Dyes and Pigments **10** (1988) 13–22

Syntheses and Some Properties of Infrared-Absorbing Croconium and Related Dyes

Shigeo Yasui

Nippon Kankoh-Shikiso Kenkyusho Co. Ltd, Nishiki, Fujita,
Okayama 701–02, Japan

Masaru Matsuoka* & Teijiro Kitao

Department of Applied Chemistry, University of Osaka Prefecture, Sakai,
Osaka 591, Japan

(Received 15 January 1988; accepted 24 February 1988)

ABSTRACT

The correlations between the structure and some properties of croconium and related cyanine dyes are discussed. It is shown by PPP MO calculations that the croconium dyes have the same chromophoric system as cyanines. The λ_{max} *of the croconium dyes undergoes a bathochromic shift of about 120 nm compared with the corresponding cyanine dyes. This shift can be calculated by the PPP MO method. Negative solvatochromism is observed for croconium dyes. Croconium dyes generally have better solubility than squarylium dyes in organic solvents and have good lightfastness in solvents, greatly improved by adding nickel complex as a stabilizer.*

1 INTRODUCTION

Some infrared-absorbing cyanine dyes have been developed as sensitizers for photographic silver halide, organic photoconductors for xerography, dye laser materials and optical information recording media for laser printers and laser optical disks.[1] The syntheses of polymethine cyanine dyes such as squarylium[2,3] and croconium dyes[4] have been reported, and the structural analysis of squarylium dyes[4] by means of X-ray has also been reported,[5,6] but correlations between their colour and structure have not yet been studied in detail.

* To whom all correspondence should be addressed.

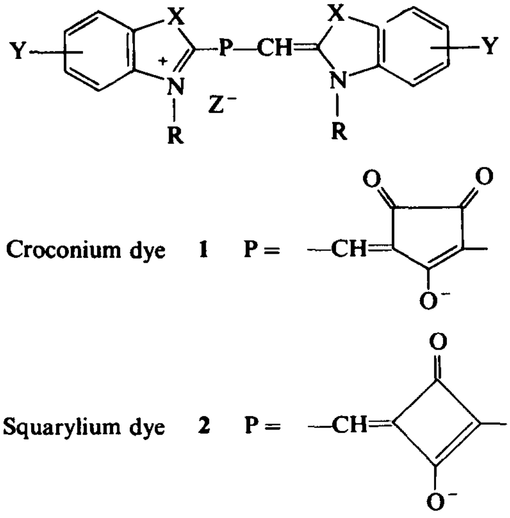
Dyes and Pigments 0143-7208/88/$03·50

In this paper, the syntheses and characteristics of croconium dyes and squarylium dyes are reported, and the colour–structure relationship of the dyes in comparison with the corresponding cyanine dyes is discussed on the basis of the PPP MO calculation method. In addition, some physical properties of these dyes, such as lightfastness and solubility in organic solvents, and some applications are reported.

2 RESULTS AND DISCUSSION

2.1 Effect of substituents in the methine chains on the absorption spectra

The structures of the cyanine dyes studied are shown in Fig. 1. The observed absorption spectra together with the calculated results are shown in Table 1. The value of $\Delta\lambda_{\text{obs.}-\text{calc.}}$, which shows the difference between the observed



Cyanine dye 3 P = -(CH=CH)_2

	X	Y
a	CH=CH	H
b	CMe_2	Benzo
c	Se	H
d	S	H
e	CMe_2	H

Fig. 1. Cyanine-type dyes used in this work.

