CHAPTER 3

LASER ACTIVITIES OF SOME STYRYL AND MEROCYANINE DYES
LASER DYES: A BRIEF REVIEW

The qualities of continuous tunability, efficient narrow band operation and a wide spectral range, have made dye lasers an important tool in many areas of laser research and applications. Since its discovery by Sorokin et al., dye lasers have attained quite advanced level of technological development.

Two excellent reviews, one by Schafer and another by Drexhage, describe most of the fundamental aspects of dye-laser operation including the desirable structure and properties of laser dyes. In a more recent review, Nair has given an exhaustive account of the state-of-art of dye lasers and a list of dyes which have been screened for their laser activity. Maeda, in a series of papers has compiled the detailed results on the laser activity of all the dyes and related organic compounds.

Principle of Dye Laser Operation:

Organic dyes are characterised by a strong absorption band in the visible region of the electromagnetic spectrum due to the presence of an extended system of conjugation. The energy levels of a typical dye molecule in solution are shown in figure 1.
At room temperature (kT \sim 200 \text{ cm}^{-1}) under thermal equilibrium conditions most of the molecules are at the lowest vibrational level $S_0$. In the absorption process stimulated either by a laser or a flash lamp, the molecule is raised from $S_0$ to a different rotational and vibrational levels of the excited singlet states $S_1$ \ldots $S_n$ according to the Franck-Condon principle. There are various ways by which a molecule can return to the ground state from the excited state. Some of them are shown schematically in figure 1. The usefulness of a dye as a laser material is determined by the relative importance of these processes. The most important is the fluorescence emission involving the radiative transition from the lowest vibronic level of $S_1$ to some of the excited vibronic levels of.
the ground state. The molecule may be excited to a higher singlet state \( S_n (n \geq 1) \). But since the internal conversion \( S_n \rightarrow S_1 \) is usually extremely fast (\( \sim 1 \) ps), the fluorescence spectra of the dye remain unaffected and is thus independent of the wavelength of excitation. If one of the photons from the spontaneous fluorescence which follows the optical excitation, strikes an excited molecule on its way out, it induces the emission of further fluorescence quanta from these molecules and is consequently amplified when it leaves the cell. If the cell is placed in a laser resonator, whose mirrors would reflect a part of the emerging light back into the cell, the process can build up into a laser emission, if the effective amplification exceeds 1. Thus a dye laser is a four level (a, b, c and d in Fig.1) laser system with all the four levels lying in the singlet manifold.

**Structure and Properties of Laser Dyes:**

A laser dye should have an absorption maximum which matches the spectral distribution of pump source. From the foregoing discussions, it follows that the efficiency of a dye as an amplifying medium for a laser, depends on the many non-radiative processes that compete and reduce its fluorescence efficiency. For an ideal laser dye, these processes should therefore be the minimum.

There are various structural and environmental factors which contribute to these nonradiative processes.
The internal conversion $S_1 \rightarrow S_0$ is affected by structural factors such as structural mobility\textsuperscript{110,111}, hydrogen vibrations\textsuperscript{103} and intramolecular charge transfer between electron-donating and electron-accepting groups present in a molecule\textsuperscript{103}. There are two structural criteria, viz. the nature of π-electron distribution\textsuperscript{103} and heavy atom substitution\textsuperscript{103,109} which influences the intersystem crossing in an organic dye.

Among the environmental effects mention may be made of fluorescence quenching by charge transfer interactions with certain anions\textsuperscript{112}, energy transfer to an external agent with an energy level equal to or lower than that of the state to be quenched (excited singlet or the triplet states)\textsuperscript{103,109}.

