Dyes and Pigments 3 (1982) 273–280

METHINE CHAIN SUBSTITUTED STYRYL CYANINE DYES—PART I

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(Received: 17 June, 1981)

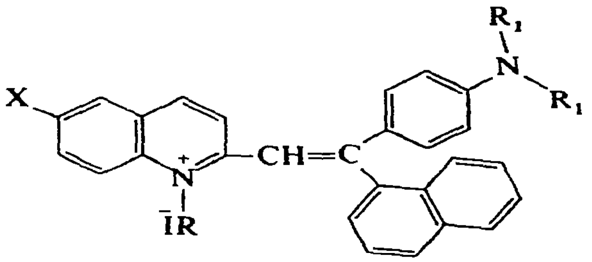
SUMMARY

Twenty-seven styryl dyes having 1-naphthyl and 2-naphthyl substituents at the β-carbon atom (β- to the heterocyclic moiety) of the methine chain have been prepared by condensing p*-diethylaminophenyl 2-naphthyl ketone,* p*-dimethylaminophenyl 1-naphthyl ketone and* p*-dimethylaminophenyl 2-naphthyl ketone with quaternised salts of variously substituted quinaldines and lepidine. The dyes obtained show hypsochromic shifts in absorption maxima compared with their analogues having no substituent in the methine chain wherever comparable data have been available in the literature. The photosensitisation properties of the dyes have also been studied.*

1. INTRODUCTION

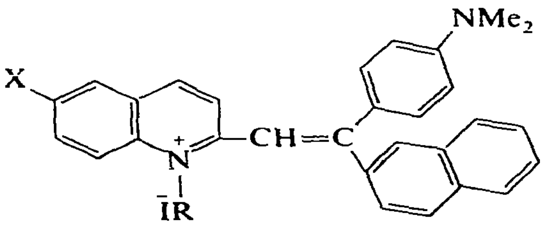
Styryl cyanine dyes have been extensively studied[1] for their usefulness as photosensitisers. Different heterocyclic bases and diversely substituted heterocyclic bases have been quaternised with different alkyl iodides and the quaternary salts thus obtained have been used for the preparation of such dyes. The carbonyl component required has also been suitably varied. The dyes obtained by the condensation of the quaternary salts and the carbonyl components have been studied with respect to their absorption and their photosensitising properties. Though it is reported that substitution in the methine chain, either α- or β- (with respect to the heterocyclic moiety), leads to hypsochromic shifts in λ_{max},[2,3] this aspect of substitution does not seem to have been thoroughly studied.[4] It was, therefore, considered to be of interest to study *inter alia* the effect of such substitution as well as to prepare new β-substituted dyes. For this purpose three ketones, viz. *p*-dimethylaminophenyl 1-naphthyl ketone (Ketone-1), *p*-dimethylaminophenyl 2-naphthyl ketone (Ketone-2)

Dyes and Pigments 0143-7208/82/0003-0273/$02·75



Dye	R_1	*R*	*X*
A_1	CH_3	CH_3	H
A_2	CH_3	CH_3	CH_3
A_3	CH_3	CH_3	Cl
A_4	CH_3	CH_3	Br
A_5	CH_3	CH_3	I
A_6	CH_3	CH_3	OCH_3
A_7	CH_3	CH_3	OC_2H_5
A_8	CH_3	C_2H_5	H

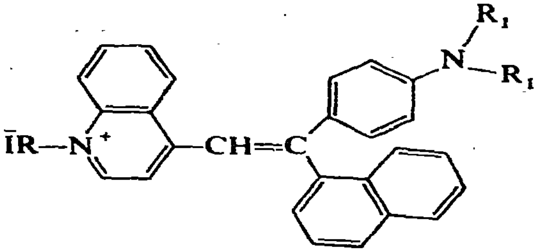
Dye	R_1	*R*	*X*
C_1	C_2H_5	CH_3	H
C_2	C_2H_5	CH_3	CH_3
C_3	C_2H_5	CH_3	Cl
C_4	C_2H_5	CH_3	Br
C_5	C_2H_5	CH_3	I
C_6	C_2H_5	CH_3	OCH_3
C_7	C_2H_5	CH_3	OC_2H_5
C_8	C_2H_5	C_2H_5	H



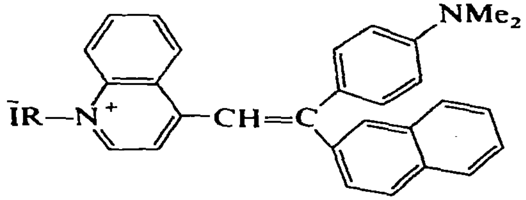
Dye	*R*	*X*
B_1	CH_3	H
B_2	CH_3	CH_3
B_3	CH_3	Cl
B_4	CH_3	Br

Dye	*R*	*X*
B_5	CH_3	I
B_6	CH_3	OCH_3
B_7	CH_3	OC_2H_5
B_8	C_2H_5	H

Fig. 1.



