

## Synthesis of some quinazolinonium styryl hemicyanines (QSH) and their spectroscopic & antimicrobial properties

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### Abstract

In our ongoing research on some novel hemicyanines scaffolds a series of novel 6-substituted -2,3 dimethyl- 4-quinazolinones were prepared from o-anthranilic acid derivatives as starting material. 6- substituted -2,3 dimethyl quinazolinonium salts are valuable intermediates in the preparation of a wide range of cyanines & hemicyanines having significant absorptiophotospectroscopic potentiality and antimicrobial susceptibility. Some quinazolinonium styryl hemicyanines were synthesised by the catalytic condensation of 4- dimethylamino benzaldehyde & 4- dimethylaminonaphthaldehyde with 6- substituted, 2- methyl quinazolinonium methiodide. These QSH were synthesised with a view to study the effect of electron donor & electron withdrawing substituents at 6- position of quinazolinonium methiodide moiety at one end & also with respect to styryl chromophoric chain 4- dimethylaminophenyl & 4- dimethylaminonaphthyl moiety at the other terminal end of dyes on absorption maxima and antimicrobial efficacy. Purified samples were also subjected to invitro antimicrobial screening to evaluate their bactericidal activity on the basis of inhibitory zone data collected at different concentrations. Conclusive findings were encouraging.

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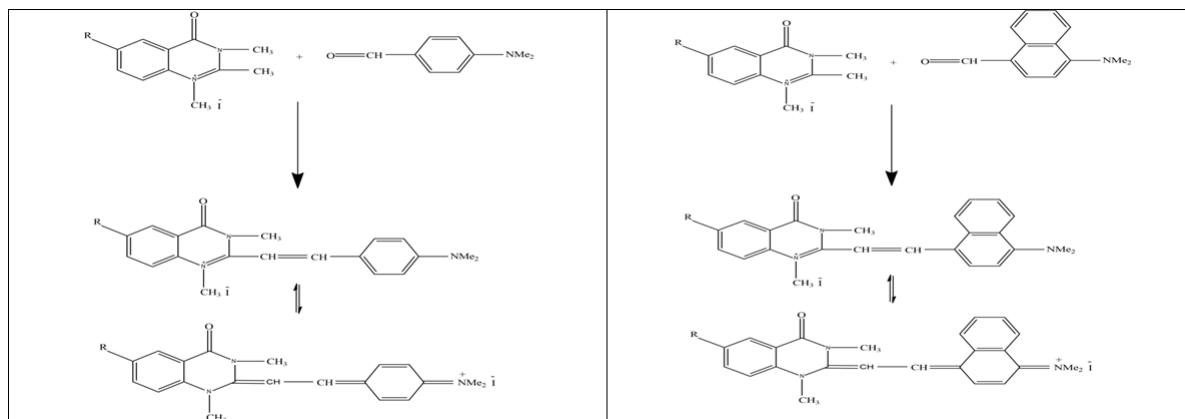
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### I. Introduction

Novel applications<sup>1-8</sup> of some polyenic cyanines & dyes, especially in solar energy conversion system, histological staining, optical information devices, antimicrobial activities & also in laser technology have been described. Hemicyanines and related dyes, have been the subject of several investigations by chemists<sup>9-18</sup> and some date have been reported in scholarly articles.<sup>19-22</sup>

In the present investigation two chalcones namely (i) 4- dimethylaminobenzaldehyde & (ii) 4- dimethylamino naphthaldehyde of extra pure Aldrich were used and each were allowed to condense catalytically with 6- substituted, 2- methyl quinazolinonium methiodide, affording two series of hemicyanines dyes were recorded and the effect of 6- substitution on the quinazolinone ring at one end as well as the effect of change in terminal moiety at the other end of styryl chromophore were studied.



