

Research Note

Substituted Benzylidene Cyanines

B. N. JHA

Department of Chemistry, S.P. College (Bhagalpur University),
Dumka (S.P.)-814101, Bihar, India.

and

J. C. BANERJI

Department of Chemistry, B.N. College, Patna University,
Patna-800004, Bihar, India

SUMMARY

Eight new chain substituted benzylidene cyanine dyes have been prepared by condensing 4-dimethylamino-2'-nitrobenzophenone and 4-dimethylamino-3',5'-dinitrobenzophenone with methiodides of quinaldine and 6-haloquinaldines, in absolute ethanol, using piperidine as a basic catalyst. The optical absorption and extra sensitisation data of the dyes have been recorded and compared with those of their methin analogues.

The dyes absorb at longer wavelengths than their unsubstituted analogues, contrary to earlier observations.¹⁻⁶ The dyes obtained from the 2'-nitroketone are good sensitizers, whereas those obtained from the 3',5'-dinitroketone, are densensitizers.

1. INTRODUCTION

Although quite a large number of 4-dialkylamino styryl dyes, containing different variously substituted heterocyclic nuclei are reported, and the effect on optical absorption and sensitisation of substituents in the hetero part of the hemicyanines has been extensively studied,⁷ very little work has been carried out to study the effect of substituents in the methin chain of the dye molecules.⁸⁻¹¹ Moreover, α - and β -methin substitutions in styryl cyanines are reported to cause a hypsochromic shift in the absorption maxima, when compared to their unsubstituted analogues,¹⁻³ but the extent of the hypsochromic shift is less pronounced in the case of β -substituted products.⁴⁻⁶ It was

therefore of interest to prepare some β -methin substituted styryl cyanines and study their optical properties systematically.

The β -methin chain substitution can be effected by using suitable 4-*p*-dialkylamino ketones in place of 4-*p*-dialkylaminoaldehydes

This paper reports the preparation of dyes derived from two ketones, 4-dimethylamino-2'-nitrobenzophenone and 4-dimethylamino-3',5'-dinitrobenzophenone, which were obtained by the method of Shah *et al.*¹² with suitable modifications. The quaternised bases required, were prepared by heating the base with methyl iodide.¹³ The synthesised ketones were separately condensed in the usual way¹⁴ with methiodides of quinaldine¹⁵ and 6-chloro-, 6-bromo- and 6-iodoquinaldines^{13,16} in absolute ethanol in the presence of a few drops of piperidine to afford eight new dyes (D₁₇-D₂₄) as in Scheme 1

The dyes (D₁₇-D₂₀) obtained from 4-dimethylamino-2'-nitrobenzophenone and dyes (D₂₁-D₂₄) from 4-dimethylamino-3',5'-dinitrobenzophenone are highly crystalline and are mostly dark violet in colour. Their alcoholic solutions are either reddish violet or violet. The colour is reversibly discharged by addition of mineral acids and regenerated on basification, indicative of the characteristic of cyanine dyes

