

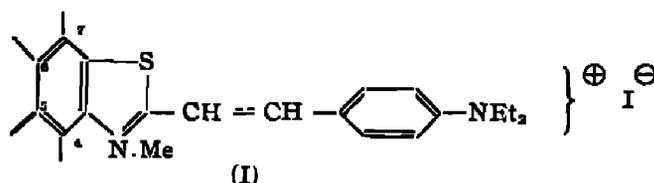
SYNTHESIS OF CYANINE DYES BY THE CONDENSATION OF
p-DIETHYLAMINO BENZALDEHYDE WITH APPROPRIATE
 HETEROCYCLIC COMPOUNDS. PART VIII

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Four new dyes have been prepared by condensing *p*-diethylaminobenzaldehyde with the methiodides of 2:4-dimethyl-, 2:5-dimethyl-, 2:7-dimethyl- and 2-methyl-6-iodo-benzthiazole, and their optical and other properties examined. Results of previous communications have been collected and it has been shown that the substitution at the 4-position of the benzthiazole nucleus affords maximum extra-sensitisation. It has also been shown that the substituents at the 4-position fall in the order: EtO->Me->Cl, Br->MeO->I- with respect to extra-sensitisation.

The present series of investigations were undertaken with a view to studying the effect of substitution on the extra-sensitisation of the *p*-diethylaminostyryl type of cyanine dyes containing a benzthiazole nucleus. For this purpose various substituents have been introduced into the 6-position of *p*-diethylaminostyrylbenzthiazole methiodide (I), and at the same time one particular substituent has been introduced at all of the four positions available for substitution in the benzthiazole nucleus. The sensitisation spectra of the dyes, thus obtained, have been compared with those of the unsubstituted dye.

Some of the results of these investigations have already been reported (Doja and Banerji, this *Journal*, 1946, 23, 217; 1949, 26, 374; 1951, 28, 7). For the sake of completeness, four new dyes have been prepared by condensing *p*-diethylaminobenzaldehyde with the methiodides of 2:4-, 2:5- and 2:7-dimethylbenzthiazoles and of 6-iodobenzthiazole in absolute ethanol, using piperidine as a catalyst. The dyes may be represented by the general expression (I) (substituents not shown):



which represents the resonance hybrid between the two extremes, in one of which the heterocyclic and in the other the exocyclic nitrogen has the positive charge.

The required methiodides were prepared in all cases by the prolonged heating of the respective base with methyl iodide in a sealed tube on the water-bath.

The rectified spirit solutions of the dyes are all magenta-coloured, the colour being reversibly discharged by the addition of mineral acids, as is the characteristic of

all cyanine dyes. The resistance to decolorisation was determined by titrating 2 c.c. of 1/2000 solution of the dyes in rectified spirit against N/100-HCl. The results are shown in Table I.

TABLE I

Dye.	Colour and shape of the crystals.	Reflex.	Pleochroism. Colour of light at one position of λ to the polariser.		N/100-HCl reqd.	λ_{\max} .	Frequency of max. (cm^{-1}).
C	Dark thin elongated needles	Weak yellowish green	Glass like	Nearly opaque	16.0 c.c.	4960 Å	60484
F	Moss-green	Green	Nearly colorless	Bottle-green	19.5	5000	60000
O	Shining dark grey needles	Pinkish yellow	Light green	Brownish green	17.5	5300	56603
H	Dull brinjal coloured needles	Nil	Slate grey	Colorless	18.0	5100	58821

The dyes produce various shades on cotton, silk and wool which, however, fade on washing and on exposure to sunlight. The shades obtained are shown in Table II.

TABLE II

Dye.	Colour developed on		
	Cotton.	Silk.	Wool.
C	Mauve	Mauve	Dull pink
F	Purple	Light magenta	Light magenta
O	Mauve	Violet-red	Bluish red
H	Bluish red	Violet-red	Pink

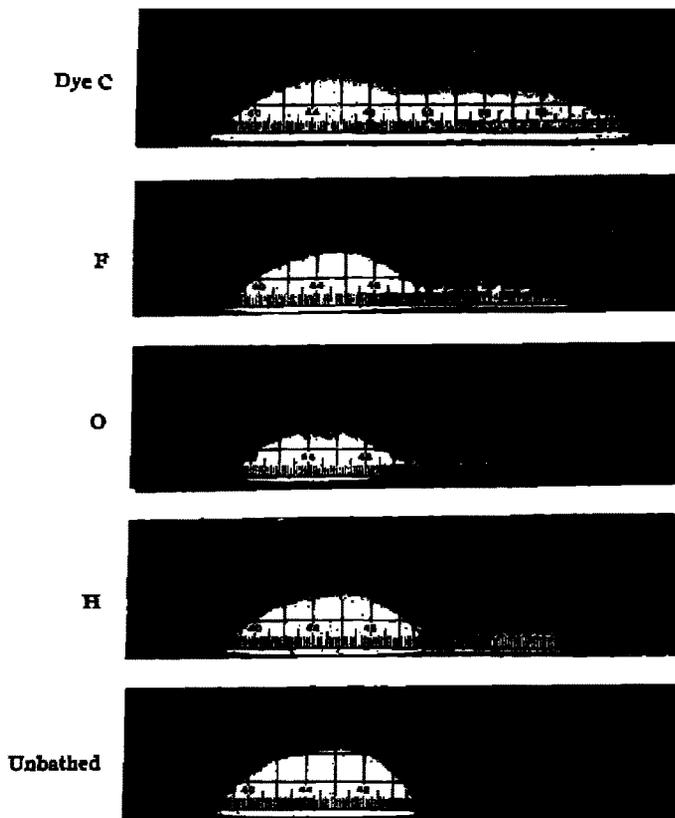
The fluorescence of weak alcoholic solutions (1/50,000) of the dyes (cf. Doja, this *Journal*, 1940, 17, 348) are shown in Table III.