2- p-dimethylaminophenyl styryl 6- substituted quinazolinone methiodide		2- p-dimethylaminophenyl naphthyl 6- substituted quinazolinone methiodide	
DYE	R	DYE	R
<sup>1</sup> C <sub>1</sub>	H	<sup>2</sup> C <sub>1</sub>	H
<sup>1</sup> C <sub>2</sub>	Cl	<sup>2</sup> C <sub>2</sub>	Cl
<sup>1</sup> C <sub>3</sub>	Br	<sup>2</sup> C <sub>3</sub>	Br
<sup>1</sup> C <sub>4</sub>	I	<sup>2</sup> C <sub>4</sub>	I
<sup>1</sup> C <sub>5</sub>	Me	<sup>2</sup> C <sub>5</sub>	Me
<sup>1</sup> C <sub>6</sub>	OMe	<sup>2</sup> C <sub>6</sub>	OMe
<sup>1</sup> C <sub>7</sub>	OEt	<sup>2</sup> C <sub>7</sub>	OEt

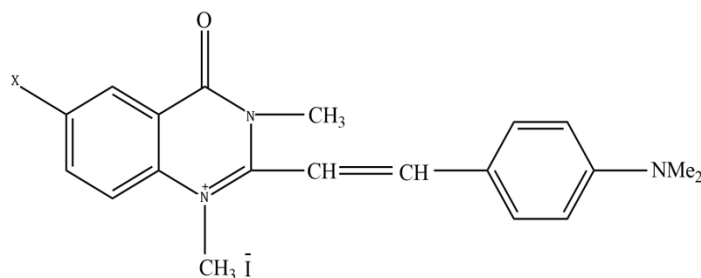
Scheme 1

## II. Result And Discussion

The absorption maxima & sensitization maxima of the dyes in ethanol are listed in Table-1 & 2.

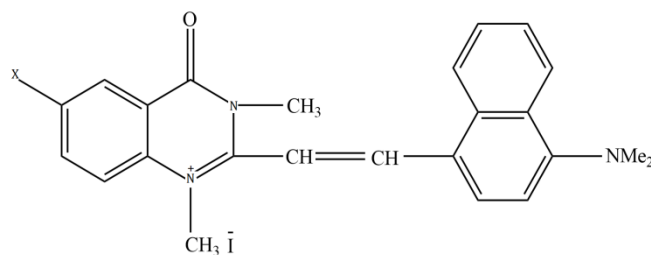
Table 1

Absorption and sensitization maxima ( $\lambda_{\max}$ ) of quinazolinone hemicyanines.



X	DYE	Absorption ( $\lambda_{\max}$ ) (nm)	Sensitization ( $\lambda_{\max}$ ) (nm)	Diff. (nm)
H	<sup>1</sup> C <sub>1</sub>	433	420	+13
Cl	<sup>1</sup> C <sub>2</sub>	442	430	+12
Br	<sup>1</sup> C <sub>3</sub>	446	440	+6
I	<sup>1</sup> C <sub>4</sub>	452	440	+12
Me	<sup>1</sup> C <sub>5</sub>	438	421	+17
OMe	<sup>1</sup> C <sub>6</sub>	441	433	+8
OEt	<sup>1</sup> C <sub>7</sub>	445	433	+12

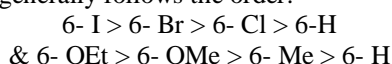
Table -2



X	DYE	Absorption ( $\lambda_{\max}$ ) (nm)	Sensitization ( $\lambda_{\max}$ ) (nm)	Diff. (nm)
H	<sup>2</sup> C <sub>1</sub>	458	444	+14
Cl	<sup>2</sup> C <sub>2</sub>	466	453	+13
Br	<sup>2</sup> C <sub>3</sub>	470	462	+28
I	<sup>2</sup> C <sub>4</sub>	475	461	+14
Me	<sup>2</sup> C <sub>5</sub>	460	442	+18
OMe	<sup>2</sup> C <sub>6</sub>	465	456	+9
OEt	<sup>2</sup> C <sub>7</sub>	470	457	+13

### 2.1 Absorption maxima

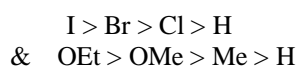
In the heterocyclic quinazolinonic system, the influence of the 6- substituents on  $\lambda_{\max}$ , although small but consistent. Progressive increase in molecular weight of the 6- substituents causes a progressive bathochromic shift in both the series. The sequence generally follows the order.



