SPECTROSCOPIC AND LASER PROPERTIES OF THE DYE CHROMOGEN RED B*

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Summary

The title compound, the xanthene merocyanine related to rhodamine B and fluorescein, shows a slightly larger Stokes shift than either dye and lases at intermediate wavelengths. A weak response under nitrogen laser pumping is ascribed to strong excited state absorption.

1. Introduction

Systematic changes of molecular structure serve as a probe of spectroscopic properties and can lead to the design of improved laser dyes.

The title compound is a xanthene merocyanine, chemically related to the laser dyes rhodamine B (the cyanine) and fluorescein (the oxonol) and to a third efficient class, the 7-aminocoumarins. Strictly, the material described in the early literature [1] included derivatives of the parent compound 6-diethylamino-9 (2-carboxyphenyl) 3H-xanthen-3-one (Fig. 1) and it is properties of the latter only that are reported here.

2. Experimental

The dye was prepared according to the method of Ghatak and Dutt [2] and was crystallized from aqueous ethanol.

Fluorescence measurements were performed on a Schoeffel RRS-1000 spectrofluorimeter which was interfaced with a Hewlett Packard 9821A programmable calculator for spectral correction and background. The excitation bandwidth was 1.6 nm, the emission bandwidth 3.5 nm and the
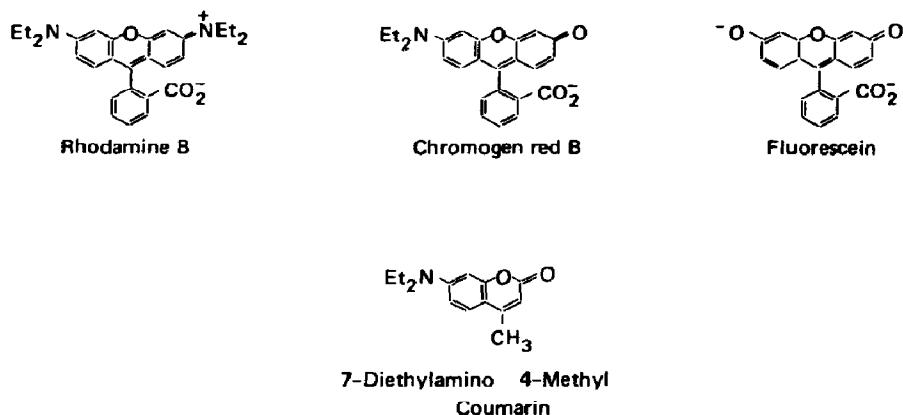

Fig. 1. A comparison of the structure of chromogen red B in basic solution with known laser dyes.

instrument took a measurement every 2 nm. Absorption measurements were performed on a Cary 14 spectrometer.

Tests of laser performance were conducted using oscillators of length 10 cm pumped by a pulsed laser. Each oscillator was composed of a dye cuvette, a borosilicate optical flat and a rotatable grating having 1 200 grooves mm^{-1} and gave outputs of linewidth 1.5 nm. Oscillator I was pumped by an NRG 0.8-8-400 nitrogen laser producing pulses of 1 mJ and 8 ns FWHM at 337.1 nm and a frequency of 5 Hz. Oscillator II was pumped from the output of oscillator I using a coumarin dye in the blue–green at 480 nm to give pulses of 100 μJ and 6 ns FWHM. The pulse energy was measured on a Laser Precision Corporation Rk 3230 energy meter and the wavelength on a Jarrell Ash 0.5 m spectrometer with a photographic attachment.

3. Results

Dilute solutions (10^{-5} M) of the dye in ether, dioxane, acetone, acetonitrile and dimethyl sulfoxide are nearly colorless, which is almost certainly the result of cyclic lactone (fluoran) formation as occurs for rhodamine B. The fluorescence of solutions in alcohols is improved in high viscosity solvents (benzyl alcohol, ethylene glycol) and methanol, particularly on the addition of a base. Such behavior again resembles that of rhodamine B and indicates a fluorescer of only moderate quantum yield which is sensitive to environment and that the carboxylate anion (Fig. 1) rather than the acid is the strongest fluorescing species. In contrast to rhodamine, the fluorescence and laser output are not enhanced in fluorinated alcohols such as trifluoroethanol. Acid produces a small red shift (about 2 nm) and a slight decrease in the absorption maxima.

Spectra of the three dyes in basic methanol are compared in Fig. 2 and Table 1 and those in basic dioxane–water mixtures are compared in Table 2. Oscillator strengths and transition moments for the low frequency absorp-
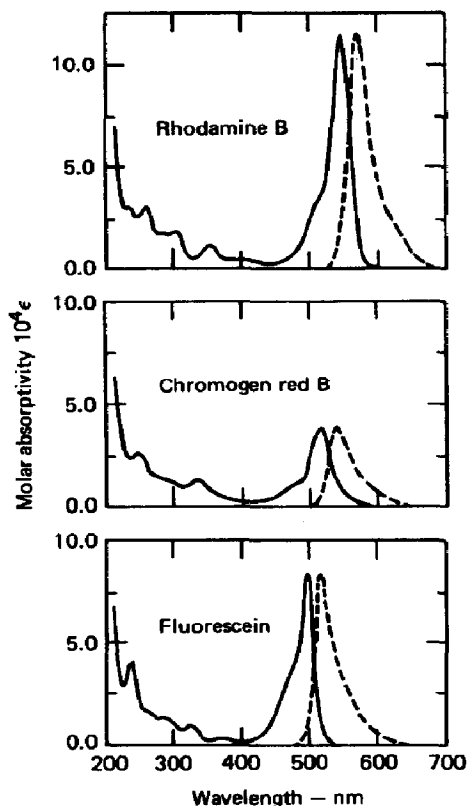
Fig. 2. Absorption and fluorescence spectra of the three dyes in 99% methanol containing 0.01 N sodium hydroxide. The fluorescences are in arbitrary units and are normalized to the absorptions.

