	47·78	4·95	25·83
2p	4′-NO_2, 2′-Cl	Toluene	Red crystals	245–246	44·09	4·20	25·72	44·04	4·09	25·43
2r	2′4′-di-NO_2	Dioxan	Purple needles	227–228	42·86	4·08	28·57	42·38	4·10	28·78
2s	4′-NO_2, 2′-CN	Dioxan	Red crystals	219–220	48·39	4·30	30·11	48·48	4·40	29·93
2u	2′,4′-di-NO_2, 6′-Br	Dioxan	Red crystals	274–275	35·74	2·34	23·83	35·46	2·08	23·53
2t	4′-NO_2, 2′,6′-di-Cl	Dioxan	Red crystals	238–239	40·38	2·65	23·61	40·55	2·56	23·62

TABLE 4
Properties and Analytical Data for Dyes **3** Derived from 3-Cyano-1,4-dimethyl-6-hydroxy-2-pyridone

Dye	*Substituent*	*Solvent*	*Appearance*	*M.p.* (°*C*)	*M*	*Required* (%)			*Found* (%)		
						C	*H*	*N*	*C*	*H*	*N*
3a	H	Dioxan	Orange crystals	257–258	268	62·68	4·56	20·89	62·69	4·53	20·87
3b	4′-NO_2	Acetone	Orange crystals	396–397	313	53·67	3·51	22·36	53·63	3·87	22·40
3k	2′-NO_2	Acetone	Yellow needles	387–388	313	53·67	3·51	22·36	53·18	3·55	22·28
3h	3′-NO_2	Acetone	Yellow crystals	359–360	313	53·67	3·51	22·36	53·83	3·66	22·33
3e	4′-Cl	Dioxan	Orange–yellow crystals	363–364	302	55·53	3·64	18·54	55·50	3·96	18·38
3l	2′-Cl	Dioxan	Yellow crystals	383–384	302	55·53	3·64	18·54	55·61	3·68	18·35
3i	3′-Cl	Dioxan	Yellow needles	357–358	302	55·53	3·64	18·54	55·55	3·69	18·99
3f	4′-CH_3	Dioxan	Orange needles	344–345	282	63·82	4·96	19·86	63·74	5·01	19·90
3d	4′-Br	Dioxan	Orange–yellow flakes	369–370	346	48·55	3·17	16·18	48·46	3·22	15·35
3g	4′-OCH_3	Dioxan	Red crystals	352–353	298	60·40	4·69	18·79	60·43	4·72	18·80
3c	4′-CN	Acetone	Yellow needles	395–396	293	61·43	3·75	23·89	61·35	3·79	23·87
3m	2′-CN	Acetone	Yellow crystals	389–390	293	61·43	3·75	23·89	61·52	3·82	23·95
3j	3′-CN	Acetone	Orange crystals	400–401	293	61·43	3·75	23·89	—	—	23·75
3n	4′-NO_2, 2′-CH_3	Dioxan	Yellow crystals	409–410	327	55·04	3·97	21·41	—	—	21·37
3o	4′-NO_2, 2′-OCH_3	Dioxan	Orange–yellow needles	384–385	343	52·47	3·79	20·41	52·40	3·82	20·35
3p	4′-NO_2, 2′-Cl	Dioxan	Green–yellow needles	391–392	347	48·41	2·88	20·17	48·45	2·86	20·09
3q	2′,4′-di-NO_2	Dioxan	Green–yellow flakes	405–406	358	46·92	2·79	23·46	46·72	2·80	23·42
3r	4′-NO_2, 2′-CN	Dioxan	Green–yellow flakes	391–392	338	53·25	2·95	24·85	51·65	3·78	24·64
3s	4′-NO_2, 2′,6′-di-Cl	Dioxan	Gold–yellow flakes	335–336	381	44·09	2·36	18·37	43·96	2·41	18·44