TABLE 1
Effect of Methine Substituents on the λ_{max} of Dyes 1–3

Dye	*X*	*R*	*Calculated* λ_{max} *(nm)*	*Observed*[a] λ_{max} *(nm)*	$\Delta\lambda_{obs-calc.}$	*Observed*		
						$\Delta\lambda_{1-2}$	$\Delta\lambda_{1-3}$	$\Delta\lambda_{2-3}$
1a	CH=CH	Et	731	832	101			
2a	CH=CH	Et	680	724	44	108		
3a	CH=CH	Et	671	706	35		126	18
1d	S	Et	709	771	62			
2d	S	Et	650	663	13	108		
3d	S	Et	617	651	34		120	12
1e	CMe_2	Me		764				
2e	CMe_2	Me		629		135		
3e	CMe_2	Me		638			126	−9

[a] Measured in acetonitrile.

and calculated λ_{max} values, is in the range 13–86 nm. The MO calculation results can be considered to be reasonable from these results.

Substituent effect on λ_{max} was evaluated by $\Delta\lambda_{1-2}$ and $\Delta\lambda_{2-3}$ values in Table 1. The introduction of a croconic moiety into the conjugated methine chains produced a 120–126 nm bathochromic shift of λ_{max}. On the other hand, that of a squarylic moiety produced a bathochromic shift of only 12 nm in **2d** and 18 nm in **2a**, respectively, and a 9 nm hypsochromic shift in **2e**. It was found that the croconium dyes **1** absorbed at much longer wavelength than the corresponding squarylium dyes **2**, and cyanine dyes **3**, and dye **1** absorbed in the near-infrared region over 700 nm.

Figure 2 shows typical absorption spectra of dyes **1a**–**3a**. The absorption maximum lies at longer wavelength in the order **1a** > **2a** > **3a**. The halfwidth values at λ_{max} are 52 nm (1·10) in dye **1a**, 36 nm (0·75) in dye **2a** and 47 nm (1·00) in dye **3a**, respectively. Relative halfwidth values based on the parent dye are shown in parentheses. The results showed that the narrowest absorption band is obtained with dye **2a**, and dye **1a** has a much broader absorption band in comparison with the cyanine dye **3a**. A narrow absorption band is important for dye lasers and recording media for laser optical storage.

The π-electron density changes accompanying the first excitation of dyes **1d** and **3d** are shown in Fig. 3. The π-electron density of dye **1d** decreases at the starred positions and increases at the unstarred positions, as defined by Dewar's rule. From the results, the croconium dye can be evaluated as having the same chromophoric system as that of the cyanine dye **3d**.

Dye **1** can be considered to have two carbonyl groups as the electron-

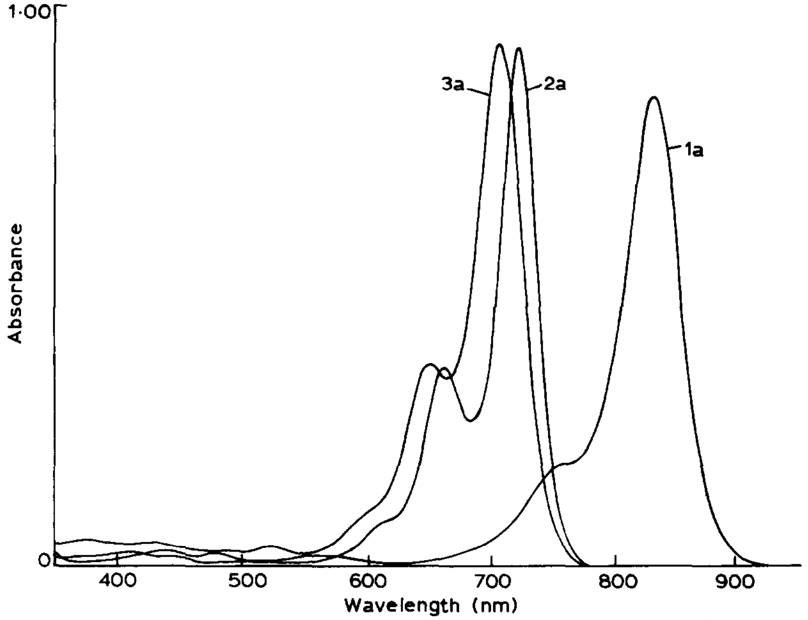
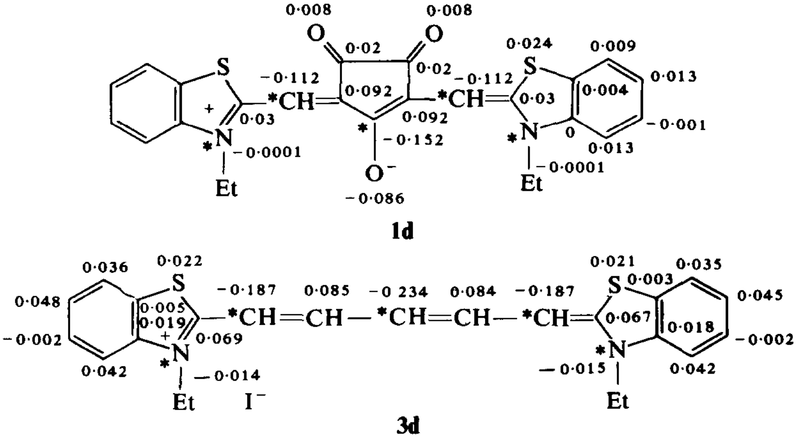


