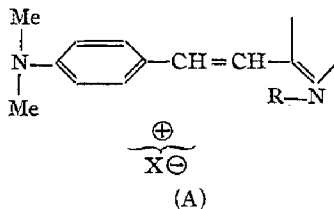


SYNTHESIS OF CYANINE DYES BY THE CONDENSATION OF *p*-DIETHYL-AMINOBENZALDEHYDE WITH APPROPRIATE HETEROCYCLIC COMPOUNDS. PART I

BY M. Q. DOJA AND MUKTIDRO PANDEY

Three new dyestuffs have been obtained by the condensation of *p*-diethylaminobenzaldehyde with the ethiodides of lepidine, *p*-toluquinaldine and 6-ethoxyquinaldine. One of these compounds, the *p*-toluquinaldine condensation product has been found to be a powerful sensitiser which can be commercially utilised. Unlike other cyanine dyes, these substances dye silk and wool in fast colours. The fluorescence and other characteristics of these dyes have also been examined and recorded.

Cyanine dyes with two methenyl groups between the two ring systems (Doja, *Chem. Review*, 1932, **11**, 293) generally conform to the formula (A) and are prepared by the condensation of *p*-dimethylaminobenzaldehyde with heterocyclic ammonium compounds possessing a



when R = an alkyl radical.
X = an acid radical.

reactive methyl group (König *J. prakt. Chem.*, 1912, **86**, 166; Barbier, *Bull. Soc. Chim.*, 1920, **28**, 427; Mills and Smith, *J. Chem. Soc.*, 1922, **121**, 2736; Hamer, *ibid.*, 1929, 2598; 1930, 995; König, *Ber.*, 1928, **61**, 2065). On account of the fact that some of the dyestuffs belonging to this series are marked sensitisers (Mills and Pope, *J. Chem. Soc.*, 1922, **121**, 946) it was considered of interest to investigate the nature of compounds produced in the above reaction by the use of *p*-diethylaminobenzaldehyde in place of the *p*-dimethylamino compound. The present work was undertaken with this object in view (*cf.* B. P. 449527; also see Cocker and Turner, *J. Chem. Soc.*, 1940, 57). In making a choice of the heterocyclic compounds, which are to be condensed with the aldehyde, we have given preference to those which were constituents of commercially valuable sensitisers. Thus (1) *p*-toluquinaldine, a constituent of the well known orthochromatic sensitiser "pinaverdol" (Wise, Adams, Stewart and Lund, *Ind. Eng. Chem.*, 1919, **11**, 460; Mills and Pope, *Phot. J.*, 1920, **60**, 183; D.R.P. 167159, 167770, 158078, 170048, 170049) and "orthochrome T" (D. R. P. 154475, 127771); (2) 6-ethoxyquinaldine, a constituent of the German commercial product "pinachrome", and (3) lepidine, a constituent of the deep and infra-red sensitisers "kryptocyanine" and "neocyanine" (Adams and Haller, *J. Amer. Chem. Soc.*, 1920, **42**, 2661; Hamer, *J. Chem. Soc.*, 1927, 2801) have been selected in the first instance. The ethiodides of these bases have been condensed with *p*-diethylaminobenzaldehyde in absolute alcoholic solution with piperidine as a catalyst, and the resulting compounds are found to possess unusual sensitising characteristics. As will be evident from the wedge spectrograms (Kenneth, Mees and Wratten, *Brit. J. Phot.*, 1907, 384) recorded in Fig. 1, the lepidine condensation product, 4-*p*-diethylaminostyrylquinoline ethiodide (E) does not confer any extra sensitisation on the photographic plate. On the other hand the condensation product