Dye	*R*	R_1
L_1	CH_3	CH_3
L_3	CH_3	C_2H_5



Dye	*R*
L_2	CH_3

Fig. 1—*contd.*

and *p*-diethylaminophenyl 1-naphthyl ketone (Ketone-3) have been condensed with diversely substituted quinaldine alkyl iodides and lepidine methiodide in boiling ethanol (with piperidine as catalyst) affording *β*-naphthyl (*β*- with respect to the hetero-nucleus) styryl cyanines. The *p*-diethylaminophenyl 1-naphthyl ketone was prepared by the method adopted by Shah *et al.*[5] The dyes under report are characterised in Fig. 1.

2. RESULTS AND CONCLUSIONS

The absorption and sensitisation of the dyes are given in Table 1.

A study of the absorption maxima of the dyes leads to some interesting conclusions.

TABLE 1

Dye	λ_{max} (*mμ*)	*Sensitisation*	
		Extended to (*mμ*)	*Remarks*
A_1	500	Nil	—
A_2	515	Nil	—
A_3	510	540	Weak sensitisation
A_4	513	600	Feeble max. at 570 μm
A_5	517	600	Uniform
A_6	505	Nil	—
A_7	508	560	Weak sensitisation
A_8	520	600	Feeble max. at 570 mμ
B_1	505	Nil	—
B_2	522	Nil	—
B_3	515	600	Weak sensitisation
B_4	518	600	Weak sensitisation
B_5	525	600	Weak sensitisation
B_6	508	Nil	—
B_7	512	600	Weak sensitisation
B_8	529	595	Weak sensitisation
C_1	502	600	Weak sensitisation
C_2	518	610	Uniform
C_3	515	540	Weak sensitisation
C_4	519	560	Weak sensitisation
C_5	524	560	Weak sensitisation
C_6	508	Nil	—
C_7	512	605	Uniform
C_8	528	610	Uniform
L_1	524	Nil	—
L_2	535	Nil	—
L_3	525	585	Weak sensitisation

2.1. *The effect of substitution in the methine chain*

The dyes reported have one or other substituent attached to the β- (β- to the heterocyclic component) position of the methine chain. A bulky substituent as in the case here, is likely to hinder sterically the planarity of the resonating system. Such hindrance to resonance may be expected to interfere with the delocalisation of the π molecular orbitals and cause a hypsochromic shift in absorption maxima. Such indeed has been found to be the case—the β-substituted dyes have shown appreciable hypsochromic shifts in absorption maxima, compared with their unsubstituted analogues (Table 2). It may be pointed out also that bond alternation will exist since the system is not electronically symmetrical and hence crowding substituents will cause hypsochromic shifts owing to rotation about essentially single bonds.[6]

The earlier observation[3] that substitution at the β-position of the methine chain of hemicyanines leads to a hypsochromic shift in absorption is thus confirmed.

2.2. *Comparison of the effects of 1-naphthyl and 2-naphthyl substitution at the β-position of the methine chain*

β-Chain substitution of 1-naphthyl and 2-naphthyl groups shows an interesting

TABLE 2
EFFECT OF β-SUBSTITUTION

β-Substituted dyes			*β-Unsubstituted dyes*			*Hypsochromic shift* ($m\mu$)
Symbol	*Substitution* (*β-chain*)	λ_{max} ($m\mu$)	*Substitution* (*β-chain*)	λ_{max} ($m\mu$)	*Reference*	
A_1	1-Naphthyl	500	Hydrogen	530	7, 8, 9, 10	30
B_1	2-Naphthyl	505	Hydrogen	530	7, 8, 9, 10	25
C_1	1-Naphthyl	502	Hydrogen	Not recorded	11	—
C_3	1-Naphthyl	518	Hydrogen	556	12	38
L_1	1-Naphthyl	524	Hydrogen	550	8, 9	26
L_2	2-Naphthyl	535	Hydrogen	550	8, 9	15
L_3	1-Naphthyl	525	Hydrogen	560	13	35

relationship. The former in all analogous dyes has caused small but definite bathochromic shifts in absorption (Table 3). This may be attributed to administration of the steric effect in the 2-naphthyl dyes as compared with the 1-naphthyl dyes caused by the *peri*-H. It is also significant that the electron density at the 1-position in the naphthyl moiety is greater than that at the 2- position.

