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QUASI-AROMATIC HETEROCYCLICS AS LASER DYES

by

Theodore G. Pavlopoulos and Joseph H. Boyer

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## QUASI-AROMATIC HETEROCYCLICS AS LASER DYES

Theodore G. Pavlopoulos, Marine Sciences and Technology Department  
U.S. Naval Ocean Systems Center, San Diego, CA 92152

Joseph H. Boyer, Department of Chemistry  
University of New Orleans, New Orleans, LA 70148

### 1. ABSTRACT

Superior laser dyes were recently discovered in the *quasi*-aromatic families of *syn*-dioxabimanes and pyrromethene-BF<sub>2</sub> complexes. The representative new dye  $\mu$ -bis-(carboethoxy) methylene-*syn*-(methylene, methyl) bimeane lased at 507 nm with 50% greater efficiency than was obtained with Coumarin 30. A similar determination showed 4,4-difluoro-1,3,5,7,8-pentamethyl-4-bora-3a,4a-diaza-s-indacene to lase at 546 nm with about 300% greater efficiency than was obtained from Coumarin 545. These *quasi*-aromatic systems are readily available and offer desirable properties of stability (photo, thermal, and chemical), solubility, and diminished triplet-triplet absorption in the lasing spectral region. Selected spectroscopic and lasing properties of these new laser dyes are presented.

### 2. INTRODUCTION

Since the first observation of laser action from organic dyes (about 20 years ago), intense research activity has taken place. The main reason for this development is the unique dye-laser feature of being tunable over a wide range of wavelengths. Other important advantages of laser dyes are the following. (1) Dye lasers are liquid lasers. This implies high optical quality of the active medium and high repetition rate (i.e., high average power output) because of the simplicity of cooling. (2) Cost of preparing the active medium (laser dye and solvent) is much less than with solid-state lasers. When flashlamps are employed as excitation sources, the flashlamps, as well as the driving power supplies, are relatively inexpensive.

However, present dye lasers, which employ commercially available laser dyes, have the following disadvantages. (1) Laser output energy (efficiency) is rather low. (2) Photodecomposition is more or less present in all presently available laser dyes. (3) Because most organic laser dyes can only be dissolved in organic solvents such as methyl alcohol, *p*-dioxane, dimethylformamide, etc., a serious fire and health hazard exists, especially for inexperienced personnel. Few laser dyes are water soluble. Unfortunately, most laser dyes are very unstable photochemically when water is employed as a solvent. (4) Another drawback is the requirement to use flashlamps with steep risetimes (in the 1- $\mu$ second range and less) to obtain laser action from the laser dye. Flashlamps meeting this stringent requirement are difficult to build for operation above 1000 Joules.

Low efficiency, low photostability, and the requirement to employ flashlamps with fast risetimes in present dye lasers using commercially available laser dyes are caused by excessive so-called triplet-state losses. If new laser dyes could be developed that exhibit reduced triplet-state losses, flashlamps for excitation could be employed that have slower pulse risetimes. Significantly, these flashlamps can be operated over much longer lifetimes, and are commercially available at several 10,000-Joule ratings.

### 3. LASER DYES

The selection of organic dyes that show laser action is, at present, accomplished by trial and error. Thousands of organic dyes have been synthesized over the last hundred years and are commercially available. Thousands of them show strong fluorescence (i.e., high quantum fluorescence yield). However, only a few exhibit laser action under flashlamp excitation. The disadvantage of low efficiency (0.2 to 1%) of presently available laser dyes is closely related to the accumulation of dye molecules in their triplet state as the result of so-called intersystem crossing. These triplet-state molecules, generated during intense excitation, in turn absorb the laser light more or less efficiently, depending on the magnitude of their triplet absorption. In addition, most organic compounds (including laser dyes) undergo photodecomposition when present in their triplet state.

Although Rhodamine 6G has been known since 1967, it is still one of the most efficient laser dyes. It lases with about 1% efficiency when flashlamp pumped. The question is, then, why haven't more efficient laser dyes been synthesized since 1967? The answer appears to be that there is excessive triplet-triplet (T-T) absorption over the fluorescence (laser action) spectral region because of the presence of benzene (or its heterocyclic) derivatives in all presently available laser dyes [1].