This corroborates the earlier observation that the nature and position of the substituent in the heterocyclic terminal residue of the dye molecule may influence visible absorption spectrum.<sup>2,3,23-26</sup> The dimethylaminophenyl & Dimethylaminonaphthyl unit at the other terminal end of the dye molecule also in consistent with the observation that additional resonance stabilization of dimethyl aminonaphthyl moiety increases wavelength of spectral absorption systematically with respect to dimethylaminophenyl residue.

### 2.2 Photo sensitization

The photosensitization data appears to be in good agreement with the spectral absorption data. The extension of optical sensitization induced by 6- substituents in the quinazolinonium moiety of all the dyes studied follows the similar sequence to that observed in absorption characteristics.



Extra sensitization  $\lambda_{\max}$  observed in case of p- dimethylaminonaphthyl vinylogues as compared to p- dimethylaminophenyl styrylogues towards longer wavelength by around 150 nm. This is presumably be due to additional  $\pi$  electrons delocalization.

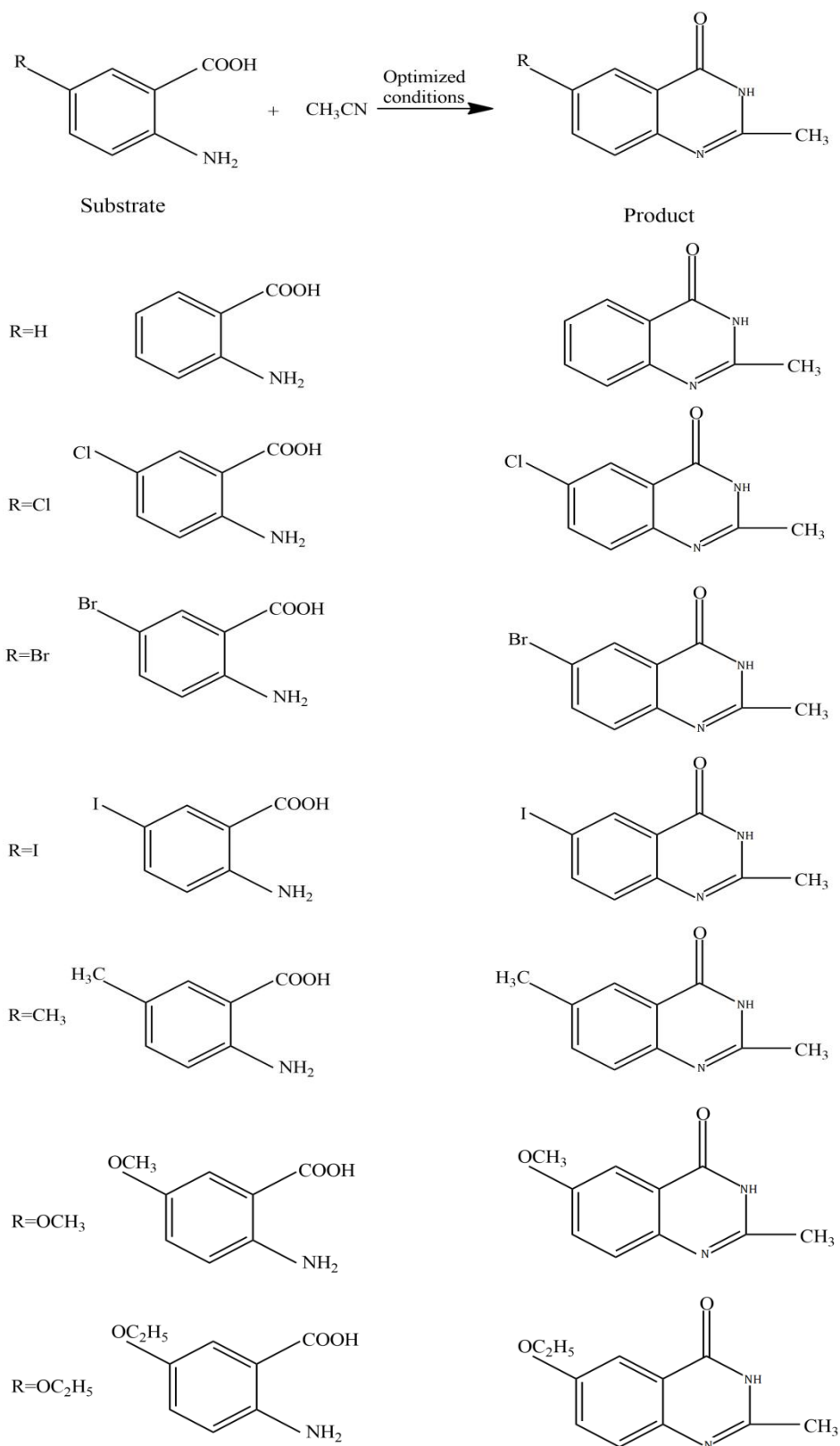
## III. Experimental

### 3.1 The chalcones

The chalcones p- dimethylaminobenzaldehyde and p- dimethylaminonaphthaldehyde were procured from Aldrich extra pure quality.

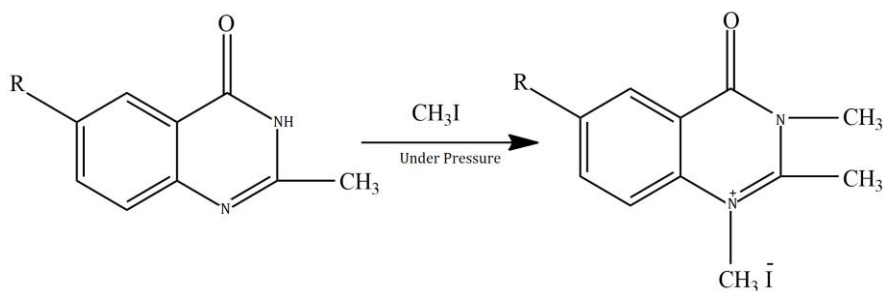