TABLE 3
COMPARISON OF λ_{max} OF 1- AND 2-NAPHTHYL DYES

β-Naphthyl-1-dyes	A_1	A_2	A_3	A_4	A_5	A_6	A_7	A_8
β-Naphthyl-2-dyes	B_1	B_2	B_3	B_4	B_5	B_6	B_7	B_8
Bathochromic shift ($m\mu$)	5	5	7	5	8	3	4	7

2.3. *Lengthening of the conjugated chain*

Bathochromic shifts in absorption of cyanine dyes with lengthening of the conjugated chain of carbon atoms between polyvalent atoms involved in the resonance system is an established fact. Using lepidine quaternised salts, a number of dyes have been prepared, wherein the lengthening of the methine chain has been annular. The absorption maxima of these dyes exhibit bathochromic shift in absorption over their quinaldine analogues (Table 4).

TABLE 4
EFFECT OF INCREASE IN THE CHAIN LENGTH

Dye	λ_{max} ($m\mu$)	*Bathochromic shift* ($m\mu$)
A_1	500	24
L_1	524	
B_1	505	30
L_2	535	
C_1	502	23
L_3	525	

2.4. *The* p-*diethylamino dyes* vis-a-vis *their dimethyl analogues*

The *p*-diethylamino dyes show a bathochromic shift, though small, in λ_{max} compared with their dimethyl analogues (Table 5), an observation also made by earlier workers[2] and presumably due to greater electron donation by the $—NEt_2$ group as compared with the $—NMe_2$ group leading to an increase in electron symmetry.

TABLE 5
p-DIETHYL AND *p*-DIMETHYL ANALOGUES

Dye	λ_{max} $(m\mu)$	*Bathochromic shift* $(m\mu)$
A_1	500	2
C_1	502	
A_2	515	3
C_2	518	
A_3	510	5
C_3	515	

2.5. *The ethiodide dyes* vis-a-vis *their methiodide analogues*

The ethiodide dyes have shown uniform bathochromic shifts of about 20–26 mμ in λ_{max} over their methiodide analogues (Table 6).

The dyes reported were found to be weak sensitisers. In several cases the extra-sensitisation was almost nil. However, the dyes derived from quinolinium ethiodide were found to possess some extra-sensitising property.

It can therefore be concluded that any substituent at the β-position of the methine chain adversely affects the extra-sensitising property of the dyes. This is, of course, not surprising considering the fact that such chain-(β-)substituted dyes absorb at shorter wavelengths than their unsubstituted analogues. Both of these effects are probably caused by the non-planarity of substituted dye molecules due to bulky substitution.

TABLE 6
ETHIODIDE AND METHIODIDE DYES

Dye	λ_{max} $(m\mu)$	*Bathochromic shift* $(m\mu)$
A_8	520	20
A_1	500	
B_8	529	24
B_1	505	
C_8	528	26
C_1	502	

3. EXPERIMENTAL

(All melting and boiling points are uncorrected.)

3.1. *Preparation of the ketones*

p-Diethylaminophenyl 1-naphthyl ketone was prepared by utilising the general procedure of Shah *et al.*[5] It was purified by distillation under reduced pressure (b.p. at 1·5 mm, 235 °C, yield 44 %).

Repeated attempts to prepare the oxime, semicarbazone and DNP of this compound were unsuccessful. The ketone, however, readily afforded the styryl derivative which gave the predicted analysis. Ultraviolet peaks at 220 mμ (intense) and at 332 mμ (weak) (α,β-unsaturated ketone).

