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T.G. Pavlopoulos

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At the present, the Coumarin laser dyes are the ones most widely used for the spectral region stretching from 440 to 550 nm. However, the Coumarin dyes have rather poor photochemical stability.

While searching for more stable and efficient laser dyes, we studied 3,4,6,7-tetramethyl-1, 5-diazabicyclo [3.3.0] octa-3, 6-diene-2, 8-dion [syn-(CH₃ⁿCH₃ⁿ)B for short]. This new heterocyclic molecule was first reported by Kosower, Pazhenchevsky, and Hershkowitz in 1978. Their work included the observation of strong and striking fluorescence properties, as well as good photochemical stability, for these compounds. It should be emphasized that strong fluorescence (high quantum fluorescence yield) of organic compounds which are not benzene derivatives is rare. The quantum fluorescence yield of the syn-(R₂ⁿ,R₁ⁿ)B ranges from 0.7 to 0.9. The isomer anti-(R₂ⁿ,R₁ⁿ)B is only weakly fluorescent.

There are two specific spectroscopic parameters of laser dyes which critically determine the laser action efficiency of flashlamp and cw laser-pumped dye lasers: (a) a high quantum fluorescence yield and (b) low triplet-triplet (T-T) absorption over the fluorescence (laser action) spectral region of the laser dye.

We, therefore, recorded the T-T absorption spectrum of syn-(CH₃ⁿCH₃ⁿ)B. We compared the laser action parameters of syn-(CH₃ⁿCH₃ⁿ)B with those of Coumarin 30. Both syn-(CH₃ⁿCH₃ⁿ)B and Coumarin 30 showed laser action in the same spectral region. syn-(CH₃ⁿCH₃ⁿ)B lased only 30% less efficient than did Coumarin 30.

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Laser action from *syn*-(methyl,methyl) bimane

Theodore G. Pavlopoulos

U. S. Naval Ocean Systems Center, San Diego, California 92152

Joseph H. Boyer, I. R. Politzer, and Chun M. Lau

Department of Chemistry, University of New Orleans, New Orleans, Louisiana 70148

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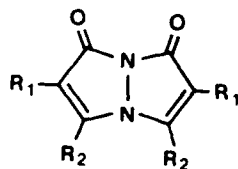
Under the flashlamp excitation from an aqueous solution of *syn*-(methyl,methyl)bimane laser action was observed at 504 nm. The absorption, fluorescence, and triplet-triplet absorption spectra of this compound were also recorded. This compound showed good photochemical stability. The laser action properties of this new laser dye were compared with those of Coumarin 30.

At present, the Coumarin laser dyes are the ones most widely used for the spectral region stretching from 440 to 550 nm. However, the Coumarin dyes have rather poor photochemical stability.

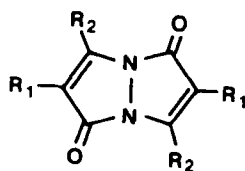
While searching for more stable and efficient laser dyes, we studied 3,4,6,7-tetramethyl-1,5-diazabicyclo[3.3.0]octa-3,6-diene-2,8-dione [*syn*-(CH₃,CH₃)B for short]. This new heterocyclic molecule was first reported by Kosower, Pazhenchevsky, and Hershkowitz in 1978.¹ Their work included the observation of strong and striking fluorescence properties, as well as good photochemical stability, for these compounds. It should be emphasized that strong fluorescence (high quantum fluorescence yield) of organic compounds which are not benzene derivatives is rare. The quantum fluorescence yield of the *syn*-(R₂,R₁)B ranges from 0.7 to 0.9.¹ The isomer *anti*-(R₂,R₁)B is only weakly fluorescent.

There are two specific spectroscopic parameters of laser dyes which critically determine the laser action efficiency of flashlamp and cw laser-pumped dye lasers: (a) a high quantum fluorescence yield and (b) low triplet-triplet (T-T) absorption over the fluorescence (laser action) spectral region of the laser dye.

We, therefore, recorded the T-T absorption spectrum of *syn*-(CH₃,CH₃)B. We compared the laser action parameters of *syn*-(CH₃,CH₃)B with those of Coumarin 30. Both *syn*-(CH₃,CH₃)B and Coumarin 30 showed laser action in the same spectral region. *syn*-(CH₃,CH₃)B lased only 30% less efficient than did Coumarin 30.



syn-(R₂,R₁)bimane



anti-(R₂,R₁)bimane

We used the same equipment described by Pavlopoulos² to measure the absorption [singlet-singlet (S-S)], fluorescence, and T-T absorption of *syn*-(CH₃,CH₃)B. As the exci-

tation source for recording the T-T absorption spectrum, we used the 351,356-nm lines of a Spectra-Physics krypton-ion cw laser.