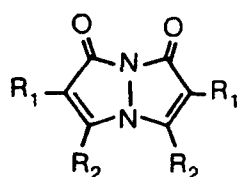
It is well known that the presence of benzene (and its heterocyclics) in organic compounds is responsible in most cases for carrying the spectroscopic property of fluorescence. Reviewing experimental data on T-T absorption of organic compounds published in the literature, it is apparent that all aromatic compounds possess strong (to very strong) T-T absorption, stretching from their fluorescence spectral region to longer wavelengths [2].

Should the search for new laser dyes concentrate on the few organic compounds (*quasi*-aromatic heterocyclic) that exhibit strong fluorescence but do not contain any homocyclic and/or heterocyclic aromatic groups? Some of these compounds seem to have low T-T absorption over their fluorescence spectral region. Laser dyes were recently discovered in the *quasi*-aromatics of *syn*-9,10-dioxabimanes (*syn*-( $R_2, R_1$ ) bimananes) and pyrromethene-BF<sub>2</sub> complexes.

#### 4. SYN-BIMANES AS LASER DYES

While searching for more stable and efficient laser dyes, we observed laser action from *syn*-(methyl, methyl) bimanane, *syn*-(acetoxymethyl, methyl) bimanane, and some other *syn*-bimananes. Under flashlamp excitation from aqueous solutions, these compounds showed laser action in the 505-to-515-nm (blue/green) spectral region [3-5].

An efficient method of synthesizing these and other bimananes was developed recently (Kosower and coworkers, 1978). They possess strong and striking fluorescence. The quantum fluorescence yield  $Q_F$  of *syn*-( $R_2, R_1$ ) bimananes ranges from 0.7 to 0.9. Significantly, these compounds are generally of good photostability and some of them are water soluble. The isomer *anti*-( $R_2, R_1$ ) bimanane is only weakly fluorescent [6,7]. The Coumarin laser dyes presently used for the spectral region from 440 to 540 nm have rather poor photochemical stability.



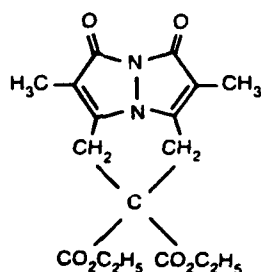
*syn*-( $R_2, R_1$ ) bimanane



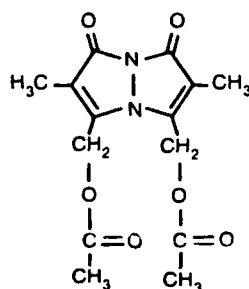
*anti*-( $R_2, R_1$ ) bimanane

We compared our *syn*-bimananes, dissolved in water, with Coumarin 30 dissolved in ethanol. This dye exhibits laser action in the same spectral region as our *syn*-bimananes. *Syn*-(methyl, methyl) bimanane lased about 30% less efficiently, but was three times more stable. *Syn*-(acetoxymethyl, methyl) bimanane lased as efficiently and was twice as stable. Other *syn*-bimananes were 50% more efficient, but had only limited water solubility.  $\mu$ -bis(carboethoxy) methylene-*syn*-(methylene, methyl) bimanane lased 50% more efficiently at 9-J input energy, and 20% more efficiently when pumped with 12-J energy, than Coumarin 30.

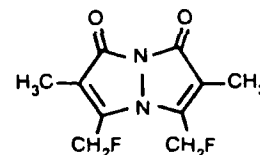
*Syn*-(acetoxymethyl, methyl) bimanane was water soluble and lased as efficiently as Coumarin 30. *Syn*-(fluoromethyl, methyl) bimanane showed weak laser action at 525 nm when dissolved in water, but also lased at 435 nm when dissolved in *p*-dioxane [5].