The other two ketones were also prepared by following the procedure adopted by Shah *et al.*[5]

TABLE 7

Symbol	*Yield* (%)	*Melting point* (°C)	*Molecular formula*	*Found* (%)		*Calculated* (%)	
				N	*Halogen*	*N*	*Halogen*
$\mathbf{A}_1$	28·59	210–1	$C_{30}H_{27}N_2I$	5·21	23·49	5·16	23·43
$\mathbf{A}_2$	19·78	221–2	$C_{31}H_{29}N_2I$	5·06	22·87	5·03	22·84
$\mathbf{A}_3$	19·25	208	$C_{30}H_{26}N_2ICl$	4·89	28·25	4·85	28·18
$\mathbf{A}_4$	19·32	204	$C_{30}H_{26}N_2IBr$	4·55	33·30	4·50	33·33
$\mathbf{A}_5$	25·44	205	$C_{30}H_{26}N_2I_2$	4·23	38·12	4·19	38·02
$\mathbf{A}_6$	19·23	203	$C_{31}H_{29}N_2OI$	4·93	22·26	4·89	22·20
$\mathbf{A}_7$	23·03	196	$C_{32}H_{31}N_2OI$	4·69	21·71	4·77	21·67
$\mathbf{B}_1$	25·18	225	$C_{30}H_{27}N_2I$	5·19	23·48	5·16	23·43
$\mathbf{B}_2$	24·28	210	$C_{31}H_{29}N_2I$	5·08	22·91	5·03	22·84
$\mathbf{B}_3$	19·42	202	$C_{30}H_{26}N_2ICl$	4·81	28·24	4·85	28·18
$\mathbf{B}_4$	23·34	186	$C_{30}H_{26}N_2IBr$	4·56	33·14	4·50	33·33
$\mathbf{B}_5$	14·97	249	$C_{30}H_{26}N_2I_2$	4·24	38·09	4·19	38·02
$\mathbf{B}_6$	19·22	205	$C_{31}H_{29}N_2OI$	4·85	22·29	4·89	22·29
$\mathbf{B}_7$	18·76	190	$C_{32}H_{31}N_2OI$	4·81	21·72	4·71	21·67
$\mathbf{C}_1$	16·66	188	$C_{32}H_{31}N_2I$	4·95	22·32	4·91	22·28
$\mathbf{C}_2$	17·29	202	$C_{33}H_{33}N_2I$	4·81	21·80	4·79	21·75
$\mathbf{C}_3$	19·85	180	$C_{32}H_{30}N_2ICl$	4·67	26·95	4·63	26·88
$\mathbf{C}_4$	21·81	210	$C_{32}H_{30}N_2IBr$	4·36	31·97	4·31	31·90
$\mathbf{C}_5$	14·36	221	$C_{32}H_{30}N_2I_2$	4·08	36·55	4·02	36·50
$\mathbf{C}_6$	16·66	183	$C_{33}H_{33}N_2OI$	4·70	21·23	4·66	21·16
$\mathbf{C}_7$	22·96	198	$C_{34}H_{35}N_2OI$	4·59	22·71	4·56	22·68
$\mathbf{A}_8$	21·58	210	$C_{31}H_{29}N_2I$	5·08	22·93	5·03	22·84
$\mathbf{B}_8$	18·45	210	$C_{31}H_{29}N_2I$	5·07	22·79	5·03	22·84
$\mathbf{C}_8$	18·83	180	$C_{33}H_{33}N_2I$	4·76	21·79	4·79	21·75
$\mathbf{L}_1$	25·83	225	$C_{30}H_{29}N_2I$	5·12	23·48	5·16	23·43
$\mathbf{L}_2$	35·96	230	$C_{30}H_{27}N_2I$	5·18	23·53	5·16	23·43
$\mathbf{L}_3$	26·31	221–2	$C_{32}H_{31}N_2I$	4·94	22·35	4·91	22·28

p-*Dimethylaminophenyl 1-naphthyl ketone:* pale yellow crystals, m.p. 115°C, yield 48·5% (lit.[5], m.p. 115–16°C, yield 35%).

p-*Dimethylaminophenyl 2-naphthyl ketone:* pale yellow crystals, m.p. 128°C, yield 56% (lit.[5], m.p. 128–9°C, yield 40%).

3.2. *General procedure for the preparation of the dyes*

The ketone and the quaternary salt in molar proportions were dissolved in absolute ethanol (20 ml) together with two drops of piperidine and the solution was gently boiled under reflux for 4 h. The solution was concentrated, when a dark viscous mass was obtained. This was repeatedly washed with ether to remove any unchanged ketone and then with boiling water to remove any unchanged quaternary salt. Finally the mass was crystallised from ethyl alcohol. The yields, m.p.s and the analytical data of the dyes are listed in Table 7.

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