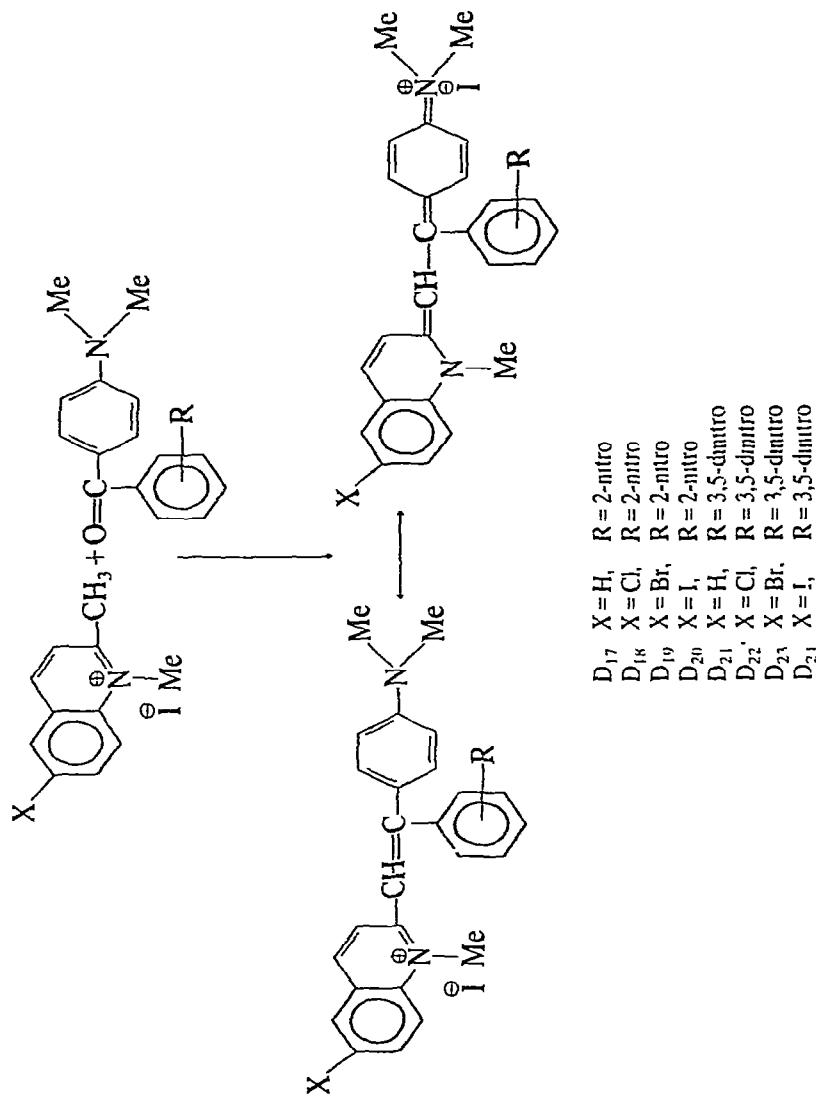
β -Methin substitution may affect the resonance stabilisation of substituted dye molecules sterically and electronically, as the substituents under study are electron attracting. The steric hindrance to resonance in the main conjugated chain due to bulkiness of the substituents is likely to be significant too.

The data for optical absorption maxima and the ranges of extra sensitisation have been recorded, analysed and compared with those of their corresponding styryl analogues wherever possible and reasonable conclusions have been drawn.

2 CONCLUSIONS

The absorption maxima and extra sensitisation of the newly prepared dyes and those of their styryl analogues, available in the literature, are shown in Table 1 for comparison.

It will be evident from the absorption data that β -methin substitution, whether by 2-nitrophenyl or by 3,5-dinitrophenyl, has caused an almost uniform bathochromic shift in λ_{max} by about 30 m μ . It will also be seen that 6-substitution of the heteronucleus has caused only a slight bathochromic shift in λ_{max} , the order being 6-H < 6-Cl < 6-Br < 6-I in both the 2-nitro series and the 3,5-dinitro series. Analysis of the sensitisation data, however, does not lead to any definite generalisation. The β -2-nitrophenyl dyes are inferior sensitisers to their unsubstituted analogues, while the β -3,5-dinitrophenyl dyes are desensitisers



Scheme 1

TABLE I
THE RECORDED DATA OF ABSORPTION MAXIMA (λ_{\max}) AND EXTRA SENSITISATION OF THE BENZYLIDENE CYANINE DYES AND THOSE OF UNSUBSTITUTED STYRYL ANALOGUES

Dye Symbol	Substituted benzylidene cyanine dyes			Unsubstituted styryl dyes (from the literature)				Reference	
	λ_{\max} (m μ)	Extra sensitisation		λ_{\max} (m μ)	Extra sensitisation				
		range (m μ)	max. (m μ)		range (m μ)	max (m μ)			
D ₁₇	564	620 w, dc, ibvr	560	530	680	580	11		
D ₁₈	578	630 mi, c	590 u	548	650	595	16		
D ₁₉	579	630 mi, c	590	550	650	595	16		
D ₂₀	583	650 i, lc	590	552	650	600	16		
D ₂₁	569	D ^a	—	530	680	580	11		
D ₂₂	578	D ^a	—	548	650	595	16		
D ₂₃	580	D ^a	—	550	650	595	16		
D ₂₄	584	D ^a	—	552	650	600	16		