of *p*-toluquinaldine, 2-*p*-diethylaminostyryl-6-methylquinoline ethiodide (F) is a powerful sensitiser, the zone of additional sensitisation extending up to λ 6700. In this respect it surpasses even the famous orthochromatic sensitiser "pinaverdol" and very nearly equals to the panchromatic sensitiser "pinaacyanol" (Mills and Pope, *Phot. J.*, 1920, 60, 253; Hamer, *J. Chem. Soc.*, 1927, 2796; D.R.P. 172118, 175034, 178688, 189942, 200207). It may be noted, in this connection, that the band of extra sensitisation is not only extensive but intense, which fact enhances the value of the compound as a practical sensitiser. For commercial purposes we have named this sensitiser "Sensitine P". The condensation product of 6-ethoxyquinaldine, 2-*p*-diethylaminostyryl-6-ethoxyquinoline ethiodide (G) is a weak sensitiser, the faint band of extra sensitisation reaching up to λ 6300. The general characteristics of the wedge spectrograms of all the three compounds are summarised in Table I.

TABLE I

Com- pound.	Total range of sensi- sation.	Range of uni- formly in- tense sensi- sation.	Extra sensitisation.	
			Maxima.	Minima.
(E)	3800-5200Å	4400-4800Å	nil	nil
(F)	3900-6700Å	5100-6400Å	5600-6200Å	5050-5850Å
(G)	3850-6300Å	5200-5900Å	5550Å	5800Å

TABLE II

Colour produced on		Cotton.
Wool.	Silk.	
(E) Violet	Sapphire blue	Weak blue-black.
(F) Maroon	Deep amethyst	Reddish blue
(G) Deep pink	Reddish violet	Deep violet

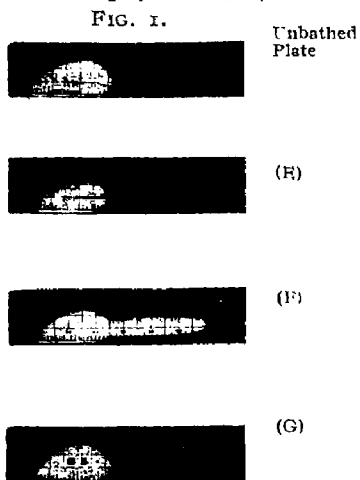
Cyanine dyes generally produce pretty but fugitive shades on cotton, wool, and silk. The compounds now synthesised, however, appear to be exceptions (*cf.* U.S.P. 1524791 and E.P. 232740). They not only dye silk and wool in beautiful colours but the shades thus produced are fairly resistant to both sunlight and washing. The shades on cotton are poor and easily removed. It appears that these substances are more suitable for the dyeing of wool than silk, because the shades in the former case are faster. In Table II are recorded the shades produced on wool, silk and cotton from a neutral bath.

All the three compounds are soluble in water and chloroform, readily so in alcohol and insoluble in ether. Their melting points, crystalline properties and optical characteristics are given in Table III. In column 4 the 'form' of the crystal is expressed as euohedral, subhedral, or anhedral, according as the crystal shows well developed partly developed or not at all developed external faces, under a microscope.

TABLE III

Compound.	Shape.	Habit	Form.	Streak.	M.P.	Colour in ordinary light.	Colour through transmitted light.	Reflex.	Pleochroism.	
									Colour of light in one position of polariser.	Colour after rotation through 90°.
(E)	Irregular earthy crystals	Nil	Anhedral	Blue	159°	Brownish black	Deep violet	Nil	Brinjal blue	Weak, light violet
(F)	Microscopic needles	Acicular	Subhedral	Reddish violet	221	Rust-red	Claret red	Moderate light green	Dark red	Strong, light orange yellow
(G)	Small glistening plates	Tubular	Euohedral	Reddish violet	218	Sage green	Smoky green	Strong, emerald green	Greenish white	Strong, opaque

Being cyanine dyes, the solution of these substances exhibits the characteristic property of



the discharge of colour by the addition of mineral acids and its restoration by caustic alkalis. In this connection Mills and Pope (*Phot. J.*, 1920, **44**, 255) noted that alcoholic solutions are more resistant to decolourisation than aqueous solutions. So far as these newly prepared dyes are concerned, as will be seen from Table IV, the case is opposite. It is the aqueous solutions which require larger quantities of acid for decolourisation (*cf.* Doja and Prasad, *J. Indian Chem. Soc.*, 1943, **20**, 154).