Fig. 2. Absorption spectra of dyes **1a–3a** at the concentration of 4×10^{-6} mol litre^{-1} in acetonitrile.

withdrawing substituents at the unstarred positions and the oxide as the electron-donating substituent at the starred position. These substituent effects would be expected to produce a large bathochromic shift of λ_{max} in comparison with dyes **3**. Dye **2** has one carbonyl group at the unstarred position and the oxide at a starred position. It can thus be expected that dye **1** will absorb at much longer wavelength than dye **2** which is also expected to



1d

3d

Fig. 3. The π-electron density changes accompanying the first excitation of dyes **1d** and **3d**.

absorb at longer wavelength than the cyanine dye **3**. These observations can be confirmed by the observed λ_{max} values shown in Table 1.

2.2 Effects of hetero-ring substituents X and solvents on the absorption spectra

The effects of hetero-ring substituents X and solvents on the absorption spectra are shown in Table 2. The bathochromic effect of substituent X on the λ_{max} is in order of **a** (CH═CH) > **b** (benzo) > **c** (Se) > **d** (S) > **e** (CMe_2), which is attributed to the larger π-systems, followed by the electron-donating property of the hetero-atom. These dyes showed negative solvatochromism and absorbed at much longer wavelength in the order liquid crystal > dichloromethane > acetonitrile > methanol. The effect of the polarity of solvents on λ_{max} is illustrated by the $\Delta\lambda$ values determined by the difference between data in dichloromethane (λCH_2Cl_2) and in methanol (λCH_3OH). The $\Delta\lambda$ values decrease in the order **1** (29–43 nm) > **2** (9–27 nm) > **3** (10–16 nm). This is caused by the dipole–dipole interaction between dyes and solvent. Dye **1** has an additional three substituents (two carbonyl and one oxide) in comparison with dye **3**. These substituents can strongly interact with the polar solvent to stabilize the ground state, that causing the hypsochromic shift. The additional two polar substituents in dye **2** also play

TABLE 2
Effects of Substituents and Solvents on the Absorption Spectra of Dyes **1**–**3**