TABLE III

Wallace colour filter No.	Colour of the fluorescent beam seen at right angle to the incident beam passing through soln. of the dyes			
	C.	F.	O.	H.
1	Weak red	Light absorbed	Light absorbed	Light absorbed
2	Do	Do	Do	Do
3	Light absorbed	Brownish yellow	Orange-yellow	Weak orange-yellow
4	Do	Brownish orange	Weak brown	Light brown
5	Dull yellow	Lemon-yellow	Orange-yellow	Yellowish brown
6	Weak rose-red	Dull yellow	Carrot-yellow	Dirty yellow
7	Yellow	Greenish yellow	Light absorbed	Greenish yellow
8	Yellow	Orange-brown	Do	Orange-brown
9	Orange-yellow	Orange-yellow	Orange-yellow	Orange-yellow
10	Do	Brownish yellow	Pink-yellow	Brownish yellow

Some of the other properties of the dyes are also recorded in Table I. The sensitisation spectra are shown in Fig. 1. For the sake of comparison, the sensitisation spectrum of an unbathed process plate is appended in Fig. 1.

FIG. 1



Acetic acid solutions of the dyes deepened in intensity on warming and the original intensity was regained on cooling, the effect being more pronounced in aqueous acetic acid solutions (cf. Doja and Banerji, *loc. cit.*).

The sensitisation spectra of some of the dyes reported previously (Doja and Banerji, *loc. cit.*) were retaken with a slight improvement in the technique. The results obtained together with those of the dyes now prepared are shown in Table IV.

TABLE IV

Dye.	Nature of substitution.	Extra-sensitisation.		Remarks.
		Range.	Maxima.	
X	Unsubstituted	5200-6350 Å	Gradual decay	Doja and Banerji (this <i>Journal</i> , 1946, 23, 217). Retaken.
C	4-Methyl	4920-6840	5440, 6020 Å	
F	5-Methyl	5100-6280	5600, 6000	
S	6-Methyl	4800-6750	5620	Doja and Banerji (<i>ibid.</i> , 1949, 26, 374). Retaken.
O	7-Methyl	5000-6620	5600, 6000	
L	6-Methoxy	4860-6520	Gradual decay	Doja and Banerji (<i>ibid.</i> , 1951, 28, 7). Retaken.
M	6-Ethoxy	5000-6760	5800	Do
N	6-Chloro	5000-6560	5500	Do
P	6-Bromo	5180-6560	5400, 5800, 6300	Do
H	6-Iodo	5160-6260	6000	
T	4 : 6-Dimethyl	5000-6540	5600	Doja and Banerji (<i>loc. cit.</i> , p. 374). Retaken.

It will be seen from Table IV that the substitution of a methyl group in the benzthiazole nucleus of the parent dye affects the sensitisation profoundly. Thus, while the unsubstituted dye (X) sensitises up to 6350 Å, the 4-, 5-, 6- and 7-methyl-substituted dyes sensitise up to 6840, 6280, 6750 and 6620 Å respectively. Arranged in order of extra-sensitisation, the available positions for substitution fall in the order : 4-Me > 6-Me > 7-Me > 5-Me. The 5-methyl dye is a weaker sensitiser than the unsubstituted parent dye.

Of the various substituents at the 6-position of the benzthiazole nucleus, the ethoxy group imparts the greatest extra-sensitisation (up to 6760 Å), the different substituents falling in the order : EtO > Me > Cl, Br > MeO > I. Curiously enough the 4 : 6-dimethyl dye is a weaker sensitiser than either of the singly methyl-substituted 4-methyl or 6-methyl dye.

EXPERIMENTAL

2 : 4-Dimethylbenzthiazole Methiodide.—2 : 4-Dimethylbenzthiazole (Kiprianov and Sitsch, *Trav. Inst. Chem.*, Charkov, 1936, 2, 25) and methyl iodide (1 : 1.5 molar) were heated for 24 hours in a sealed tube in a water-bath and the salt was recrystallised from absolute ethanol, m.p. 223°, yield 77%. (Found : I, 41.72. C₁₀H₁₂NIS requires I, 41.64%).