### 3.2 Synthesis of quinazolinone derivatives

This is prepared by the following typical procedure. To a flask containing sodium (23 mg, 1 mmol) was added anhydrous Me OH (5ml), then acetonitrile (0.95ml, 15 mmol) with a syringe via a rubber septum, and the solution was stirred at ambient temperature for about 40 min under nitrogen. A solution of appropriate o- aminobenzoic acid (5mmol) in anhydrous MeOH (25 ml) was then added. The reaction mixture was stirred at this temperature for about 2h under nitrogen. The precipitate was collected by filtration, washed with MeOH (8ml), H<sub>2</sub>O (8ml) and MeOH (5 ml), respectively, and then dried under vacuum at room temperature to obtain the corresponding 6-subst. 2- methyl quinazolinone derivatives.



### 3.3 The quaternised bases

The 6- substituted quinazolinonium methodides were prepared according to the general methods of Johnson & Adams<sup>27</sup> with slight modifications<sup>2,19</sup> under following scheme.



Scheme 2

### 1.1.1 2,3 Dimethyl 4- quinazolinone Methiodide

Analysis:-

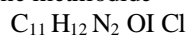
Found: C = 41.6%; H = 4% ; N = 8.8 % ; O = 4.9% I = 40 %

Calculated: C=41.78%; H = 4.11%; N = 8.86% O = 5.06%; I = 40.17%

IR Spectra (KBr) (cm<sup>-1</sup>): 1690(C = O); 1600(C = N), 3010 (C – H)

(Str. Aromatic)

### 3.3.2 2, 3 Dimethyl, 6- Chloro, 4- Quinazolinone methiodide



Analysis:

Found: C=37.6%, H = 3.3%, N = 7.9%, O= 4.5%, I = 36.1%,  
Cl= 10%

Calculated: C=37.67%, H=3.42%, N = 7.99%, O= 4.56%, I = 36.21%,  
Cl= 10.13%

IR Spectra (KBr) (cm<sup>-1</sup>): 1690(C = O); 1600(C = N), 3010 (C – H)

