CHAPTER-IV

EXPERIMENTAL

All the dyes except those derived from benzoxazolyl and benzothiazolyl malondialdehydes have been reported earlier by various workers of this laboratory. It is, therefore, considered not necessary to give the detailed methods of their preparation. In some cases, viz. symmetrical cyanines, symmetrical oxonols and symmetrical azacyanines, the absorption data reported in various sources \(41-43\) have been straightway used for the purpose of comparison or computing the isoenergetic wavelengths of merocyanines.

Dyes derived from 2-(2-benzoxazolyl) and 2-(2-benzothiazolyl)-malondialdehydes:

The methyl group in 2-methylbenzoazole \(44\) and 2-methyl benzothiazole \(45\) has been diformylated using Wilsmeier reagent derived from dimethyl formamide and phosphorus oxychloride to yield, among others, 2-(2-benzoxazolyl)- and 2-(2-benzothiazolyl) malondialdehydes. The present investigation deals with the synthesis of some dyes viz. cyanines(I), oxonols(II) derived from these malondialdehydes.

\[
\begin{align*}
B & \quad \text{N} \quad \text{CH}_3 \quad \text{I} \quad \text{H}_3\text{C} \quad \text{N} \\
& \quad \text{- CH = CH - C = CH - CH =} \quad \text{B}
\end{align*}
\]

(I)
Preparation of the dye nuclei:

2-Methyl heterocyclic compounds and 4-methyl quinoline were procured and quaternised by using the standard method of heating them in sealed tubes with methyl iodide.

The ketomethylene compounds for the oxonols and merocyanines were prepared and purified by the standard methods reported in the literature. 2-(2-benzoxazolyl) and 2-(2-benzo-thiazolyl) malondialdehydes were also prepared by the literature method (44, 45).

Preparation of the dyes:

(i) Cyanines: These were prepared by heating methiodides (2 moles) of 2-methyl or 4-methyl heterocyclic compounds and malondialdehyde (1 mole) in ethanol (acetic anhydride in the case of the dye C6) in the presence of a base (pyridine for the dyes C1-C4 and piperidine for the dyes C5-C8) for 15-20 mins. The dyes
separated on cooling, crystallised from ethanol and finally purified by repeated washing with benzene. The purity was checked on a Silica gel TLC plate using benzene-ethanol(10:90) mixture as the solvent. The melting points and U.V. data of the dyes are given in Table-1.

(ii) Oxonols: These are prepared by heating malondialdehyde (1 mole) with ketomethylene compound (2 moles) in ethanol in the presence of piperidine for 20-35 mins. The reaction mixture was kept in ice-bath and the free oxonols were obtained by the addition of 2 N HCl (till just acidic). The product was filtered, washed repeatedly with water and finally crystallised from ethanol or benzene (Table-1). The purity was checked on a Silica gel TLC plate using benzene-ethylacetate - pyridine-ethanol(40:40:5:15% v/v) as the solvent.

In addition to the analytical data, the structure of the dyes were confirmed from the close similarity of their U.V. absorption spectra with the corresponding methine analogues. Such technique for establishing the structure has been reported by earlier workers in this field(46).

**Table 1: U.V. data of the dyes**

<table>
<thead>
<tr>
<th>Nature of A or B</th>
<th>U.V.,(nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>R=H</td>
</tr>
<tr>
<td>B= Cyaninesa</td>
<td></td>
</tr>
<tr>
<td>Benzoazolone</td>
<td>520</td>
</tr>
<tr>
<td>Benzthiazole</td>
<td>665</td>
</tr>
<tr>
<td>Quinoline-2</td>
<td>710</td>
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<td>Quinoline-4</td>
<td>810</td>
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Table 1 (Contd.)

<table>
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<th>Nature of A or B</th>
<th>U. V. (nm)</th>
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<tr>
<td></td>
<td>R=H</td>
</tr>
<tr>
<td>A = Oxonols&lt;sup&gt;b&lt;/sup&gt;</td>
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</tr>
<tr>
<td>N-methyl rhodanine</td>
<td>620</td>
</tr>
<tr>
<td>3-Phenyl thiohydantoin</td>
<td>610</td>
</tr>
<tr>
<td>Indane-1,3-dione</td>
<td>555</td>
</tr>
<tr>
<td>Diphenylthiobarbituric acid</td>
<td>540</td>
</tr>
<tr>
<td>1-Ph-3-methyl pyrazolone</td>
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</tr>
<tr>
<td>3-Phenyl isooxazolone</td>
<td>535</td>
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</table>

<sup>a</sup> data in ethanol,
<sup>b</sup> data in pyridine

Analytical data of the dyes

<table>
<thead>
<tr>
<th>Dyes</th>
<th>M.P. (°C)</th>
<th>% C</th>
<th></th>
<th>% N</th>
<th></th>
<th>% H</th>
<th></th>
</tr>
</thead>
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<tr>
<td>&lt;sup&gt;c&lt;/sup&gt;1</td>
<td>193</td>
<td>58.4</td>
<td>58.2</td>
<td>6.9</td>
<td>6.8</td>
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<td>190</td>
<td>55.3</td>
<td>55.1</td>
<td>7.3</td>
<td>7.2</td>
<td>3.6</td>
<td>3.5</td>
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<tr>
<td>&lt;sup&gt;c&lt;/sup&gt;5</td>
<td>195</td>
<td>64.3</td>
<td>64.0</td>
<td>7.03</td>
<td>7.0</td>
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<td>4.5</td>
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<td>67.3</td>
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<td>3.4</td>
<td>3.2</td>
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### Analytical data of the dyes (Contd.)

<table>
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<th>Dyes</th>
<th>M.P. (°C)</th>
<th>% C Calc.</th>
<th>% C Obs.</th>
<th>% N Calc.</th>
<th>% N Obs.</th>
<th>% H Calc.</th>
<th>% H Obs.</th>
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<td>O4</td>
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(d) - denotes decomposition.


- (49) -

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