TABLE 1

Spectroscopic properties of the three dyes in 99% methanol containing 0.01 N NaOH

	Rhodamine B	Chromogen red B	Fluorescein
Absorption maxima (nm)	545	517	497
$10^4\ \epsilon_{max}$	11.4	3.9	8.4
Oscillator strength	0.76	0.34	0.59
Transition moment (debye)	9.4	6.0	8.2
Fluorescence maxima (nm)	569	542	518
Fluorescence quantum yield[a]	0.52	0.58	1.00
Fluorescence Stokes shift (10^3 cm^{-1})	0.78	0.89	0.81

[a]Compared with a quantum yield of 1.00 for the fluorescein solution.

tion bands from absorption onsets to minima were estimated using the formulae

$$f = 4.32 \times 10^{-9} \int \epsilon\, d\nu \tag{1}$$

TABLE 2

Absorption maxima (nm) in water–dioxane mixtures[a]

	Water content (mol.%)				
	100	70	50	30	1
Rhodamine B	553	548	546	—	—
Chromogen red B	522	518	516	514	512
Fluorescein	491	501	502	—	—

[a]Containing 0.01 N tetramethylammonium hydroxide.

and

$$D = 0.0958\{\int(\epsilon/\nu)\ \mathrm{d}\nu\}^{1/2} \tag{2}$$

Quantum yields were determined for the same 500 nm excitation. In Table 2 the absorptions diminish with increasing dioxane content, less so for chromogen red B than the others, in accordance with increasing fluoran formation.

As expected for a merocyanine, chromogen red B shows a Brooker deviation of the absorption maximum (517 nm compared with the mean value of 521 nm), a larger Stokes shift than the cyanine or oxonol and a red shift of the absorption maximum with increasing polarity of the solvent. However, such shifts are small and the change with solvent medium is no larger than that for rhodamine B or fluorescein. The transition moment and particularly the oscillator strength are smaller for chromogen red B.

Solutions for laser testing were prepared that gave identical absorption depths (0.3 mm for an absorbance of 1.0) at (a) the nitrogen laser wavelength, i.e. 5.0×10^{-3} M for the cyanine, 3.0×10^{-3} M for the merocyanine and 7.5×10^{-3} M for the oxonol, and (b) at 480 nm, i.e. 3.0×10^{-3} M, 3.0×10^{-3} M and 1.0×10^{-3} M respectively. The wavelength 480 nm was chosen because it is within the low frequency absorption bands but is blue shifted from all fluorescences.

Responses of oscillator I and oscillator II are shown in Fig. 3. Chromogen red B shows laser operation at intermediate wavelengths although in both cases this is weaker than those of either rhodamine B or fluorescein. The shifts between tuning maxima and absorption maxima are each larger than those for rhodamine B or fluorescein. The relative response is much greater for 480 nm pumping than for 337.1 nm.

Such comparisons depend critically on oscillator construction and pumping fluxes and permit only first order generalizations. A weaker response for chromogen red B can arise from either strong excited state absorption at the pump wavelengths or larger excited state absorption across the fluorescence band. Certainly the marked difference between 337.1 nm and 480 nm pumping implies a strong excited state absorption at the nitrogen laser wavelength.
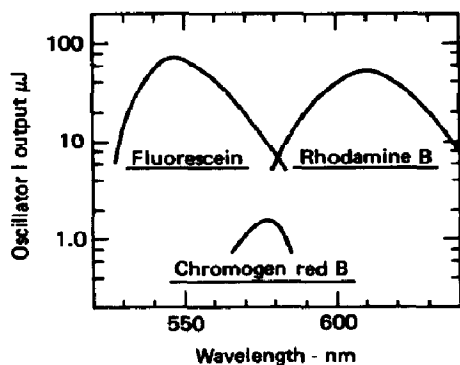
(a)
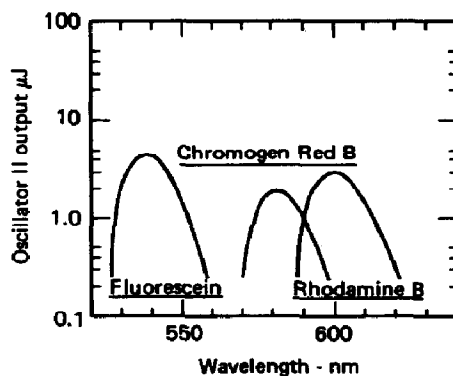
(b)

Fig. 3. The tunable laser responses of the three dyes in 99% methanol containing 0.01 N sodium hydroxide for pump wavelengths of (a) 337.1 nm and (b) 480 nm.

References

1 K. Venkataraman, in Synthetic Dyes, Vol. 2, Academic Press, New York, 1952, p. 750.
2 N. N. Ghatak and S. Dutt, J. Indian Chem. Soc., 6 (1929) 465.