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NOTE

Synthesis of Some New Photosensitizer Cyanine Dyes

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A series of new cyanine dyes has been synthesized by the reaction of *p*-dimethylamino cinnamaldehyde with meth and ethiodide of 5-arylamino-2-methyl-1,3,4-thiadiazole and quinaldines in ethanol using piperidine as catalyst. Absorption spectra structure relationships of the synthesized cyanine dyes were discussed.

Key Words: Synthesis, 5-Arylamino-2-methyl-1,3,4-thiadiazole, Cyanine dyes.

Cyanine dyes find extensive applications as sensitizers for photographic emulsions[1,2]. Other noted applications of these dyes especially in voltage sensitivity[3], producing offset printing plates[4,5] and also as tools for lasers[6] have been described. Some of these dyes are growth inhibitors to bacteria[7], posses antifungal activity[8] and can be used for the determination of the sensitivity of microorganism to antibiotics[9].

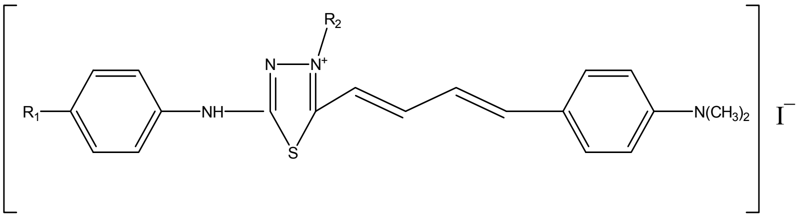
All melting points are uncorrected, purity of the compounds is checked on TLC using silica Gel-G. Absorption spectra were carried out on a Perkin-Elmer Lambda 15 UV/Vis spectrophotometer.

5-Arylamino-2-methyl-1,3,4-thiadiazoles and their salts were prepared by reported procedure[10]. Quinaldines and their salts were prepared by procedure given in the literature[11-13].

Cyanine dyes derived from 5-arylamino-2-methyl-1,3,4-thiadiazole (a): To the solution of the aldehyde (0.175 g, 0.001 mol), 5-phenylamino-2-methyl-1,3,4-thiadiazole ethiodide (0.347 g, 0.001 mol) in absolute ethanol (10 mL), piperidine (two drops) was added and the mixture was refluxed for 3 h, when deep red needles shaped crystals separated. The dye was filtered under suction and washed successively with ethanol and ether. Yield; 0.37 g (73.41 %), m.p. 255 °C. Anal. found (%): N 11.01, S 6.23, $C_{22}H_{25}N_4SI$ required: N 11.11, S 6.34 %. Other cyanine dyes (Table-1a) were synthesized by similar procedure.

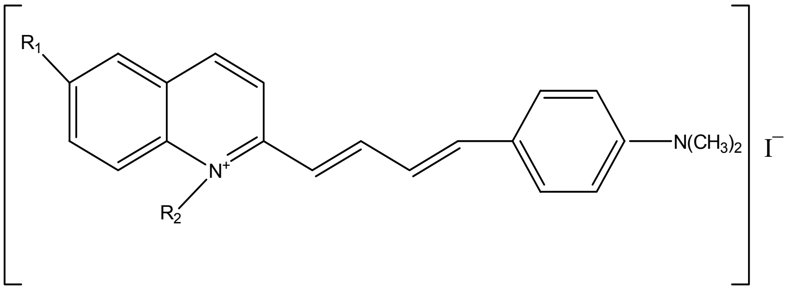
Cyanine dyes derived from salts of quinaldines (b): Solution of the *p*-dimethylamino cinnamaldehyde (0.175 g, 0.001 mol), 6-iodoquinaldine methiodide (0.411 g, 0.001 mol) in absolute alcohol (10 mL) together with piperidine (two drops) was gently refluxed for 3 h. Deep violet crystals of the dye separated during the heating.The dye was filtered under suction and washed successively with ethanol and ether, when it was obtained as deep violet needles. Yield; 0.41 g (72.18 %) m.p. 238 °C. Anal. Found (%): N 4.89; $C_{22}H_{22}N_2I_2$ required: N 4.92. Other cyanine dyes (Table-1b) were synthesized by similar procedure.

TABLE-1
(a) CYANINE DYES DERIVED FROM SALTS OF 5-ARYLAMINO-2-METHYL-1,3,4-THIADIAZOLES



S. No.	R_1	R_2	Colour	Yield (%)	m.p. (°C)	λ_{max} (nm)	ϵ_{max}
1	H	CH_3	Red	71.42	248	490	1100
2	H	C_2H_5	Deep Red	73.41	255	485	1200
3	CH_3	CH_3	Red	64.47	243	490	1600
4	CH_3	C_2H_5	Deep red	75.28	253	510	1800

(b) CYANINE DYES DERIVED FROM SALTS OF QUINALDINES



S. No.	R_1	R_2	Colour	Yield (%)	m.p. (°C)	λ_{max} (nm)	ϵ_{max}
1	H	CH_3	Deep brown	43.98	233	450	1000
2	Cl	CH_3	Violet	40.02	249	520	1800
3	Br	CH_3	Violet	61.22	235	536	2400
4	Br	C_2H_5	Violet	56.07	259	560	3400
5	I	CH_3	Deep violet	72.18	238	539	2600
6	I	C_2H_5	Deep violet	67.01	252	544	2400

A number of cyanine dyes (a$_{1-4}$ and b$_{1-6}$) (Table-1) using *p*-dimethylamino cinnamaldehyde have been synthesized by the condensation of the aldehyde with methiodides and ethiodides of 5-phenylamino-2-methyl-1,3,4-thiadiazole, 5-(*p*-tolylamino)-2-methyl-1,3,4-thiadiazole, quinaldine, 6-chloroquinaldine, 6-bromoquinaldine and 6-iodoquinaldine. The condensations were carried out in ethanolic medium using a few drops of piperidine as the condensing agent. The aldehyde reacted readily with the salts of heterocyclic compounds yielding deeply coloured crystalline products.

The synthesized cyanine dyes are highly coloured, lustrous, crystalline solids with varying degree of reflux. Colour of the dyes obtained from quinaldine and substituted quinaldine are generally deeper than the dyes obtained from 5-arylamino-2-methyl-1,3,4-thiadiazole. All these dyes are insoluble in ether. The new dyes are soluble in conc. H_2SO_4, liberating iodine vapours on warming. They are also pH sensitive dyes, hence their ethanolic solutions give changeable colours in acid/base media. The dyes from 5-arylamino-2-methyl-1,3,4-thiadiazoles are soluble in ethanol, methanol and acetone forming red to purple coloured solutions. The dyes from quinaldines have low solubility, their alcoholic solutions are violet to deep violet in colour.

Deep colour of new cyanines may be attributed to the increase in the intensity of light absorption and displacement of absorption maxima to longer wavelengths, consequent upon greater mobility of electrons of the chromophoric system stimulated by additional contribution of resonance structures. Spectral behaviour of the prepared cyanine dyes were determined by studying their electronic absorption spectra in 95 % ethanol. The position and molar extinction coefficients of absorption bands in the spectra were influenced by the nature of heterocyclic quaternary residue. As compared with the dyes (a_{1-4}) cyanine dyes (b_{1-6}) showed absorption spectra bands, their positions underwent bathochromic or hypsochromic shifts depending upon the type of substituent R_1 in the quinoline ring.

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