Abbreviations c connected, i intense, u unpronounced. w weak, dc disconnected, lc loosely connected, mi moderately intense ibvr intense in blue-violet range, D desensitiser

^a In all cases, intensity in blue-violet range is decreased. The desensitising property varies in the order D₂₀ < D₁₉ < D₁₈ < D₁₇

3. EXPERIMENTAL

3.1. The ketones

For the preparation of ketones, the general method of production of alkylaminobenzophenones and their substituted products by Shah *et al.*¹² was adopted with some procedural modifications.

(i) *4-Dimethylamino-2'-nitrobenzophenone*: Dimethylaniline (8 ml) was added in portions to a mixture of *o*-nitrobenzaldehyde (3 g) and phosphorus oxychloride (8 ml) and warmed (40–45°C) for 8 h. The viscous mass, on extracting with hydrochloric acid, was almost neutralised with sodium hydroxide solution and rendered homogeneous with alcohol. The ketone, which separated after addition of a few drops more of sodium hydroxide solution and chilling, was recrystallised from toluene as shining deep orange leaflets (yield 30%, m.p. 249–50°C; ref. 12, yield not mentioned, m.p. 251–53°C).

(ii) *4-Dimethylamino-3',5'-dinitrobenzophenone*: 3,5-Dinitrobenzaldehyde (5 g) and dimethylaniline (7 ml) were mixed together and phosphorus oxychloride (7 ml) was slowly added. The mixture was heated on a steam bath for

TABLE 2
ANALYTICAL DATA OF THE SUBSTITUTED BENZYLIDENE CYANINE DYES

Dye symbol	Methiodide of base used	Dye as methiodide	Crystal colour and shape ^a	Yield (%)	M.p. (°C)	Molecular formula	Found (%)		Calc (%)	
							N	Hal	N	Hal
D ₁₇	Quinaldine	2- <i>p</i> -Dimethylamino(β-2-nitrophenyl)styryl quinoline	dv lc	61	208	C ₂₆ H ₂₄ N ₃ IO ₂	7.77	23.61	7.82	23.65
D ₁₈	6-Chloroquinaldine	2- <i>p</i> -Dimethylamino(β-2-nitrophenyl) styryl-6-chloroquinoline	dv sn wrt	58	224	C ₂₆ H ₂₃ N ₃ ClIO ₂	7.29	28.41	7.35	28.45
D ₁₉	6-Bromoquinaldine	2- <i>p</i> -Dimethylamino(β-2-nitrophenyl) styryl-6-bromoquinoline	dv sn wrt	41	231	C ₂₆ H ₂₃ N ₃ BrIO ₂	6.77	33.58	6.82	33.62
D ₂₀	6-Iodoquinaldine	2- <i>p</i> -Dimethylamino(β-2-nitrophenyl) styryl-6-iodoquinoline	dv sn wrt	37	247	C ₂₆ H ₂₃ N ₃ I ₂ O ₂	6.27	38.34	6.33	38.31
D ₂₁	Quinaldine	2- <i>p</i> -Dimethylamino(β-3,5-dinitrophenyl) styryl-quinoline	dv lc	67	145	C ₂₆ H ₂₃ N ₄ IO ₄	9.57	21.78	9.62	21.82
D ₂₂	6-Chloroquinaldine	2- <i>p</i> -Dimethylamino(β-3,5-dinitrophenyl) styryl-6-chloroquinoline	dv lc wrt	71	153	C ₂₆ H ₂₂ N ₃ ClIO ₄	9.01	26.31	9.08	26.35
D ₂₃	6-Bromoquinaldine	2- <i>p</i> -Dimethylamino(β-3,5-dinitrophenyl) styryl-6-bromoquinoline	dvc wrt	73	161	C ₂₆ H ₂₂ N ₃ BrIO ₄	8.42	33.84	8.47	33.88
D ₂₄	6-Iodoquinaldine	2-[<i>p</i> -Dimethylamino(β-3,5-dinitrophenyl) styryl-6-iodoquinoline	dvc wrt	75	189	C ₂₆ H ₂₂ N ₄ I ₂ O ₄	7.86	35.83	7.91	35.88

^a dv dark violet, sn small needles, lc tiny crystals, dvc dark violet crystals, wrt with blue reflex, wrt with green reflex, wrt with reddish tinge, wrt with red reflex, wrt with reddish tinge.