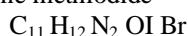
(Str. Aromatic)

Table 3

DYE	DYE NAME	Yield%	M.P (°C)	Molecular Formula	Found %		Calc%	
					N	Halo	N	Halo
<sup>1</sup> C <sub>1</sub>	2-p DMAPSQMeI	68.3	146	C <sub>20</sub> H <sub>22</sub> N <sub>3</sub> OI	9.3	28.2	9.39	28.39
<sup>1</sup> C <sub>2</sub>	2-p DMAPS 6-Cl QMeI	73.1	189	C <sub>20</sub> H <sub>21</sub> N <sub>3</sub> OICl	8.6	33.6	8.72	33.73
<sup>1</sup> C <sub>3</sub>	2-p DMAPS 6-Br QMeI	66.7	193	C <sub>20</sub> H <sub>21</sub> N <sub>3</sub> OIBr	7.9	39.1	7.98	39.33
<sup>1</sup> C <sub>4</sub>	2-p DMAPS 6-I QMeI	67.8	200	C <sub>20</sub> H <sub>21</sub> N <sub>3</sub> OI <sub>2</sub>	7.2	44.2	7.33	44.30
<sup>1</sup> C <sub>5</sub>	2-p DMAPS 6-Me QMeI	74.2	166	C <sub>21</sub> H <sub>24</sub> N <sub>3</sub> OI	9.0	27.4	9.11	27.53
<sup>1</sup> C <sub>6</sub>	2-p DMAPS 6-OMe QMeI	69.6	176	C <sub>21</sub> H <sub>24</sub> N <sub>3</sub> O <sub>2</sub> I	8.7	26.5	8.80	26.60
<sup>1</sup> C <sub>7</sub>	2-p DMAPS 6-OEt QMeI	71.3	189	C <sub>22</sub> H <sub>26</sub> N <sub>3</sub> O <sub>2</sub> I	8.4	25.8	8.55	25.85
<sup>2</sup> C <sub>1</sub>	2-p DMANS QMeI	72.7	165	C <sub>24</sub> H <sub>24</sub> N <sub>3</sub> OI	8.3	25.4	8.45	25.53
<sup>2</sup> C <sub>2</sub>	2-p DMANS 6-Cl QMeI	74.3	211	C <sub>24</sub> H <sub>23</sub> N <sub>3</sub> OICl	7.8	30.5	7.90	30.56
<sup>2</sup> C <sub>3</sub>	2-p DMANS 6-Br QMeI	69.3	218	C <sub>24</sub> H <sub>23</sub> N <sub>3</sub> OIBr	7.2	35.8	7.29	35.91
<sup>2</sup> C <sub>4</sub>	2-p DMANS 6-I QMeI	70.1	222	C <sub>24</sub> H <sub>23</sub> N <sub>3</sub> OI <sub>2</sub>	6.6	40.6	6.74	40.75
<sup>2</sup> C <sub>5</sub>	2-p DMANS 6-Me QMeI	72.7	188	C <sub>25</sub> H <sub>26</sub> N <sub>3</sub> OI	8.1	24.7	8.22	24.83
<sup>2</sup> C <sub>6</sub>	2-p DMANS 6-OMe QMeI	72.1	191	C <sub>25</sub> H <sub>26</sub> N <sub>3</sub> O <sub>2</sub> I	7.8	23.9	7.97	24.08
<sup>2</sup> C <sub>7</sub>	2-p DMANS 6-OEt QMeI	73.6	204	C <sub>26</sub> H <sub>28</sub> N <sub>3</sub> O <sub>2</sub> I	7.6	25.3	7.76	23.46

Abbreviations: QMeI, quinazolinone methiodide; DMAPS, dimethylaminophenyl styryl; DMANS, dimethylaminonaphthyl styryl.