Dye	*X*	*Y*	*Z*	*R*	λ_{max} *(nm)*				$\Delta\lambda$[b]	$\varepsilon \times 10^{-5}$ CH_3CN
					CH_3OH	CH_3CN	CH_2Cl_2	*LC*[a]		
1a	CH═CH	H		Et	807	832	850	865	43	2·22
1b	CMe_2	Benzo		Me	772	791	804	824	32	1·08
1c	Se	H		Et	771	789	804	808	33	2·00
1d	S	H		Et	755	771	784	795	29	2·23
1e	CMe_2	H		Me	746	764	775		29	0·97
2a	CH═CH	H		Et	707	724	734		27	2·63[c]
2d	S	H		Et	649	663	669		20	2·56[c]
2e	CMe_2	H		Me	625	629	634		9	2·99[c]
3a	CH═CH	H	I	Et	707	706	718		11	2·36
3b	CMe_2	Benzo	ClO_4	Me	676	674	692		16	2·19
3c	Se	H	I	Et	662	661	674		12	2·28
3d	S	H	I	Et	652	651	662		10	2·37
3e	CMe_2	H	ClO_4	Me	638	638	652		14	2·42[c]

[a] Measured in a liquid crystal of ZLI – 1565.

[b] $\Delta\lambda = \lambda_{CH_2Cl_2} - \lambda_{CH_3OH}$.

[c] Measured in methanol.

the same role and produce a smaller hypsochromic shift than in dye **1**. It is well known that the ground state has much more polar structure than the excited state in these cyanine dyes,[7] and negative solvatochromism is generally observed for these ionic dyes.

It is also well known that steric hindrance can be evaluated by the ε values of similar types of dyes. The ε value of dye **1e** is 0·97 and it is 1·08 for **1b**, while that of **2e** is 2·99, 2·19 for **3b** and 2·42 for **3e**. Steric hindrance between the geminal methyl groups and the carbonyl groups in dyes **1b** and **1e** are proposed. It was generally observed that the ε values of dye **1** are smaller than those of dyes **2** and **3**, which may be caused by the rather broad absorption band of dye **1**, compared with dyes **2** and **3** as discussed above.

2.3 Effect of solvent on the solubility

Solvent effects on the solubility of cyanine dyes are summarized in Table 3. The solubility decreases in the order **3** > **1** > **2** in methanol, cyclohexanone and the mixed solvent methanol–chloroform, whereas the order is **1** > **3** > **2** in chloroform. Dye **2** is scarcely soluble in all solvents but dye **1** has good solubility in non-polar solvents. The solubilities of these dyes are largely improved in the mixed solvent in comparison with those in each individual solvent. Dyes **1a** and **3a** have good solubility in the mixed solvent and these dye solutions can be applied to make a wet-coating thin film for the heat-mode optical recording media for semiconductor laser disks.

2.4 Effect of substituent on the lightfastness

The effect of substituents on the lightfastness of dyes **1–3** is shown in Fig. 4. The lightfastness is in the order E > D > C > B > A and e > d > b > c > a.

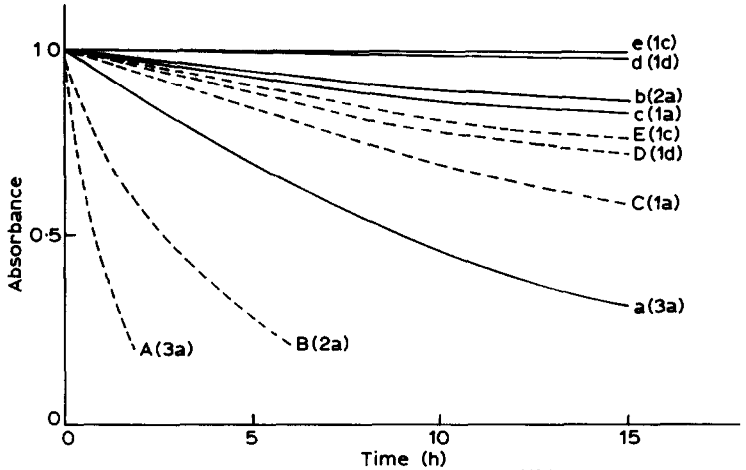
TABLE 3

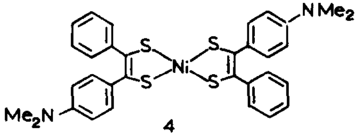
Effects of Solvents on the Solubility of Dyes **1–3**