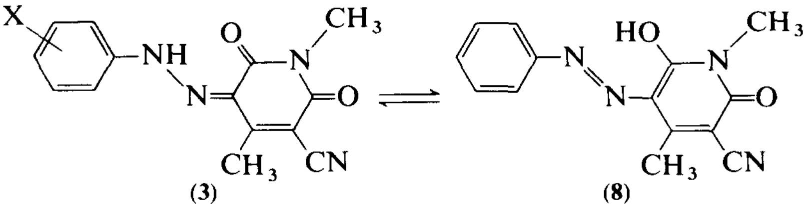
2.1. Structure of the dyes

The two most probable tautomeric forms for the pyrimidine dyes are the aminoazo form **1** or **2**, and the iminohydrazone form **7**.



The infrared spectroscopic properties of dyes **1** and **2** (KBr disc) show typical NH_2 group absorptions near 3400, 1630 and 1310 cm^{-1}, which correspond closely to similar absorptions for the parent couplers **5** and **6**. The close correspondence of the two series of spectra suggests that the dyes preferentially adopt the aminoazo tautomeric form. In support of this, it is found (Table 5) that the λ_{max} values for the dyes move progressively to longer wavelengths as the electron-withdrawing strength of substituents in the aryl ring increases. This is typical of a donor–acceptor aminoazo chromogen.[4] In a recent paper by Hutchings *et al.* various arylazo dyes based on diamino-pyridines, -pyrimidines and -pyrazines were assumed to exist exclusively in the azo tautomeric form, and the light absorption properties of these compounds could be explained satisfactorily by MO theory in terms of such an assumption.[3] The planar intramolecularly hydrogen-bonded structures **1** and **2** have thus been assumed in the following discussion of colour and constitution properties.

In contrast to the pyrimidine dyes, the arylazopyridone series **3** show clear evidence for preferential adoption of the hydrazone tautomeric form, rather than the alternative azo form **8**. The dyes show no detectable



hydroxyl absorption in their IR spectra (in Nujol and in $CHCl_3$), but do show two intense carbonyl peaks at 1600 and 1700 cm^{-1}. Parent has

TABLE 5

Experimental (Toluene) and Calculated Absorption Spectroscopic Properties of Pyrimidine Dyes **1** and **2**

Dye **1** *or* **2**	*Substituents*	σ^a	*Dyes* **1**				Dyes **2**	
			λ_{max} *(nm)*	*10*$^{-3}\varepsilon(f)^b$	$\lambda_{max}(f)^b$ *(nm)*	$\Delta\lambda^c$ *(nm)*	λ_{max} *(nm)*	*10*$^{-3}\varepsilon$
			(Exptl)		*(Calc.)*		*(Exptl)*	
a	H	0	389	25·3 (0·43)	396 (0·92)	−7	386	26·4
b	4'-CH$_3$	−0·170	391	25·9 (0·55)	398 (0·93)	−7	389	25·9
c	4'-Cl	0·227	397	26·2 (0·58)	395 (0·91)	2	395	28·5
d	4'-Br	0·232	398	27·2 (0·57)	395 (0·91)	3	397	28·0
e	4'-CN	0·660	409	27·2 (0·59)	413 (1·17)	−4		
f	4'-NO$_2$	0·778	423	30·6 (0·69)	421 (1·11)	2	426	28·5
g	3'-CH$_3$	0·07	385	24·1 (0·53)	396 (0·92)	−11	390	23·1
h	3'-Cl	0·37	395	20·9 (0·47)	396 (0·92)	−1	395	28·5
i	3'-CN	0·56	397	26·4 (0·55)	396 (0·96)	1		
j	3'-NO$_2$	0·71	400	26·0 (0·58)	398 (0·92)	2	400	26·9
k	2'-CH$_3$	—	397	23·9 (0·52)	397 (0·92)	0	398	26·1
l	2'-Cl	—	403	26·1 (0·53)	396 (0·91)	7	404	26·0
m	2'-CN	—	413	30·4 (0·60)	424 (0·86)	−11		
n	2'-NO$_2$	—	415	23·4 (0·56)	479 (0·52)	−64	416	23·1
o	4'-NO$_2$, 2'-CH$_3$	—	403	23·6 (0·54)	423 (1·12)	−20	403	24·1
p	4'-NO$_2$, 2'-Cl	—	445	29·5 (0·61)	420 (1·11)	25	445	30·2
q	4'-NO$_2$, 2'-OCH$_3$	—	450	25·8 (0·58)	445 (1·09)	5	450	27·4
r	2,4'-di-NO$_2$	—	468	30·9 (0·60)	479 (0·69)	−11	469	32·3
s	4'-NO$_2$, 2'-CN	—	470	31·1 (0·57)	449 (0·83)	21	472	33·2
t	4'-NO$_2$, 2',6'-di-Cl	—	435	21·7 (0·61)	420 (1·11)	15	434	22·4
u	2',4'-di-NO$_2$, 6'-Br	—	480	29·7 (0·66)	472 (0·68)	8	475	31·3