A small EG&G model no. FX139C-2 flashlamp pumped dye laser was used for the experiments. The flashlamp produced pulses of approximately 200-ns rise time and 600-ns length at the half-width of the pulse. It delivered 2 J at 6.32 kV, 5 J at 10.0 kV, and 10 J at 14.14 kV. The dye laser was used in the nonflowing (static) mode. The dye cell was about 2.5 mm in diameter and 50 mm long, positioned in a single ellipsoidal cavity of small eccentricity. The intensity of the laser pulses, which were measured with a photomultiplier, were reduced by several Jenaer Glaswerk neutral-density filters and displayed on the screen of a Tektronix 7834 storage oscilloscope.

The preparation of *syn*-(methyl,methyl)bimane was carried out from ethyl methylacetoacetate in three steps according to Kosower and Pazhenchevsky.³ It was purified by recrystallization from acetonitrile. Coumarin 30 was obtained from the Eastman Kodak Company. Hexafluoroisopropanol was purchased from PCR.

Another unusual property of the *syn*-bimanes is their remarkable dependence on the spectral location of their lowest-energy absorption band (S-S) on the solvent employed. Consequently, the spectral location of the fluorescence is also very much solvent dependent.^{1,3} For example, the fluorescence maximum for *syn*-(CH₃,CH₃)B, the compound we studied shifts from 420 nm in *p*-dioxane to 460 nm in ethanol to 480 nm in water. However, we found laser action under flashlamp excitation from this compound only in water and hexafluoroisopropanol solutions.

The T-T absorption spectra of organic compounds are measured at liquid-nitrogen temperatures to extend the lifetime of the triplet-state molecules. For this measurement, the organic compound must be dissolved in a solvent which freezes in clear, glasslike solid at liquid-nitrogen temperature. We dissolved the *syn*-(CH₃,CH₃)B in the following solvents: ethanol/ethyl ether in a 2:1 ratio, 2-methyltetrahydrofuran, EPA, and *n*-butanol/isopentane in a 3:7 ratio.

syn-(CH₃,CH₃)B showed a fluorescence intensity maximum in the blue region (450–460 nm) of the spectrum in all of these glassy solvents we tried. We did not find any

glassy solvents in which *syn*-(CH₃,CH₃)B would give blue-green (480 nm) fluorescence as in water and hexafluoroisopropanol.

Figure 1 shows the absorption (S-S), the T-T absorption, and the fluorescence spectrum of *syn*-(CH₃,CH₃)B dissolved in 2:1 ratio ethanol/ethyl ether. It is apparent that some T-T absorption overlaps the fluorescence spectral region. This compound has a T-T absorption band located in the fluorescence region with its maximum at 490 nm. The intensity of this T-T absorption bands drops rather rapidly toward the long wavelengths. This would then explain why this compound showed laser action in the green spectral region and not in the blue spectral region.

The photostability under krypton-ion cw laser excitation at 351,356 nm of *syn*-(CH₃,CH₃)B was remarkably good in the different glassy solvents we employed. This exceptional stability under irradiation with 360-nm light was already observed by Kosower and Pazhenchevsky.³ This is in contrast to the Coumarin laser dyes where photodecomposition reduces measurement accuracy when recording the T-T absorption spectra.²

We observed laser action from the *syn*-(CH₃,CH₃)B broadband at 504 nm, with a threshold at 9.6 kV, using a 5×10^{-4} M solution in distilled water. A 2×10^{-4} M solution had its threshold at 13.4 kV. We did not observe any laser action in a 1×10^{-4} M solution pumping with 14.5 kV. By comparison, a 2×10^{-4} M solution of Coumarin 30 in ethanol did exhibit laser action at 506 nm with a threshold at 6.7 kV.

The pulses were displayed on the storage oscilloscope

and photographed. By measuring the area (integration) of the intensity-time curve, the relative intensity of the laser pulses were obtained. From these measurements it was concluded that *syn*-(CH₃,CH₃)B lases with about $\frac{1}{3}$ less efficiency than does Coumarin 30. Both dyes were pumped at 12 kV. In solvents conventionally used to dissolve laser dyes, such as *p*-dioxane, ethanol, and dimethyl formamide, we did not observe any laser action when pumped up to 14.5 kV. In all these solvents, the fluorescence maximum was located in the 420–460 nm spectral region. However, we observed laser action of *syn*-(CH₃,CH₃)B in a 1×10^{-3} M solution of hexafluoroisopropanol, where *syn*-(CH₃,CH₃)B showed blue-green fluorescence, with an intensity maximum at 480 nm. Laser emission occurred at 501 nm with a threshold at 9.9 kV. In a 5×10^{-4} M solution, however, pumping with up to 14.5 kV failed to produce laser action.