$\mu$ -bis(carboethoxy)methylene-*syn*-(methylene, methyl) bimanane

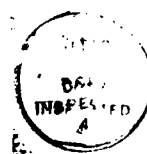


*syn*-(acetoxymethyl, methyl) bimanane



*syn*-(fluoromethyl, methyl) bimanane

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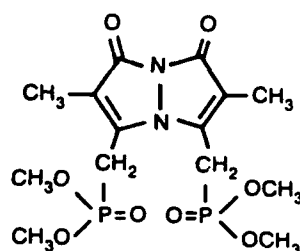


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This can be explained from the intensity and shape of the T-T absorption spectrum of the *syn*-bimanes. They exhibit some T-T absorption stretching from the violet to the blue/green portion of the spectrum, with intensity maximum at about 480 nm. This maximum does not appear to shift with change of solvent. Intensity decreases steeply toward longer wavelengths. Toward shorter wavelengths, T-T intensity decreases more gradually.

In Figure 1, we show the fluorescence, (S-S) absorption, and T-T absorption of *syn*-((CH<sub>3</sub>O)<sub>2</sub>OPCH<sub>2</sub>, CH<sub>3</sub>) bimane dissolved in water, which is a typical representation of the *syn*-bimane laser dyes. It lases about 80% as efficiently as Coumarin 30 when dissolved in water (Figure 2) and about 30% as efficiently as Coumarin 120 (at 438 nm) when dissolved in *p*-dioxane (Figure 3).

To further improve the laser action properties of the *syn*-bimane laser dyes, one has to shift the fluorescence intensity maximum to longer wavelengths without affecting the T-T absorption band. By selective substitution (dye synthesis) into the R<sub>1</sub> (long-axis) or R<sub>2</sub> (short-axis) position, one should be able to move the S-S absorption band at about 360 nm sufficiently that the fluorescence intensity maximum falls into the 525-nm spectral region, where only little T-T absorption would be present (see Figure 1). With reduced T-T absorption, very efficient laser action should be observable.



*syn*-(dimethylphosphonomethyl, methyl) bimane.

## 5. PYRRMETHENE-BF<sub>2</sub> COMPLEX AS LASER DYES

As shown in Figures 1 and 3, laser dyes derived from *syn*-bimanes have rather low T-T absorption in the spectral region of fluorescence. We speculated that other *quasi*-aromatic heterocyclics possessing a high quantum fluorescence yield might also possess low T-T absorption over their fluorescence spectrum.

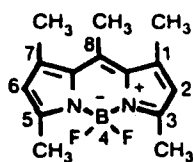
Because the pyrromethene-BF<sub>2</sub> complex, 4,4'-difluoro-1,3,5,7-tetramethyl-4-bora-3a,4a-diaza-*s*-indacene (TMP-BF<sub>2</sub>) [8] has a Q<sub>F</sub> = 0.80, this compound was synthesized and tested for its spectroscopic as well as its laser action properties.

A 2 × 10<sup>-4</sup> molar solution of TMP-BF<sub>2</sub> dissolved in methanol lased broadband at 533 nm with about 10% more efficiency than a 2 × 10<sup>-4</sup> molar solution of Coumarin 540A. Surprisingly, TMP-BF<sub>2</sub> had rather low T-T absorption (ε<sub>T</sub>(λ<sub>lss</sub>) = 1.8 × 10<sup>3</sup> l/mole cm) over the fluorescence spectral region [9].

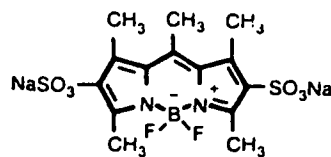
For efficient laser action to occur from flashlamp-pumped laser dyes, the following spectroscopic parameters are of importance. Besides low T-T absorption over the fluorescence (laser action) spectral region, (a) the onset of the (S-S) absorption reaching into the fluorescence spectral region should be small (i.e., a small Stoke's shift is required); and, as already mentioned, (b) the quantum fluorescence yield Q<sub>F</sub> of the laser dye should be high (Q<sub>F</sub> ≈ 1).

Condition (a) and low T-T absorption seemed to be fulfilled for TMP-BF<sub>2</sub>, but not (b). A Q<sub>F</sub> = 0.80 is not really high. We therefore synthesized the 1,3,5,7,8-pentamethyl-BF<sub>2</sub> complex (PMP-BF<sub>2</sub>), hoping that this new pyrromethene complex might have a higher quantum fluorescence yield than TMP-BF<sub>2</sub> [10].

