

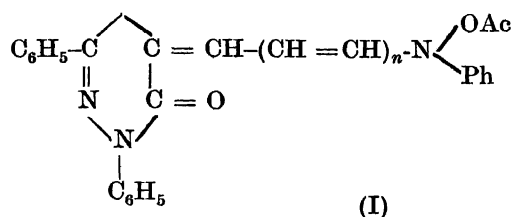
## Merocyanines Derived from 1, 3-Diphenyl-6-oxo-Pyridazine

E. Jena\*

1,3-Diphenyl-6-oxo-pyridazine was condensed separately with diphenyl formamidine and beta-anilino acrolein anil hydrochloride. The resulting acetanilidomethylene and acetanilido allylidene derivatives were finally condensed with the quaternary compounds of few 2-methyl heterocyclic compounds yielding merocarbo and merodicarbo cyanines. Their absorption and photosensitising action were studied.

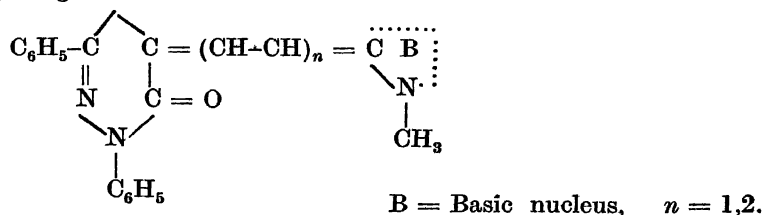
Merocyanines have been known as good photographic sensitisers<sup>1</sup>. It is also known that the absorption maxima increases with the increase in chain length between the acid and basic nuclei<sup>2</sup>. The variation in the basic component is also likely to cause much change in the absorption of the corresponding successive vinylenes homologues<sup>3</sup>. It was, therefore, considered worthwhile to synthesise some merocyanines containing 1,3-diphenyl-6-oxo-pyridazine as the fixed acid nucleus.

In the present investigation, the 1,3-diphenyl-6-oxo-pyridazine was condensed with diphenyl formamidine and beta-anilino-acrolein-anilhydrochloride yielding acetanilido compounds of type I ( $n' = 0,1$ ). These intermediate acetanilido compounds (I :  $n' = 0,1$ ) were



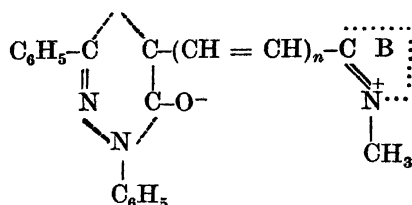
subsequently condensed with methiodides of different 2-methyl heterocyclic compounds which served as the basic nuclei. The reaction was accomplished in absolute alcohol in presence of triethylamine.

Expression for final dye is given below :



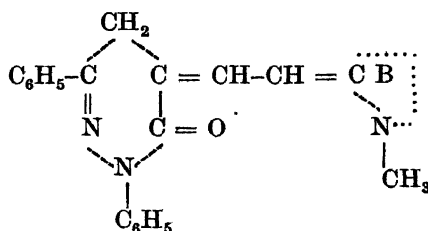
\* Present address : Department of Chemistry, S. B. W. College, Cuttack.

1. F. M. Hamer, *Quant. Review*, 1950, 327.
2. N. I. Fisher and F. M. Hamer, *Proc. Roy. Soc.*, 1936, A, **154**, 703;  
Fisher, Hamer, Beilson, *ibid.*, 1937, A, **163**, 1938;  
L. G. S. Brooker *et al.*, *J. Amer. Chem. Soc.*, 1941, **63**, 3192.
3. M. K. Rout *et al.*, *J. Indian Chem. Soc.*, 1964, **41**, 407;  
L. G. S. Brooker, *J. Amer. Chem. Soc.*, 1951, **73**, 5332.



It is well known that the colour of polymethine dyes is explained by resonance theory according to which a given dye is regarded as a hybrid of contributing structures both in the general and in the excited states<sup>4</sup>. When applied to the present series of dyes it is seen that there will be resonance between the two structures shown above. Table I shows the

TABLE I



B=Basic nucleus

No.	Nature of 'B'	$\lambda$ max m $\mu$	Sensitisation range	Sensn. max.	Remarks
a.	Benzothiazole	530	500—540	530	Poor
b.	Quinaldine	550	520—580	560	„
c.	Lepidine	580	530—540	575	„
d.	4-Ph.thiazole	520	520—560	540	„

results of the photographic sensitising activity of the pyridazine ( $n = 1$ ) dyes. The dicarbo-cyanines could not be used for such study owing to their instability. An examination of Table I shows that these dyes are sensitisers in the region where the dyes absorb maximum. Table II indicates the  $\lambda$ max values and other physical properties that were studied in the present investigation. From the  $\lambda$ max values it can be seen that with the increase in chain length (increase in one vinyl group) the absorption maxima increases to an extent of about 110 m $\mu$ . When the chain length remains same the  $\lambda$ max values also increase with the increase in basicity of the basic nucleus. Methanol was used as the solvent for the measurement of  $\lambda$ max values of the dyes.