The reason that *syn*-(CH₃,CH₃)B shows laser action only in water and in hexafluoroisopropanol and only at higher concentrations is somewhat difficult to explain. We mentioned the solvent dependency of the spectral location of the lowest energy S-S absorption band and consequently of the spectral location of the fluorescence spectrum of *syn*-(CH₃,CH₃)B. Unfortunately, we do not know whether the spectral location of the lowest energy T-T absorption band, which is located at about 490 nm in the ethanol/ethyl ether solution, is solvent dependent or not. The fact that we do observe laser action in the two solvents, which causes the largest red shift of the fluorescence band (peak), suggests that the T-T absorption band located at 490 nm was probably not much red-shifted. However, the observation that

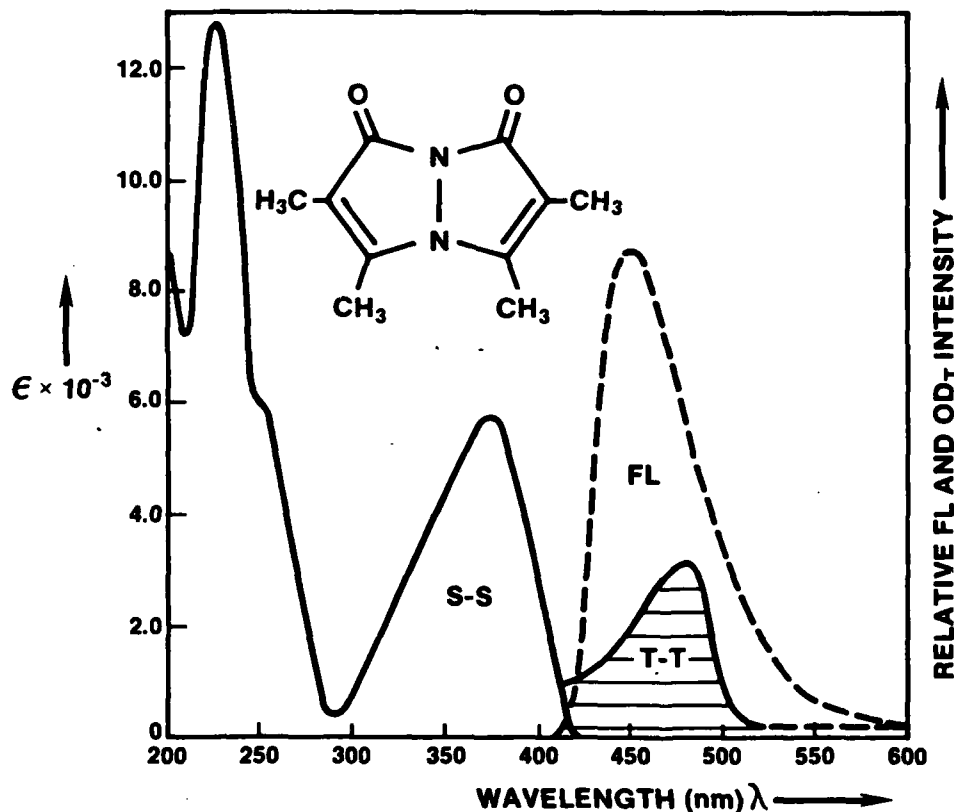


FIG. 1. Absorption (S-S), fluorescence FL, and triplet-triplet (T-T) absorption of *syn*-(CH₃,CH₃)B in ethanol/ethyl ether 2:1 ratio. The T-T absorption spectrum was recorded at the temperature of liquid nitrogen.

laser action takes place only at higher *syn*-(CH₃,CH₃)B concentrations may suggest that some sort of triplet-triplet annihilation mechanism is present. It is well known, from experiments on pure crystals of organic compounds, that no T-T absorption is observed due to triplet-triplet annihilation. Nevertheless, other explanations cannot be ruled out.

In conclusion, the bimanes appear to be a new class of potential laser dyes. By using different groups (e.g., auxochromic substituents) for R₁ and R₂,⁴ one should be able to shift the T-T absorption band out of the fluorescence emission (laser action) region.

Higher efficiency resulting from the reduced T-T absorption combined with the high quantum efficiency of the

bimanes, their good solubility in many solvents (including water), and their good photochemical stability should make these new laser dyes very competitive with the currently available laser dyes.

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