Besides those shown in figure 1, there are a few other processes which contribute to the loss mechanism (i) absorption of laser light by excited singlet ($S_1$) and triplet ($T_1$) states following which molecules may go to the higher, $S_n$, states\textsuperscript{111}. The rapid radiationless decay from $S_n$ brings the molecule back to the lowest vibrational level of $S_1$. This type of excited state absorption (ESA) may affect the dye laser performance by the optical loss associated with it, particularly the absorption at the laser wavelength would reduce the gain and efficiency of the laser. If the molecules are accumulated in the triplet, $T_1$, state, due to relatively long triplet state life, they are trapped there and can not participate in the lasing action, (ii) excited state reactions - In a majority of organic compounds,
fluorescence is quenched by increasing the concentration, due to a strong interaction between the molecules in the excited state and those in the ground state. An excited molecule may also react with a molecule of solvent or another solute to form an excited complex (exciplex). Since their ground state is unstable, these species, if do not disturb the triplet effects and have high fluorescence efficiency, may sometimes be ideal lasing compounds.

The usefulness of a dye as a laser material is limited by its thermal and photochemical stability. All dyes undergo photochemical decomposition to varying extent and the 'half life' of a dye solution is generally expressed in terms of total energy input / volume of the dye solution for which the laser output drops to 1/e of its initial value. The amount and the nature of the photochemical products formed during the pumping primarily determines the life of the dye solution.

**Solvent Effects:** The most commonly used solvents for laser dyes are methanol, ethanol, ethyleneglycol, dimethylsulfoxide and cyclohexane. The thermo-optical properties of water and its deuterated analogue (D₂O) make them the most ideal solvents for high power dye lasers. There is, however, one disadvantage associated with these solvents. Dyes have a tendency to form dimers and higher aggregates which have absorption and fluorescence characteristics different from the monomer. The dimers usually have a hypsochromic shift in the absorption, and additional
band in the long wavelength side of the monomer and have weak fluorescence or none at all. Such dimers not only absorb a part of the pump light, but also increase cavity losses by their long wavelength band which often overlaps the fluorescence spectrum of the monomers\textsuperscript{103}. A number of workers have discussed the various factors responsible for dye aggregation\textsuperscript{103,117-123}.

Certain detergents such as N,N-dimethyldodecylamine-N-oxide (sold under the trade name Ammonyx-LO)\textsuperscript{124}, hexafluoroisopropanol and N,N-dipropylacetamide\textsuperscript{117} help to solubilize dyes that are insoluble in water\textsuperscript{125}. It has, however, been found that there is a deterioration in the thermo-optical properties of water on addition of these detergents\textsuperscript{126}.

The fluorescence spectra of xanthene dyes containing the mobile diethylamino substituents (the rhodamine series) are strongly affected by the temperature and viscosity of the solvent\textsuperscript{103}.

**Laser Dyes:**

By considering the various structure-laser activity relationships, it has been possible to synthesize a large number of dyes which act as excellent laser materials. A good deal of work is still being carried out to improve the laser performance of these dyes by some structural modification or to synthesize new class of laser dyes.
As already mentioned, Maeda\textsuperscript{105-108} and Nair\textsuperscript{104} have given a comprehensive list of all the dyes which have been screened for their laser efficiency along with their structure, absorption and lasing wavelengths. Their lists which include the dyes that have been reported till 1981, contain the following classes of dyes.

(i) Cyanines, (ii) Merocyanines, (iii) Phthalocyanines, (iv) Xanthene dyes\textsuperscript{101,103}, (v) Triphenylmethane dyes, (vi) Acridine dyes, (vii) Azine dyes, (viii) chlorophylls, (ix) Coumarine derivatives\textsuperscript{101}, (x) Quinolones\textsuperscript{127-131}, (xi) Oxadiazole derivatives\textsuperscript{132,133}, (xii) Oxazine dyes\textsuperscript{134}.

A relatively recent report on a new class of efficient laser dyes is a series of seven benzoxazinone derivatives\textsuperscript{135} (I).

![Chemical structure](image)

(I)

Systems of dye mixtures have been investigated by several authors\textsuperscript{136-140}, to extend the tuning range and improve the lasing efficiency. These systems utilize the energy transferred from an auxiliary dye whose fluorescence band coincides with the absorption band of the lasing dye. Multiple dye systems exhibit higher output energy by exploiting the pump light more efficiently, particularly the UV region of the broad band emission of flash lamps, which is weakly absorbed by the primary lasing dye.
Schafer et al., and Liphardt et al. have synthesized bifluorophoric dyes that utilize the principle of intramolecular energy transfer. In these compounds, two dyes are linked with a short saturated hydrocarbon chain that insulates the conjugation of π-electron system of two moieties. Structure - II illustrates one such dye in which p-terphenyl (PT) and dimethyl-POPOP (DMP), have been linked together.