2-p-Diethylaminostyryl-4-methylbenzthiazole Methiodide (Dye C).—The above methiodide (0.3 g.), *p*-diethylaminobenzaldehyde (0.18 g.), absolute ethanol (5 c.c.) and piperidine (2 drops) were refluxed for 4 hours. The dye (10%) separated on cooling and it was recrystallised from methanol as indigo-blue slender needles, m.p. 210°. (Found : N, 5.98; I, 27.30. C₂₁H₂₂N₂IS requires N, 6.04; I, 27.37%).

2 : 5-Dimethylbenzthiazole Methiodide.—2 : 5-Dimethylbenzthiazole (Banerji, this *Journal*, 1955, 32, 135) and methyl iodide (1 : 1.5 molar) were heated in a sealed tube for 24 hours on a water-bath and the salt was recrystallised from hot water as colorless needles, m.p. 211°, yield 81%. (Found : I, 41.57. C₁₀H₁₂NIS requires I, 41.64%).

2-p-Diethylaminostyryl-5-methylbenzthiazole Methiodide (Dye F).—On refluxing the above methiodide (0.6 g.), *p*-diethylaminobenzaldehyde (0.36 g.), absolute ethanol (5 c.c.) and piperidine (2 drops) for 14 hours, the dye separated (45%) as greenish golden yellow platelets and it was recrystallised from methanol, m.p. 218°. (Found: N, 6.18; I, 27.21. $C_{21}H_{28}N_2IS$ requires N, 6.04; I, 27.37%).

2:7-Dimethylbenzthiazole Methiodide.—2:7-Dimethylbenzthiazole (Banerji, *loc. cit.*) and methyl iodide (1:1.5 molar) were heated in a sealed tube in a water-bath for 24 hours and the salt was recrystallised from hot water as faint pink, elongated needles, m.p. 240°, yield 88%. (Found: I, 41.48. $C_{10}H_{12}NIS$ requires I, 41.64%).

2-p-Diethylaminostyryl-7-methylbenzthiazole Methiodide (Dye O).—The above methiodide (0.6 g.), *p*-diethylaminobenzaldehyde (0.36 g.), absolute ethanol (10 c.c.) and piperidine (2 drops) were refluxed for half an hour. The dye began to separate even while the solution was boiling. On cooling, the dye (63%) was obtained as woolly needle clusters and was recrystallised from methanol, m.p. 227°. (Found: N, 6.12; I, 26.96. $C_{21}H_{28}N_2IS$ requires N, 6.04; I, 27.37%).

***p*-Iodothioacetanilide.**—*p*-Iodoacetanilide (20 g.) and phosphorus pentasulphide (12 g.) were intimately mixed and the mixture was treated with boiling xylene (50 c.c.) for a short time. The hot xylene extract, decanted from the tarry residue, deposited on cooling *p*-iodothioacetanilide (4 g.) as buff-coloured needles, m.p. 147-48°. Worrall (*J. Amer. Chem. Soc.*, 1924, 46, 2837), who prepared it from substituted aromatic mustard oils, reported m.p. 149°. The crude product was used in the subsequent preparation without further purification.

2-Methyl-6-iodobenzthiazole.—To a filtered solution of *p*-iodothioacetanilide (4 g.) in 2*N*-NaOH solution (100 c.c.) a 20% potassium ferricyanide solution (50 c.c.) was added and the mixture allowed to stand overnight. The base settled down as a thick viscous mass. The aqueous layer was removed and the residue was washed repeatedly with water. The residue on recrystallisation from hot aqueous ethanol (bone charcoal) furnished the thiazole as long white needles (25%), m.p. 140-41°. This compound was prepared by Kiprianov, Ushenko and Sitsch (*J. Gen. Chem. USSR.*, 1945, 15, 200) by Sandmeyer's reaction on 6-amino-2-methylbenzthiazole, m.p. 142°.

2-Methyl-6-iodobenzthiazole Methiodide.—On heating the above base with methyl iodide (1:1.5 molar) in a sealed tube in a water-bath for 24 hours, the salt was obtained and was recrystallised from hot water (bone charcoal) as stout colorless needles, (79%), m.p. 239°. (Found: I, 60.1. $C_9H_9NI_2S$ requires I, 60.9%).

2-p-Diethylaminostyryl-6-iodobenzthiazole Methiodide (Dye H).—On refluxing a mixture of the above methiodide (0.45 g.), *p*-diethylaminobenzaldehyde (0.2 g.), absolute alcohol (5 c.c.) and piperidine (2 drops) for 2 hours, the dye was obtained (33%) and was recrystallised from methanol as greenish blue needles, m.p. 253-54° (Found: N, 4.91; I, 43.87. $C_{20}H_{22}N_2I_2S$ requires N, 4.86; I, 44.09%).

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