[a] Hammett sigma constant.

[b] Oscillator strength.

[c] $\Delta\lambda = \lambda_{max}(\text{exptl}) - \lambda_{max}(\text{calc.})$.

quoted characteristic peaks for the pyrazolone hydrazones at 1500–1520 cm^{-1} (C=N) and at 1230–1280 cm^{-1} (C=C—NH—),[2] and similar peaks were present in the spectra of dyes **3**. Additional evidence for the hydrazone tautomeric form is provided by the visible absorption spectra of the dyes, where it is found (Table 6) that electron-donating groups in the aryl ring exert a bathochromic shift on the visible band. This behaviour is typical of hydrazone dyes.[4]

2.2. Colour and constitution properties

Visible absorption spectra of the dyes **1**, **2** and **3** were measured in toluene with an SPM-5000 spectrophotometer, and the results are listed in Tables 5 and 6. Wavelength and absorbance data were fed into an APPLE-II-PLUS minicomputer and with a suitable program (CHSP2) were converted to molar absorption coefficient–wavenumber plots. The experimental oscillator strength was then computed from the integrated area under the curve according to the relationship:

$$f = 4{\cdot}139 \times 10^{-9} \int_{v_1}^{v_2} \varepsilon \, dv$$

where v_1 and v_2 are the limits of the absorption band (in wavenumbers) and f is the oscillator strength.

PPP–MO calculations were carried out with the aid of a program CP11 based on an original PPP package (COPRED) created at Leeds University (L. Cheng, 1982). Calculations were carried out on a PDP-11-34 microcomputer in the Department of Chemical Engineering, Dalian Institute of Technology. For these calculations parameters described elsewhere were used,[5] except in the case of the hydrazones **3**, for which new parameters were derived empirically. The new values are summarised in Table 7.

2.2.1. *The pyrimidine dyes* **1** *and* **2**

It can be seen from the data of Table 5 that the arylazopyrimidines exhibit the typical properties of a donor–acceptor azo chromogen. Although the pyrimidine ring in dyes **1** and **2** contains two strong electron-donor (—NH$_2$) groups, this is largely offset by the two electron-withdrawing ring nitrogen atoms. Thus the dyes are relatively hypsochromic, giving yellow to orange colours, even when the arylazo

TABLE 6

Experimental (Toluene) and Calculated Absorption Spectroscopic Properties of Dyes **3** Derived from 3-Cyano-1,4-dimethyl-6-hydroxy-2-pyridone