#### EXPERIMENTAL

1. *Preparation of 1,3-diphenyl-6-oxo-pyridazine*: beta-Benzoyl propionic acid (1 mole) 8.6 g., and phenyl hydrazine (1 mole) 5 c.c. were taken in a porcelain dish and was heated in a steam bath for 2 to 3 hrs. The whole reaction mixture became homogeneous and thick red syrupy mass was obtained. It was cooled and stirred well with 200 ml. of ether. On stirring crystalline solids separated out. It was washed well with ether till the solid is free from any coloured impurities. The solid was crystallised from ethanol as plates.

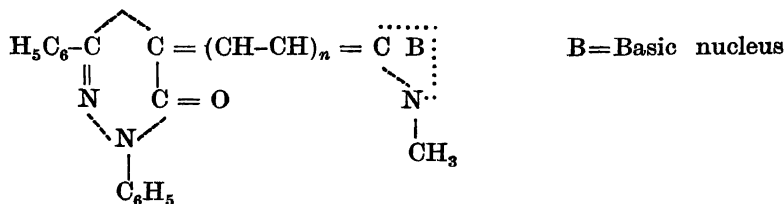
Yield —80%. M.P. 201°. Found : C, 76.54, H, 5.50%;  $C_{16}N_2OH_{14}$  requires C, 76.80; H, 5.60%.

2. *Preparation of 1,3-diphenyl-5-acetanilido methylene-6-oxo-pyridazine* : 1,3-Diphenyl-6-oxo-pyridazine (0.1 mole) 2.5 g. and diphenyl formamidine (0.1 mole) 1.96 g. were refluxed with 10 ml. of acetic anhydride and 1 g. of fused sodium acetate for 1 hr. Then the reaction mixture was cooled and poured into water. Then it was filtered and recrystallised from ethanol. Found : C, 76.03; H, 5.51%;  $C_{25}N_3O_2H_{21}$  requires : C, 75.94; H, 5.31%. Yield—80%. M.P. 95°.

3. *Preparation of 1,3-diphenyl-5-acetanilidoallylidene-6-oxo-pyridazine* : 1,3-Diphenyl-6-oxo-pyridazine (0.1 mole) 2.5 g. and beta-anilinoacrolein-anil-hydrochloride (0.1 mole) 2.5 g. were refluxed with 15 c.c. of acetic anhydride and 2 g. of fused sodium acetate for 1 hr. The reaction mixture was then poured into water and filtered. The solid was recrystallised from ethanol. Found : C, 76.77; H, 5.12%;  $C_{27}N_3O_2H_{23}$  requires : C, 76.95; H, 5.46%. Yield—70%. M.P. 85°.

4. *Preparation of 5-(3-methyl benzothiazoline-2-ylidene) ethylidene-1,3-diphenyl-6-oxo-pyridazine (a)* : The above dimethin merocyanine was prepared by refluxing an equimolecular proportion of 2-methyl benzothiazole methiodide and 1,3-diphenyl-5-acetanilido methylene-6-oxo-pyridazine in absolute alcohol for 10 mins. in a water bath in the presence of few drops of triethylamine. The solid which separated was filtered and recrystallised from ethanol. Yield—45%. M.P. 201°.

TABLE II



No.	Nature of 'B'	'n'	$\lambda$ max $m\mu$	m.p. °C	Yield %	% of Carbon		% Hydrogen	
						Calc.	Found	Calc.	Found
a.	Benzothiazole	1	530	201	45	73.63	73.68	4.98	4.81
b.	Quinaldine	1	550	226	42	80.57	80.82	5.51	5.50
c.	Lepidine	1	580	261	46	80.57	81.35	5.51	5.62
d.	4-Ph.thiazole	1	520	211	40	74.83	75.03	5.10	5.23
e.	Benzothiazole	2	640	180(d)	40	74.72	74.70	5.14	5.40
f.	Quinaldine	2	650	195(d)	35	81.26	81.09	5.64	5.78
g.	Lepidine	2	690	200(d)	35	81.26	81.36	5.64	5.60
h.	4-Ph.thiazole	2	635	190(d)	30	75.78	76.00	5.26	5.35

(d) Denotes decomposition

5. *Preparation of 5-(3-methyl benzothiazoline-2-ylidene)butylidene-1,3-diphenyl-6-oxo-pyridazine (e)* : The above tetramethin merocyanine was prepared by taking equimolecular

proportion of 2-methyl benzothiazole methiodide and 1,3-diphenyl 5-acetanilido allylidene-6-oxo-pyridazine in absolute alcohol and a few drops of triethylamine. It was refluxed for 10 mins. in a water bath. It was cooled and filtered. The solid was recrystallised from ethanol. Yield-40%. M.P. 180°(d).

The other dimethin and tetramethin merocyanines from various basic nuclei were prepared accordingly. The analytical data, m.p. etc., are given in Table II.

The author is thankful to Dr. P. B. Tripathy, for his valuable suggestion. The author is also thankful to the authorities of Utkal University for a research grant and to the Principal, Ravenshaw College, Cuttack-3, for the laboratory facilities.

Mayurbhanj Chemical Laboratory,  
Ravenshaw College,  
Cuttack-3.

*Received September 19, 1969*