It is interesting to note here that the difference in the quantity of acid required for the aqueous and alcoholic solutions goes hand in hand with the sensitising power of the dye. The toluquinaldine condensation product (F) which has the maximum sensitising power has also got the largest difference; on the other hand (E) with practically no sensitising power has the smallest difference.

Weak solutions of these dyestuffs in rectified spirit (1 : 50,000) exhibit fluorescence, which is given in Table V. The method of recording the fluorescence is the same as described by Doja (*J. Indian Chem. Soc.*, 1940, **17**, 348).

TABLE IV

Compound.	Volums in c.c. of <i>N</i> /100 HCl required for decolourisation of 2 c.c. of 1 : 10,000.	
	Aqueous solution	Alcoholic solution.
(E)	3'0	2'2
	3'05	2'2
(F)	3'1	2'2
	15'4	3'2
(G)	15'4	3'25
	4'7	1'1
	4'65	1'15
	4'6	1'2

TABLE V

Wallace colour filter No.	Colour of the fluorescent beam seen at right angles to the incident beam.		
	(E)	(F)	(G)
1	Dark blue (seen with difficulty)	Weak yellow (seen with difficulty).	Very faint pink
2	Weak yellowish blue.	Yellowish red	Weak yellowish blue.
3	Blue	Reddish yellow	Red
4	Bluish red	Yellow	Yellowish red
5	Yellowish green	Greenish yellow	Yellow
6	Green	Greenish yellow	Reddish yellow
7	Faint blue	Light absorbed	Light absorbed
8	Light absorbed	Light absorbed	Light absorbed
9	Light absorbed	Weak blue (seen with difficulty)	Reddish blue
10	Greenish yellow	Crimson	Yellowish red

EXPERIMENTAL

Streak.—The "streak" of the crystal was determined by rubbing it on a piece of white unglazed porcelain Streak Plate and noting the colour of the powder.

4-p-Diethylaminostyrylquinoline-ethiodide.—A solution of lepidine ethiodide (1.7 g.), *p*-diethylaminobenzaldehyde (1 g.) and piperidine (0.3 c.c.) in 30 c.c. of absolute alcohol was refluxed for a couple of hours. On cooling earthy crystals separated out which were recrystallised from absolute methyl alcohol, yield 1.6 g. (61.5%). (Found: I, 27.71. $C_{23}H_{27}N_2I$ requires I, 27.73 per cent).

2-p-Diethylaminostyryl-6-methylquinoline-ethiodide.—*p*-Diethylaminobenzaldehyde (1 g.) *p*-toluquinaldine ethiodide (1.7 g.), piperidine (0.5 c.c.) and absolute alcohol (36 c.c.) were heated together in a flask under reflux for 1½ hours. The solution turned violet and after leaving overnight was filled with tiny reddish needles. These were filtered off and recrystallised from methyl alcohol, yield 2.5 g. (92.5%). (Found: I, 27.12. $C_{24}H_{29}N_2I$ requires I, 26.90 per cent).

2-p-Diethylaminostyryl-6-ethoxyquinoline-ethiodide.—A solution of *p*-diethylaminobenzaldehyde (1 g.), 6-ethoxyquinaldine ethiodide (1 g.), piperidine (0.6 c.c.) and absolute alcohol (40 c.c.) was briskly boiled for 2 hours. The separated crystals were recrystallised from methyl alcohol, yield 2.4 g. (82.7%). (Found: I, 25.32. $C_{25}H_{31}ON_2I$ requires I, 25.29 per cent).

We wish to express our gratitude to Professor L. M. Chatterjee of the Physics Department of this College for help in recording wedge spectrograms.

SCIENCE COLLEGE,
PATNA.

Received January 17, 1944