Dye	*Substituents*	σ^a	*Experimental*		*Calculated* λ_{max} *(nm)* $(f)^b$			
			λ_{max} *(nm)*	$10^{-3}\varepsilon(f)^b$	*Azo*	$\Delta\lambda^c$	*Hydrazone*	$\Delta\lambda^c$
3a	H	0	433	36·3 (0·61)	408 (0·69)	25	433 (1·52)	0
3b	4′-NO_2	0·778	435	44·2 (0·65)	389 (1·47)	46	433 (1·78)	2
3c	4′-CN	0·660	429	39·8 (0·62)	429 (1·07)	0	446 (1·80)	−17
3d	4′-Br	0·232	435	39·2 (0·67)	408 (0·66)	27	429 (1·55)	6
3e	4′-Cl	0·227	437	32·1 (0·51)	408 (0·67)	29	431 (1·54)	6
3f	4′-CH_3	−0·170	442	41·3 (0·69)	407 (0·72)	35	437 (1·51)	5
3g	4′-OCH_3	−0·268	457	36·9 (0·65)	408 (0·93)	49	449 (1·54)	8
3h	3′-NO_2	0·71	423	35·8 (0·57)	384 (1·40)	39	431 (1·69)	−8
3i	3′-Cl	0·37	430	33·8 (0·54)	408 (0·68)	22	433 (1·52)	−3
3j	3′-CN	0·56	423	26·7 (0·42)	414 (0·77)	9	429 (1·53)	−6
3k	2′-NO_2	—	437	30·3 (0·45)	379 (1·42)	58	448 (1·22)	−11
3l	2′-Cl	—	434	33·3 (0·52)	408 (0·70)	26	431 (1·53)	3
3m	2′-CN	—	425	39·8 (0·62)	436 (0·85)	−11	450 (1·21)	−25
3n	2′-CH_3, 4′-NO_2	—	431	24·2 (0·43)	382 (1·46)	49	435 (1·77)	−4
3o	2′-OCH_3, 4′-NO_2	—	455	42·4 (0·64)	449 (1·15)	6	466 (1·63)	−11
3p	2′-Cl, 4′-NO_2	—	434	41·9 (0·62)	390 (1·48)	44	432 (1·79)	2
3q	2′,4′-di-NO_2	—	448	36·6 (0·52)	475 (0·77)	−27	474 (1·36)	−26
3r	2′-CN, 4′-NO_2	—	435	47·6 (0·69)	493 (0·56)	−58	462 (1·39)	−27
3s	2′,6′-di-Cl, 4′-NO_2	—	425	29·6 (0·61)	389 (1·49)	36	429 (1·79)	−4

[a] Hammett sigma constant.

[b] Oscillator strength.

[c] $\Delta\lambda = \lambda_{max}(\text{exptl}) - \lambda_{max}(\text{calc.})$.

TABLE 7

PPP-MO Parameters for the Hydrazone Tautomeric Form of 3

Bond X—Y	$Z_Y{}^a$	$\beta_{X-Y}{}^b$ (*eV*)	$VSIP_Y{}^c$ (*eV*)	$A_Y{}^d$ (*eV*)	$r_{X-Y}{}^e$ (*Å*)
>C=O	1	−2·46	15·0	0·71	1·22
>C=O (hydrogen bonded)	1	−2·46	17·7	2·47	1·22
=N—NH—	2	−2·62	21·0	9·26	1·35
−C=N—	1	−2·90	15·0	0·97	1·26
−HN—C<	1	−2·65	11·16	0·03	1·38

[a] Core charge.

[b] Resonance integral.

[c] Valence state ionisation potential.

[d] Electron affinity.

[e] Bond length.

residue contains strong electron-withdrawing groups (e.g. the 2,4-dinitro dye **1r** absorbs at only 468 nm, and is orange). In addition, the molar absorption coefficients are in the region of 20 000–30 000 litre mol^{-1} cm^{-1}, which is typical of aminoazobenzene dyes. Comparison of the dyes **1** and **2** shows not unexpectedly that the alkyl group attached to sulphur has a negligible influence on the absorption spectrum. Hammett sigma correlations with the observed absorption wavelengths are shown in Fig. 1, and it can be seen that these are poor, although some improvement is observed if *meta* and *para* substituents are considered separately. The positive slope of the plots indicates the donor–acceptor character of the chromogen, in which the diaminopyrimidine ring plays the role of electron donor. Dyes **1a–1j** and **2a–2j** contain no substituents in the aryl ring *ortho* to the azo group, and thus may reasonably be regarded as planar. Comparison of the experimental and calculated λ_{max} values for these dyes shows that the PPP method duplicates the light absorption properties remarkably well, with a maximum discrepancy of 11 nm. Oscillator strength trends are also reasonably well accounted for (allowing for the usual near-doubling of the calculated value relative to the observed value).