We observed efficient laser action under flashlamp excitation from PMP-BF<sub>2</sub>, dissolved in ethanol (1.5 × 10<sup>-4</sup> molar). This new dye lased at 546 nm. A 2 × 10<sup>-4</sup> molar solution of Coumarin 545 in ethanol also lased at 546 nm.



pentamethylpyrromethene-BF<sub>2</sub>  
complex  
PMP-BF<sub>2</sub>



disodium pentamethylpyrromethene-  
2,6-disulfonate-BF<sub>2</sub> complex  
PMPDS-BF<sub>2</sub>

In Figure 4, we present the energy output  $\Delta E$  (in mJoule) of a  $1.5 \times 10^{-4}$  molar solution of PMP-BF<sub>2</sub> in ethanol as a function of flashlamp pump energy  $E$  (in Joules). In the same figure, we also show the energy output of a  $2 \times 10^{-4}$  molar solution of Coumarin 545 in ethanol and a  $2 \times 10^{-4}$  molar solution of Rhodamine 6G also dissolved in ethanol. Rhodamine 6G lased BB at 595 nm. From Figure 1, it is apparent that PMP-BF<sub>2</sub> lases about 300% more efficiently than Coumarin 545 and about 20% less efficiently than Rhodamine 6G. PMP-BF<sub>2</sub> was about as photostable as Rhodamine 6G. Our experimental results on the lasing efficiency on the new laser dye (shown in Figure 4) place it among the most efficient laser dyes known. We also measured the quantum fluorescence yield of PMP-BF<sub>2</sub> and found that it was only 0.73.

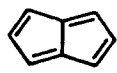
In Figure 5, we show the fluorescence, (S-S) absorption, and T-T absorption of PMP-BF<sub>2</sub>. Noteworthy is the exceptionally low T-T absorption over the laser action spectral region, which is only about  $1 \times 10^3$  l/mole cm. It appears, then, that the improvement in laser action efficiency of PMP-BF<sub>2</sub> over TMP-BF<sub>2</sub> is probably the result of reduced T-T absorption. Consequently, if pyrromethene-BF<sub>2</sub> complexes could be synthesized with the same low T-T absorption as PMP-BF<sub>2</sub>, but with quantum yields in the range of 0.90 to 0.98, very efficient laser action should be observable.

To achieve water solubility, the disodium 2,6-disulfonate derivative (PMPDS-BF<sub>2</sub>) was prepared. This dye lased about 75% as efficiently as PMP-BF<sub>2</sub> when dissolved in water and exhibited some photoinstability. However, in methanol it was highly resistant to photodegradation.

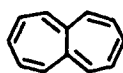
## 6. DISCUSSIONS

The *syn*-bimanes and pyrromethene complexes studied in this paper are related to the following compounds.

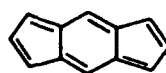
### Pseudoaromatic Compounds



pentalene

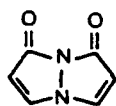


heptalene

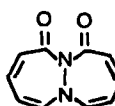


s-indacene

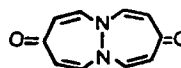
### Quasiaromatic Heterocyclics



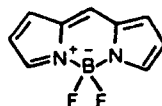
*syn*-dioxabimane



unknown



unknown



boradiaza-s-indacene

Vast areas of *quasi*-aromatic heterocyclics (derivatives of the above compounds) are now seen as potentially rich sources of new lasing molecules.