\[ \text{Structure - II} \]

Considerable interest is being shown in recent years to develop dye-vapour lasers, in which direct optical excitation of the dyes is affected in the vapour phase for high conversion efficiencies and tunable laser actions. Though, electrically discharged excited dye-vapour laser has not so far been demonstrated, important steps towards this goal have been achieved and optically as well as electron beam dye-vapour lasers have been reported.
LASER ACTIVITY OF SOME STYRYL AND MEROCYANINE DYES:

One of the main objectives in researches on laser dyes is to find dyes which will aid not only in obtaining a laser that is tunable over a wide range, but would also be free from the defects of other laser active materials. Ever since the initial reports on the use of dyes in laser technology appeared during early 60's, although a large number of both new and commercially available compounds have been screened for their laser activities, only a few have been found to be useful. Therefore any experimental and/or theoretical studies which would reduce the number of compounds to be tested, was considered worthwhile both from a scientific and commercial point of view. The specific objective of the present work was therefore to study the effect of structural and environmental changes on the laser activities of organic dyes that would aid the design and synthesis of dyes with improved laser efficiency.

Some p-dimethylamino styryl dyes as well as a number of merocyanines and benzylidene compounds derived from various ketomethylene compounds and heterocyclic bases (Structures given in page 137) were synthesized to study their laser activities.
There were several consideration for the choice of these dye series.

(a) These classes of dyes which have very strong absorption in the wavelength region 400-600 nm, have not been screened for their laser activity,

(b) They are photochemically quite stable and soluble in most of the solvents that are commonly used in dye laser work,

(c) Their relatively simple method of preparation enables one to get appreciable quantities of these dyes in very high grade purity required for laser activity,

(d) The cationic cyanines derived from the heterocyclic bases used in the work are known to be very efficient laser dyes. So it was considered worthwhile to test the laser activities of the compounds in which these moieties are present in the form of nonionic merocyanines.

The laser tests were carried out with nitrogen (337 nm), XeCl (308 nm) and the second harmonic YAG / Nd^3+ (530 nm) lasers. The results of these studies are described below:

(i) Excitation of fluorescence with nitrogen laser (337 nm) showed dyes V, VI, VIII, XVI and XVII to have some fluorescence, with that for V and XVI being the strongest. All dyes were tested for laser emission in ethanol solution using nitrogen laser of 10 ns pulsewidth and 200 kW peak power. In combination
1. STYRYL DYES

\[
\text{(CH}_3\text{)}_3\text{N} - \text{CH} = \text{CH} - \underset{\text{B}}{\bullet} \quad \underset{\uparrow}{\sigma}
\]

\( B = \)

(III) \quad (IV) \quad (V) \quad (VI)

(Quinoline-4) \quad (Quinoline-2) \quad \text{(Benzothiazole)} \quad \text{(Benzoxazole)}

(VII) \quad (VIII) \quad (IX)

(4-Phenylthiazole) \quad \text{(Pyridine-4)} \quad \text{(Thianaphthalenium)}

2. BENZYLIDENE DERIVATIVES

\[ A = \text{CH} - \text{CH} - \text{N} \]

\( A = \)

(X) \quad (XI) \quad (XII) \quad (XIII)

(2-Methyl-1-Oxazolone) \quad (2-Phenyloxazolone) \quad (1-Phenyl-3-Methyl Pyrazolone) \quad \text{(Chroman-2,4-Dione)}

3. MEROCYANINES FROM 2-PHENYL OXAZOLONE

\[ \text{B} = \text{CH} - \text{CH} - \text{N} \]

\( B = \)

(XIV) \quad (XV) \quad (XVI) \quad (XVII)

(Quinoline-4) \quad (Quinoline-2) \quad \text{(Benzothiazole)} \quad \text{(Benzoxazole)}
with Coumarin 500 (lasing max. 503 nm at the concentration used),
dyes XVI and XVII showed weak laser emission with maximum at
525 nm and 560 nm respectively. No detectable lasing was observed
in other cases. Visual inspection of day light induced fluore-
scence in glycerol indicates good quantum yield for the dye V.
There was, however, no lasing when pumped with a nitrogen laser,
even in presence of booster like disodium fluorescein.