In the dyes **1k–1u**, bulky *ortho* substituents are present and this will cause some loss of planarity. Consequently the agreement between observed λ_{max} values and calculated values is less satisfactory, the latter

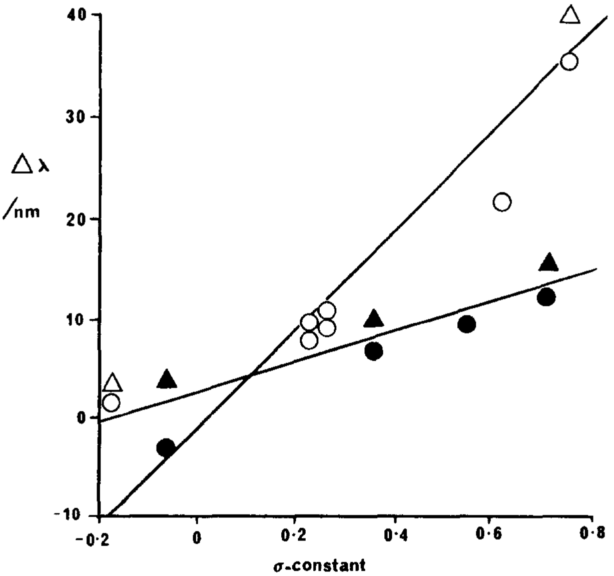


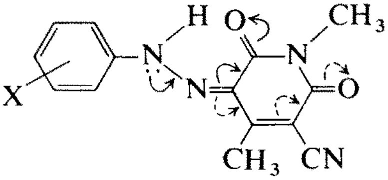
Fig. 1. Relationship between $\Delta\lambda$ and the Hammett sigma constant of aryl substituents for dyes **1** and **2**. $\Delta\lambda = \lambda_{max}$(substituted dye) − λ_{max}(unsubstituted dye); ●, *meta* substituted **1**; ▲, *meta* substituted **2**; ○, *para* substituted **1**; △, *para* substituted **2**

being based on an assumed planar geometry. For example, the calculated value for the 2-nitro dye **1n** is 479 nm, whereas the observed value is 415 nm. In simple aminoazobenzene dyes, a single *ortho* substituent in the acceptor ring does not usually cause a significant loss of planarity because the molecule can rotate about the C—N bond to relieve strain.[6] However, the presence of two *ortho* amino groups in the donor ring of dyes **1** and **2** may accentuate steric crowding about the azo group, and thus it needs only one *ortho* group in the acceptor ring to cause loss of planarity. This can be seen by comparing dye **1f** with **1o**, both of which contain a *para*-nitro group, whereas the latter also has an *ortho*-methyl group in the acceptor ring. The former dye absorbs at 423 nm (calc. 421 nm), whereas the latter absorbs at 403 nm (calc. 423 nm). The loss of planarity in the latter case is also evidenced by the low molar absorption coefficient (23 600 litre mol^{-1} cm^{-1}) compared with **1f** (30 600 litre mol^{-1} cm^{-1}).

Steric crowding is further accentuated when two *ortho* substituents are present in the acceptor ring. Thus the 2,6-dichloro-4-nitro derivative **1t** has λ_{max} = 435 (ε_{max} = 21 700 litre mol^{-1} cm^{-1}), and absorbs at shorter wavelengths and with a lower intensity than the corresponding 2-chloro-4-nitro dye **1p**, even though the former has an additional electron-withdrawing chlorine atom in the acceptor ring.