## 7. ACKNOWLEDGMENTS

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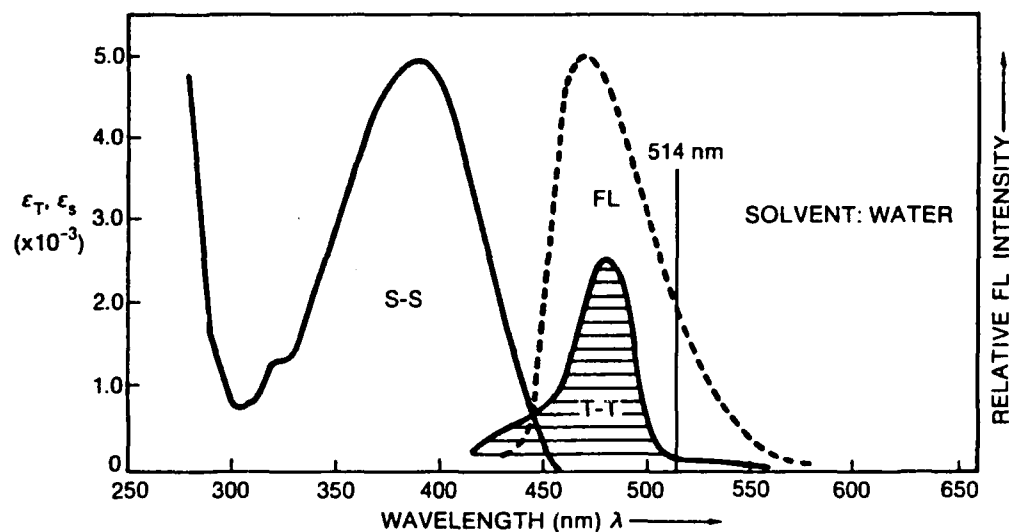


Figure 1. S-S, T-T, and fluorescence spectra FI of *syn*-(dimethylphosphonomethyl,methyl) bimeane. The T-T absorption spectrum was recorded at 77 K, employing a  $2 \times 10^{-4}$  molar solution of 2-methyltetrahydrofuran. The S-S and FI ( $1 \times 10^{-3}$  molar) were recorded with water as a solvent. Broadband laser action occurred at 514 nm, which is indicated by a vertical line in the graph.

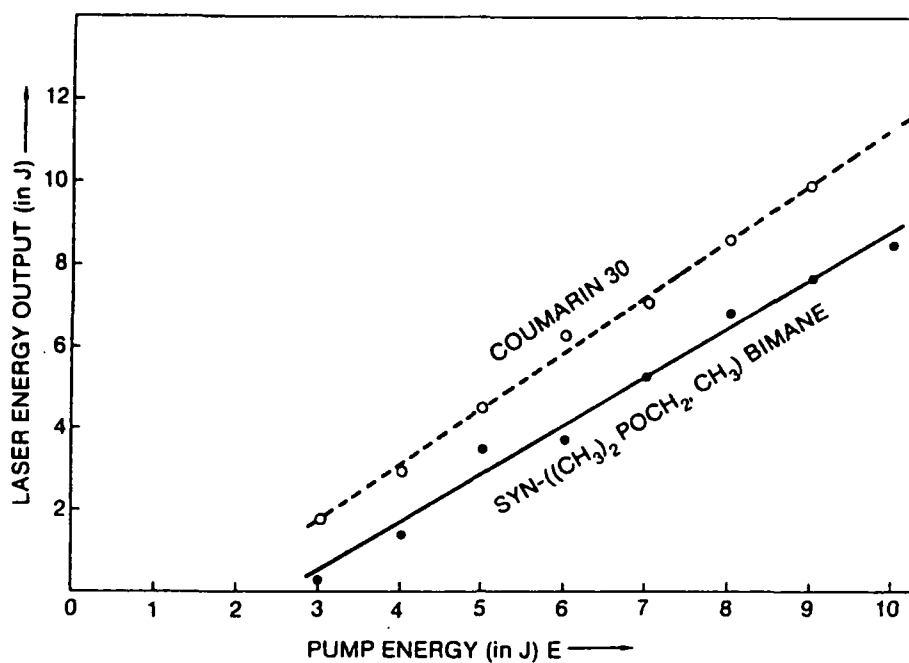


Figure 2. Laser energy output  $\Delta E$  (in mJ) as function of flash-lamp pump energy  $E$  (in J) of a  $1 \times 10^{-3}$  molar solution of *syn*-(dimethylphosphonomethyl,methyl) bimane dissolved in water and of Coumarin 30,  $7.5 \times 10^{-4}$  molar in ethanol.