Dye	*X*	*Y*	*Z*	*R*	*Solubility* ($g\ litre^{-1}$)[a]			
					CH_3OH	$C_5H_{10}CO$	$CHCl_3$	CH_3OH–$CHCl_3$[b]
1a	CH=CH	H		Et	0·18	0·08	4·10	10·75
1b	CMe_2	Benzo		Me	0·56	4·27		
1c	Se	H		Et	0·02	0·42	1·66	3·69
1d	S	H		Et	0·49	1·00		
2a	CH=CH	H		Et	0·008	0·003	0·04	0·18
3a	CH=CH	H	I	Et	1·13	0·48	0·33	11·11

[a] Measured at 25°C after stirring for 4 h.

[b] Mixed solvents, 1:1 v/v.





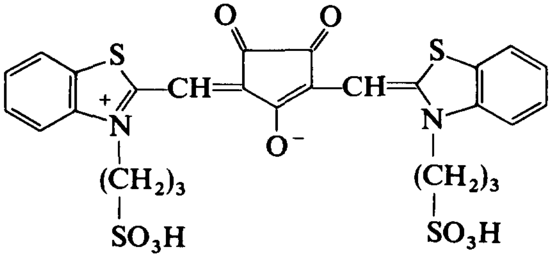
4

Fig. 4. Effect of substituents on the lightfastness of cyanine dyes in solution. Irradiated by a 1·2 kW xenon lamp. A–E: dye 1 × 10^{-4} mol/l in CH_2Cl_2; a–e: dye with nickel complex[4] (2:1) in CH_2Cl_2.

The dye solutions of a–e show better lightfastness in comparison with the corresponding solutions A–E. This means that the nickel complex **4** acts as an effective quencher and hence improves the lightfastness. In general the croconium dyes **1** have better lightfastness than squarylium dyes **2**, which in turn have better lightfastness than the cyanine dyes **3**. Croconium dyes **1c** and **1d** with nickel complex did not fade after an irradiation of 15h.

2.5 Adsorptivity of cyanine dyes on zinc oxide

The adsorptivity of cyanine dyes on zinc oxide is one of the most important factors in securing the compensated light sensitivity in xerography systems. The adsorption ratio is 14·1% in dye **3d**, 20·7% in dye **1d**, but 80·5% in dye **1f**.



1f
λ_{max} 760 nm in methanol

TABLE 4
Identification of Cyanine Dyes

Dye	*Molecular formula*	*MW*	*M.p.*[a] (*°C*)	*Analysis, obs. (calcd.) (%)*		
				C	*H*	*N*
1a	$C_{29}H_{24}N_2O_3.H_2O$	466	248–249[a]	74·55 (75·00)	5·47 (5·58)	5·99 (6·03)
1b	$C_{37}H_{32}N_2O_3.H_2O$	570	192–193	76·91 (77·89)	5·58 (5·96)	4·89 (4·91)
1c	$C_{25}H_{20}N_2O_3Se_2.H_2O$	572	277[a]	52·49 (52·45)	3·64 (3·85)	4·97 (4·90)
1d	$C_{25}H_{20}N_2O_3S_2.H_2O$	478	252–253	62·59 (62·76)	4·08 (4·60)	5·77 (5·86)
1e	$C_{29}H_{28}N_2O_3.H_2O$	470	190–191	74·92 (74·04)	6·34 (6·38)	6·33 (5·96)
2a	$C_{28}H_{24}N_2O_2$	420	>300	79·47 (80·00)	5·62 (5·71)	6·33 (6·67)
2d	$C_{24}H_{20}N_2O_2S_2$	432	295[a]	65·86 (66·67)	4·69 (4·63)	6·96 (6·48)
2e	$C_{28}H_{28}N_2O_2.H_2O$	442	>300	75·88 (76·02)	7·02 (6·79)	6·13 (6·33)
3a	$C_{27}H_{27}IN_2$	506	261–262[a]	63·53 (64·03)	5·27 (5·34)	5·36 (5·53)
3b	$C_{35}H_{35}ClN_2O_4$	582·5	252–253[a]	72·41 (72·10)	5·94 (6·01)	5·55 (4·81)
3c	$C_{23}H_{23}IN_2Se_2$	612	232–233[a]	45·05 (45·10)	3·58 (3·76)	4·45 (4·58)
3d	$C_{23}H_{23}IN_2S_2$	518	248–249[a]	52·78 (53·28)	4·26 (4·44)	6·00 (5·41)
3e	$C_{27}H_{31}ClN_2O_4$	482·5	222–223	66·71 (67·15)	6·82 (6·42)	6·88 (5·80)