6 h and then on an oil bath (115–120°C) for a further 4 h. The acid extract of the crude product was neutralised with sodium hydroxide solution and the separated ketone recrystallised from a mixed solvent, ethanol: benzene (3:1), as light orange coloured shining woolly crystals, (yield 40%, m.p. 193–94°C).

Found: C, 57.11; H, 4.06; N, 13.28%

$C_{15}H_{13}N_3O_5$ requires: C, 57.14; H, 4.14; N, 13.33%

3.2. *The quaternary quinaldinium salts*

The quaternised salts were obtained by adopting the general method of preparation of Johnson and Adams.¹³ The bases and methyl iodide (1:1.5 M) were heated in a pressure bottle on a steam bath for 24 h and the product recrystallised from hot water.

3.3. *The benzylidene cyanine dyes*

A mixture, containing requisite amounts of the ketone, the quaternary salt, ethanol and a few drops of piperidine was refluxed mildly under a moisture trap for about 2 h. The resulting solution, on cooling, afforded the dye, which was recrystallised from methanol.

The percentage analysis, yield, m.p. (uncorrected), etc. of the dyes are given in Table 2.

3.4. *Recording of optical properties*

The absorption maxima of the dyes were recorded on an Beckmann Spectrophotometer, Model DU in 1/1000 ethanolic solutions. The sensitisation spectra were recorded on an Adam Hilger Wedge Spectrograph on Ilford N40 process plates, bathed in dilute ethanol (1.3) solutions (1/50 000) of dyes. The plates after 4 min bathing were dried, exposed for 4 min to light from a 150 c.p. point-o-lite lamp.

ACKNOWLEDGEMENTS

The authors wish to thank Dr A. K. Sinha, Reader in Chemistry, B. N. College, Patna-800004 for his support during this investigation.

REFERENCES

- 1 A I KIPRIANOV and I K USHENKO *Izvest Akad Nauk. USSR, Otd Khim Nauk.* 492 (1950). *Chem Abst* **45**, 3265 (1951)
- 2 I K USHENKO *Ukr Khim Zh*, **20**, 384 (1954). *Chem Abst*, **50**, 6049 (1956)
- 3 I K USHENKO *Ukr Khim Zh* **21**, 738 (1955). *Chem Abst*, **50**, 16752 (1956)

4. I G FARBEN, Brit Pat 498, 012
5. A I KIPRIANOV and I. K USHENKO, *J Gen. Chem USSR*, **20**, 514, English translation, 543 (1950)
6. F. M HAMER, *J. Chem Soc*, 1480 (1956)
7. F. M HAMER, *Cyanine dyes and related compounds* New York, Interscience Publishers Inc (1964) Gives a comprehensive survey of the subject covered by this paper
8. W H. MILLS and J L B SMITH, *J Chem Soc*, **121**, 2724 (1922)
9. J C BANERJI, K. D. BANERJEE, N P BHATTACHARYA and S N SANYAL, *J. Indian Chem Soc*, **45**, 496 (1968).
10. J C BANERJI and S N SANYAL, *Indian J Chem*, **6**, 346 (1968)
11. S N. SANYAL, Ph D. Thesis, Bihar University, India, p 105 (1966)
12. R C SHAH, R. K DESHPANDEY and J S CHAUBAL, *J Chem Soc*, 645 (1932)
13. J R JOHNSON and R ADAMS, *J Amer Chem Soc*, **43**, 2257 (1921)
14. W H MILLS and W. Z POPE, *J Chem Soc*, **121**, 946 (1922)
15. O DOEBNER and W V MILLER, *Chem Ber.* **16**, 2468 (1883)
16. R J N SAHAY, A K SINHA and J C BANERJI *J Indian Chem Soc*, **43**, 255 (1966)