

Dimethin and Tetramethin Merocyanines Derived from Thiadiazoles

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The preparation of some dimethin and tetramethin merocyanines derived from 5-*p*-tolyl, 5-*p*-anisoyl, 5-*p*-phenitoyl and 5-*p*-bromophenyl imino-2-methyl-1,3,4-thiadiazole and *N*-phenyl rhodanine, 1-phenyl-3-methyl-5-pyrazolone, 2-phenyl-5-oxazolone and *N,N*-diphenyl thiobarbituric acid has been described. The absorption maxima have been determined with a view to study the use of the dyes as possible photographic sensitisers.

Merocyanines are useful as photographic sensitisers¹⁻⁴. A merocyanine contains a basic nucleus and an acidic nucleus joined by a polymethin chain⁵. In the present investigation few substituted thiadiazoles like 5-*p*-tolyl, 5-*p*-anisoyl, 5-*p*-phenitoyl and 5-*p*-bromophenyl imino-2-methyl-1,3,4-thiadiazoles have been used as the basic nuclei. The quaternary salts of each of them were condensed separately with acetanilido vinyl and acetanilido allylidene derivatives of various ketomethylene compounds, which act as the acidic nuclei, to give dimethin and tetramethin merocyanines respectively. Structure given below represents the general structure of the merocyanines prepared :

Here R represents $-\text{CH}_3$, $-\text{OCH}_3$, $-\text{OC}_2\text{H}_5$, $-\text{Br}$ and acidic nuclei used are 2-Phenyl-5-oxazolone; 1-Phenyl-3-methyl-5-pyrazolone, *N*-Phenyl rhodanine and *N,N*-diphenyl thiobarbituric acid.

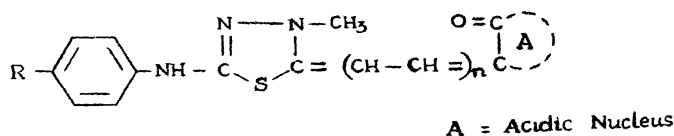
The absorption maxima of these dyes were measured in ethanol by using Unicam SP.600. The bathochromic shift with the increase in the chain length has been extensively studied^{6,7}. It was observed just for the increase of a vinyl group in the polymethin chain there is an increase of absorption maxima by about 100 $\text{m}\mu$. The absorption maxima of different merocyanines with the basic nucleus fixed was found to be different. This is due to the fact that the ketomethylene compounds used differ in their relative acidity⁸.

EXPERIMENTAL

1. Ethoxy methylene and acetanilido allylidene derivatives of 1-Ph.-5-oxazoline, 1-Ph-3-Me-5-pyrazolone-*N*-Ph-rhodanine and *N,N*-diphenyl thiobarbituric acid were prepared by standard procedure⁹.

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TABLE I



Sl. no.	Nature of A	Nature of R	Yield %	M.P. °C	max in $m\mu$	% C		% H	
						Found	Calc.	Found	Calc.
<i>Dimethin merocyanines (n = 1)</i>									
1.	Oxazolone	CH ₃	43	240	510	64.20	64.61	4.21	4.61
2.	"	OCH ₃	48	185	508	62.23	62.06	4.53	4.43
3.	"	OC ₂ H ₅	38	190	505	62.05	62.85	4.86	4.76
4.	"	Br	35	195	490	52.94	52.74	4.59	3.29
5.	Pyrazolone	CH ₃	45	140	480	65.10	65.50	5.02	5.21
6.	"	OCH ₃	55	128	465	62.01	63.00	5.62	5.01
7.	"	OC ₂ H ₅	40	190	465	63.15	63.74	5.73	5.31
8.	"	Br	40	130	475	54.24	53.84	3.27	3.84
9.	Rhodanine	CH ₃	60	186	530	58.01	57.53	4.37	4.10
10.	"	OCH ₃	55	178	520	56.00	55.50	3.90	3.96
11.	"	OC ₂ H ₅	45	228	525	56.21	56.41	4.29	4.27
12.	"	Br	35	205	525	47.01	47.71	3.03	2.98
13.	Thiobarbituric acid.	CH ₃	55	135	438	64.65	64.00	4.39	4.38
14.	"	OCH ₃	55	152	440	62.82	62.10	4.72	4.25
15.	"	OC ₂ H ₅	40	168	450	62.24	62.70	5.02	4.50
16.	"	Br	35	88	460	54.31	54.91	3.85	3.39
<i>Tetramethin merocyanines (N = 2)</i>									
17.	Oxazolone	CH ₃	55	118	610	66.14	66.34	4.27	4.80
18.	"	OCH ₃	53	120	608	63.28	63.88	4.93	4.62
19.	"	OC ₂ H ₅	45	124	612	64.11	64.57	4.92	4.93
20.	"	Br	35	132	605	54.29	54.88	3.53	3.53
21.	Pyrazolone	CH ₃	50	95	580	67.12	67.13	5.12	5.36
22.	"	OCH ₃	45	108	568	64.45	64.71	5.39	5.16
23.	"	OC ₂ H ₅	40	172	570	65.87	65.36	5.81	5.44
24.	"	Br	40	185	565	55.97	55.87	4.72	4.04
25.	Rhodanine	CH ₃	55	146	610	59.12	59.48	4.69	4.31
26.	"	OCH ₃	50	166	612	57.12	57.50	4.07	4.17
27.	"	OC ₂ H ₅	48	102	615	58.95	58.41	4.82	4.45
28.	"	Br	35	102	605	49.97	49.90	3.91	3.21
29.	Thiobarbituric acid.	CH ₃	60	154	550	65.12	65.33	4.12	4.53
30.	"	OCH ₃	55	162	545	63.89	63.49	4.89	4.40
31.	"	OC ₂ H ₅	50	175	552	64.34	64.02	4.23	4.65
32.	"	Br	45	123	555	55.73	55.59	4.02	4.51

2. The quaternary salts of 5-*p*-tolyl-5-*p*-anisoyl, 5-*p*-phenitoyl and 5-*p*-bromophenyl imino-2-methyl-1,3,4-thiadiazoles were prepared by the method of Tripathy and Rout¹⁰.

3. (5-*p*-Tolylimino-3-methyl-1,3,4-thiadiazole) (*N*-phenyl rhodanine) dimethin merocyanine⁹: 3-Phenyl-5-ethoxy methylene rhodanine (0.53 g) and 5-*p*-tolylimino-2,3-dimethyl-1,3,4-thiadiazolium iodide (0.69 g.) were refluxed in ethanol in the presence of triethyl amine (5 drops) for ten minutes. Excess of solvent was removed under reduced pressure and the solid was recrystallised from ethanol.

4. (5-*p*-Tolylimino-3-methyl-1,3,4-thiadiazole) (*N*-Phenyl rhodanine) tetramethin merocyanine. 3-Phenyl-5-acetanilido methylene rhodanine (0.55 g.) and 5-*p*-tolylimino-2,3-dimethyl-1,3,4-thiadiazolium iodide (0.69 g.) were refluxed in acetic anhydride in the presence of triethylamine (10 drops) for ten minutes. The solvent was removed under reduced pressure and the solid was washed with water and acetone. It was finally recrystallised from ethanol.

Other dyes were similarly prepared. Their absorption maxima in ethanol, melting point and other analytical data are given in Table-I.

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