[a] Decomposition.

It was found that dye **1d** has better adsorptivity than dye **3d**, and the introduction of 3-sulfopropyl groups in **1f** instead of ethyl groups in **1d** greatly improved the adsorptivity to zinc oxide; dye **1f** can be applied as a sensitizer for xerography.

3 EXPERIMENTAL AND MO CALCULATION METHOD

The dyes used were synthesized in Nippon Kankoh-Shikiso Kenkyusho Co. Ltd. Dye **1** was synthesized following the procedures reported by Depoorter *et al.*,[4] dye **2** by Sprenger & Ziegenbein,[2] and dye **3** by Ogata.[8] The dyes **1a**, **1b**, **1c**, **1d**, **1e** and **2a** were purified by column chromatography over silica gel followed by recrystallization. The others were purified by repeated recrystallization. The results of elemental analysis were consistent with the theoretical values as summarized in Table 4. Some dyes have one molecule of water of crystallization which was determined by differential thermal analysis.

Absorption spectra were measured in acetonitrile at a concentration of $2{\cdot}5 \times 10^{-6}$ mol litre^{-1} using a Hitachi U-3400 spectrophotometer. Solubility was measured by the spectroscopic method using the saturated solution at 25°C. The fading test was performed in dichloromethane at a concentration of 1×10^{-4} mol litre^{-1} by irradiation with a 1200 W xenon lamp, using a Shimadzu fademeter. Adsorptivity of dyes to zinc oxide was determined by the spectroscopic method. The mixture of dye (5 mg) and ZnO (1 g) in acetonitrile was stirred for 6 h with a magnetic stirrer and the decrease of optical density of dye determined at λ_{max}. The modified PPP MO calculations were carried out by the method described previously.[9]

ACKNOWLEDGEMENT

The authors would like to express their thanks to Mr Mitsuru Nakamura and Mr Yuzo Kato of Nippon Kankoh-Shikiso Kenkyusho Co. Ltd for their cooperation.

REFERENCES

1. Yasui, S., *Shikizai Kyokai-shi*, **60** (1987), 212.
2. Sprenger, V. H. E. & Ziegenbein, W., *Angew. Chem.*, **78** (1967), 581.
3. Tanaka, M., Sekiguchi, T., Kawabata, Y., Nakamura, T. & Manda, E., *Nippon Kagakukai-shi* (1987), 714.
4. Alfred, G. *et al.*, Ger. Offen. (Agfa-Gevaert AG), 1 930 224 (1970).

5. Kobayashi, Y., Goto, M. & Kurahashi, M., *Bull. Chem. Soc. Jpn*, **59** (1986), 311.
6. Bernstein, J., Kendra, M. T. & Eckhardt, C. J., *J. Phys. Chem.*, **90** (1986), 1069.
7. Griffiths, J., *Colour and Constitution of Organic Molecules.* Academic Press, London, 1976.
8. Ogata, K., *Kanko-Shikiso.* Sankaido Co. Ltd, Tokyo, 1933.
9. Yasui, S., Matsuoka, M. & Kitao, T., *Shikizai Kyokai-shi*, **61** (1988), 375.