2.2.2. *Pyridone dyes*, 3

The 'azo' dyes **3** derived from 3-cyano-1,4-dimethyl-6-hydroxy-2-pyridone show little variation in colour, and are yellow to orange. Thus the λ_{max} values measured in toluene range from 423 nm to 457 nm (Table 6). This is to be expected for hydrazone structures, in which the principal chromophore encompasses the pyridone ring and the hydrazone residue only, substituents in the aryl ring exerting only a secondary effect. In such systems the visible absorption band corresponds to a transition in which electron density is transferred from the hydrazone —NH group to the pyridone carbonyl groups:



Thus one would anticipate that electron-withdrawing groups in the aryl ring should cause a hypsochromic shift of the absorption band, and this is confirmed by the data of Table 6 in the case of *meta* substituents. In the *para* position, the strong —*M* nitro group in fact exerts a small bathochromic effect, which may be due to the counteracting influence of extended conjugation. The *para*-cyano group, however, exerts a hypsochromic effect. When +*M* groups are present in the *para* position, a more significant bathochromic shift of the absorption band is observed, and the most bathochromic dye in the series is the *para*-methoxy derivative **3g**, with λ_{max} 457 nm in toluene. The weak +*M* groups chlorine and bromine also provide small bathochromic shifts, in spite of their strong −*I* effects. As expected, halogen atoms in the *meta* position have a hypsochromic effect. A plot of wavelength shift against Hammett sigma constants for *para* and *meta* groups shows a poor correlation, but the general negative slope of the plot confirms the proposed direction of charge migration in these dyes (Fig. 2), and may be compared with a similar plot for dyes **1** and **2** (Fig. 1).

The *ortho* substituted derivatives **3k–3s** show similar trends to the

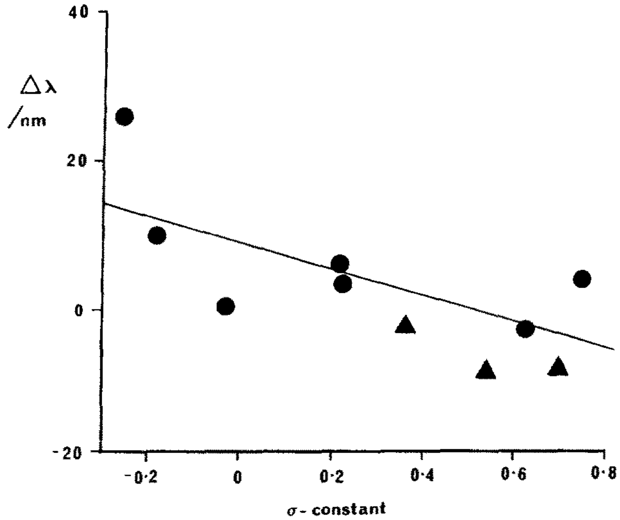


Fig. 2. Relationship between $\Delta\lambda$ and the Hammett sigma constant of aryl substituents for dyes **3**. $\Delta\lambda = \lambda_{max}$(substituted dye) − λ_{max}(unsubstituted dye); ▲, *meta* substituents; ●, *para* substituents.

para substituted derivatives, where a group with a $+M$ effect exerts a dominating bathochromic effect, as does an *ortho*-nitro substituent. Steric effects are only counteractive to these observations in the case of the 2,6-dichloro-4-nitro derivative **3s** when the two chlorine atoms induce a significant hypsochromic shift.

PPP-MO calculations were carried out for both the hydrazone and azo tautomeric forms of the pyridone dyes, and the results are summarised in Table 6. It is apparent that the calculated λ_{max} values of the hydrazone forms are in much closer agreement with experiment than values for the azo tautomeric forms. Thus the largest discrepancy between theory and experiment was 17 nm for the *meta* and *para* substituted dyes **3a–3j**, and in general agreement between calculated and observed λ_{max} values was within ±8 nm. For corresponding azo structures the discrepancy was generally of the order of *ca* 30 nm. The correlation between calculated and experimental λ_{max} values for the *ortho* substituted hydrazone forms **3k–3s** was poorer than for the *meta* and *para* dyes, presumably because of the intrusion of steric crowding.