### 3.3.3 2, 3 Dimethyl, 6- Bromo, 4- Quinazolinone methiodide



Analysis:

Found: C = 33.4%, H = 3%, N = 7%, O = 3.9%,

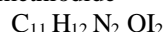
I = 32%, Br = 20.1%

Calculated: C = 33.43%, H = 3.03%, N = 7.09%, O = 4.05%,

I = 32.14%, Br = 20.23%

IR Spectra (KBr) ( $\text{cm}^{-1}$ ): 1690(C = O); 1600(C = N), 3015 (C – H)  
(Str. Aromatic)

3.3.4 2, 3 Dimethyl, 6- Iodo, 4- Quinazolinone methiodide



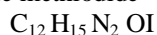
Analysis:

Found: C = 29.8%, H = 2.6%, N = 6.2%, O = 3.6%,  
I = 57.4%

Calculated:- C = 29.87%, H = 2.71%, N = 6.33%, O = 3.62%,  
I = 57.44%

IR Spectra (KBr) ( $\text{cm}^{-1}$ ): 1700(C = O); 1620(C = N), 3000 (C – H)  
(Str. Aromatic)

3.3.5 2, 3 Dimethyl, 6- Methyl, 4- Quinazolinone methiodide



Analysis:

Found: C = 43.5%, H = 4.5%, N = 8.4%, O = 4.8%,  
I = 38.3%

Calculated:- C = 43.64%, H = 4.54%, N = 8.48%, O = 4.84%,  
I = 38.46%

IR Spectra (KBr) ( $\text{cm}^{-1}$ ): 1690(C = O); 1600(C = N), 3017 (C – H)  
(Str. Aromatic)

3.3.6 2, 3 Dimethyl, 6- Methoxy, 4- Quinazolinone methiodide



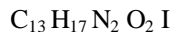
Analysis:

Found:- C = 41.5%, H = 4.2%, N = 8%, O = 9.1%,  
I = 36.5%

Calculated:- C = 41.63%, H = 4.33%, N = 8.09%, O = 9.25%,  
I = 36.68%

IR Spectra (KBr) ( $\text{cm}^{-1}$ ): 1680(C = O); 1610(C = N), 3010 (C – H)  
(Str. Aromatic)

3.3.7 2, 3 Dimethyl, 6- Ethoxy, 4- Quinazolinone methiodide



Analysis:

Found: C = 43.2%, H = 4.7%, N = 7.6%, O = 8.8%,  
I = 35.1%

Calculated: C = 43.34%, H = 4.72%, N = 7.77%, O = 8.89%,  
I = 35.25%

IR Spectra (KBr) ( $\text{cm}^{-1}$ ): 1690(C = O); 1620(C = N), 3015 (C – H)  
(Str. Aromatic)

### 3.4 The substituted styryl dyes.

For the dye condensation, the general method of preparation previously reported was used.

A mixture of the quaternary base and the chalcone dissolved in absolute alcohol was refluxed in the presence of a basic catalyst for about 2 hours. The separated crude product was recrystallised from methanol.

Analytical data, yield, m.p. etc of the dyes are summarised in Table 3.

### 3.5 Absorption and photo sensitization spectra.

The absorption maxima ( $\lambda_{\text{max}}$ ) were recorded on a Beckmann spectrophotometer, model DU, and the photosensitization spectra on an Adam Hilger wedge spectrograph, using process plates (N40, Ilford Ltd, UK).

### 3.6 Antimicrobial activity

The purified and screened samples of the cyanines were tested for bactericidal activity at different concentrations in ethanolic medium, using the 'disc sensitivity technique' against staphylococcus aureus (Gram Positive Cocci) and Escherichia coli (Gram negative bacilli) in nutrient agar medium and McConkey's medium respectively at an optimum temperature (35-37°C).

The  $\beta$ - haloaryl derivatives particularly the chloro derivative were found to be highly active against *S. aureus* and *E. Coli*, whilst the alkyl and alkoxy derivatives were moderately effective. The antimicrobial activity of the compounds was less pronounced than that of known antibiotics.

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