(ii) Excitation of fluorescence with XeCl laser (308 nm) showed
dyes V, VI, VII, VIII and XI to have the highest fluorescence,
all others showing very weak fluorescence. All dyes were tested
for laser emission in DMF solution in a 1 sq cm cuvette with
transverse excitation using a f = 40 mm focussing cylindrical
lens and a XeCl laser with 60 mJ pulse energy for pumping.
As a resonator for the dye laser, on one end the Fresnel reflection from the cell window and on the other hand a fully-
reflecting mirror was used. Only dyes V, VI, VII, and VIII showed laser emission.

(iii) Screening with a mode-locked YAG / Nd³⁺ laser deliv-
ering on the second harmonic (530 nm) with a single pulse of
25 ps pulse width, dyes III, IV, V, VI, and VIII showed laser
action with the following characteristics in methanol.
Table - 1: Lasing characteristics of dyes

<table>
<thead>
<tr>
<th>Dye</th>
<th>Centre of laser emission (nm)</th>
<th>Remarks</th>
</tr>
</thead>
<tbody>
<tr>
<td>III</td>
<td>653.3</td>
<td>Very weak laser action</td>
</tr>
<tr>
<td>IV</td>
<td>679.7</td>
<td>Lases when highly concentrated</td>
</tr>
<tr>
<td>V</td>
<td>606.0</td>
<td>Very good laser action, intense emission</td>
</tr>
<tr>
<td>VI</td>
<td>565.3</td>
<td>Very good laser action, intense emission</td>
</tr>
<tr>
<td>VII</td>
<td>596.1</td>
<td>Good laser action</td>
</tr>
<tr>
<td>VIII</td>
<td>617.0</td>
<td>Good laser action</td>
</tr>
<tr>
<td>IX</td>
<td></td>
<td>No laser action</td>
</tr>
</tbody>
</table>

It is quite evident from the results described above that from among the dyes synthesized and tested, the styryl dyes (dyes III – VIII, belonging to series 1) have very good potential as laser dyes for practical applications with an appropriate pump source. Failure to observe any significant laser emission, when pumped with a nitrogen or XeCl laser, is most likely due to very weak absorption by the dyes at the laser wavelength (337 nm and 308 nm respectively). The weak lasing of the dye III and IV even with YAG / Nd<sup>3+</sup> laser could be on
account of their distortion from planarity due to steric crowding, a conclusion based on theoretical studies (Section 1.4B). It is quite well known that rigid, planar molecules generally have high fluorescence efficiency. Steric crowding tends to degrade excited dye molecules by torsional interconversion and photoisomerism. It is, however, not possible to pin point the exact loss mechanisms operating here.

Failure of other dyes to show any significant lasing property may be due to any of the following reasons:

(a) loss of coplanarity due to ortho hydrogen interaction with relatively high rotational barrier,

(b) steric crowding due to the presence of bulky phenyl group in case of XI, XV - XVIII,

(c) presence of trace impurities which has escaped detection by thin layer chromatographic method employed in the present work.

Synthesis of dyes: Synthesis of the styryl dyes III - VIII have been described earlier (Section 2.2). IX was synthesized by the method described by Tilak et al.\textsuperscript{143}. Dyes X and XI were prepared by condensing acetylglycine and benzoylglycine respectively with p-dimethylamino benzaldehyde in acetic anhydride and fused sodium acetate, following the procedure for similar compounds
described in Vogel\textsuperscript{144} and were finally characterised by element analysis. Dyes XII and XIII were prepared by condensing the appropriate ketomethylene compounds (1-phenyl-3-methyl pyrazolone, and 4-hydroxy coumarin respectively) with p-dimethylaminobenzaldehyde in acetic anhydride and fused sodiumacetate and were characterized by element analysis. The merocyanines belonging to series 3 were prepared by the method described in the literature\textsuperscript{145-147}. 