One of the most interesting features of the spectra of the dyes **3**, and a feature of considerable technical value, is the relatively high intensity of these dyes. Thus values of ε_{max} near 40 000 litre mol^{-1} cm^{-1} are common, and are approximately 30% higher than the pyrimidine azo dyes **1** and **2**. Comparison of the oscillator strengths, however, shows that these are not significantly higher than those for the arylazopyrimidines **1** and **2**, and this may be attributed to the fact that the hydrazones have narrower absorption bands than the azo dyes. Thus the two types of dye have a similar peak area, which is proportional to oscillator strength, but the pyridone dyes have higher ε_{max} values, which are proportional to peak height. The practical effect of this is that the hydrazones **3** provide characteristically bright colours on textile substrates.

The oscillator strengths for dyes **3** calculated by the PPP-MO method are higher than might be expected in comparison with corresponding values for dyes **1**, and do not correlate well with observed trends, both in the case of the *meta* and *para* substituted dyes and with the *ortho* substituted dyes **3k**–**3s**. This tends to be a recognised weakness of the PPP method, at least when parameters derived exclusively from λ_{max} considerations are employed.

It is also observed that a single *ortho* substituent in the aryl residue of hydrazone dyes **3** does not generally influence the absorption intensity greatly, unlike the situation found with azo dyes **1** and **2**. (The 2-methyl-4-nitro dye **2n** is an exception, however, and the reasons for this are not clear.) Steric crowding does become apparent in the 2,6-dichloro-4-nitro dye **3s**, when the molar absorption coefficient falls to 29 600 litre mol^{-1} cm^{-1}. A molar absorption coefficient as high as 47 600 litre mol^{-1} cm^{-1} can be obtained in the case of the 2-cyano-4-nitro dye **3r**, whilst the yellow colour is retained (λ_{max} 435 nm) together with the characteristic brightness of this class of dye.

3. EXPERIMENTAL

Melting points are uncorrected. Infrared spectra were recorded on a Hitachi 260-5U spectrophotometer, using Nujol mull, potassium bromide discs, or chloroform solution. Visible absorption spectra were recorded with an SPM-5000 spectrophotometer, using toluene as solvent.

4,6-Diamino-2-mercaptopyrimidine **4** was prepared according to the literature method, by refluxing malononitrile and thiourea in ethanol in the presence of sodium ethoxide, and then neutralising the solution with acid.[7]

2-Thioethyl-4,6-diaminopyrimidine **5** was prepared by heating 4,6-diamino-2-mercaptopyrimidine with bromoethane in ethanolic sodium ethoxide solution.[8] 2-Thio-*n*-butyl-4,6-diaminopyrimidine **6** was prepared similarly, using 1-bromobutane as alkylating agent.

The azo dyes **1** and **2** were prepared by conventional azo coupling between **5** and **6** respectively and various diazotised arylamines under aqueous acidic conditions. The dyes were purified by recrystallisation from the solvents specified in Tables 2 and 3, and the purities were confirmed by tlc analysis (silica/toluene–AcOH, 4:1), and microanalysis. Relevant data are summarised in Tables 2 and 3.

3-Cyano-1,4-dimethyl-6-hydroxy-2-pyridone was commercial material provided by the Shangshi Dyestuff Company, and was purified by recrystallisation twice from aqueous ethanol.

The hydrazone dyes **3** were prepared by coupling various diazotised arylamines to 3-cyano-1,4-dimethyl-6-hydroxy-2-pyridone under aqueous alkaline conditions. The dyes were recrystallised from acetone–dioxan, and their purity confirmed by tlc analysis (silica/toluene–AcOH, 4:1), and microanalysis. Mass spectrometric, microanalytical and melting point data are summarised in Table 4.

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