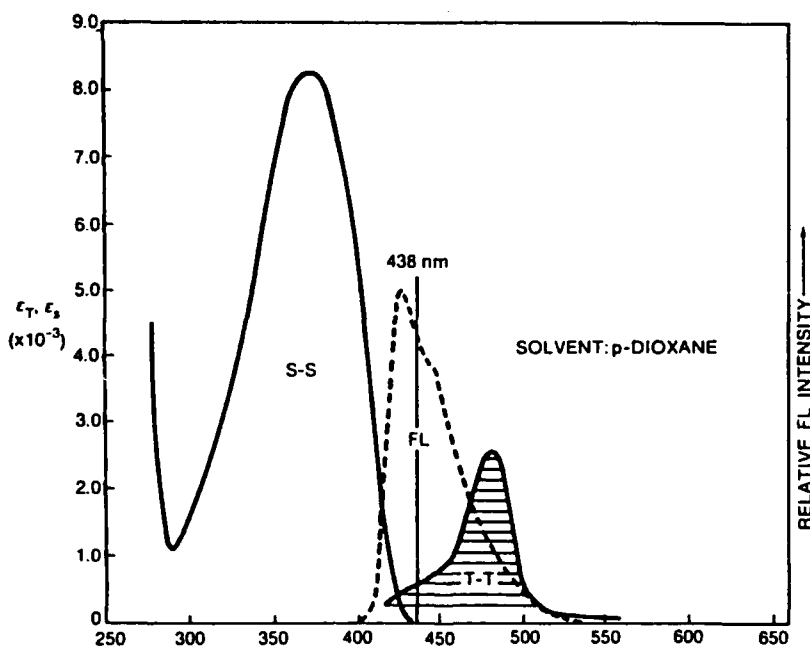


Figure 3. S-S, T-T, and fluorescence spectra FI of *syn*-(dimethylphosphonomethyl,methyl) bimane. The T-T absorption spectrum was recorded at 77 K, employing a  $2 \times 10^{-4}$  molar solution of 2-methyltetrahydrofuran. The S-S and FI ( $1 \times 10^{-3}$  molar) were recorded with p-dioxane as solvent. Broadband laser action occurred at 438 nm, which is indicated by a vertical line in the graph.



Figure 4. Laser energy output  $\Delta E$  (in mJoules) as a function of energy  $E$  (in Joules) of a  $1.5 \times 10^{-4}$  molar solution of the pentamethylpyrromethene- $\text{BF}_2$  complex (PMP- $\text{BF}_2$ ) dissolved in ethanol; a  $2 \times 10^{-4}$  molar solution of Coumarin 545 dissolved in ethanol; a  $2 \times 10^{-4}$  molar solution of  $2 \times 10^{-4}$  molar solution of Rhodamine 6G dissolved in ethanol; and a  $2 \times 10^{-4}$  molar solution of pentamethylpyrromethene- $\text{BF}_2$  sulfonate (PMP- $\text{BF}_2$ -sulfonate), also dissolved in ethanol.

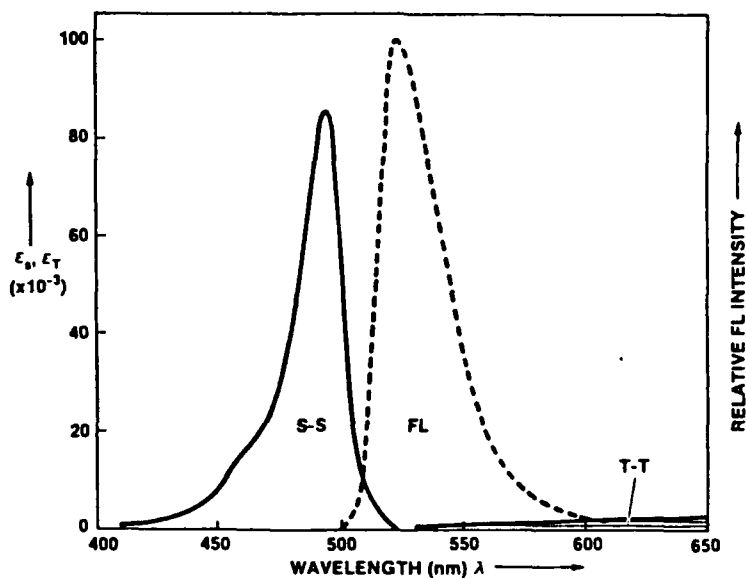
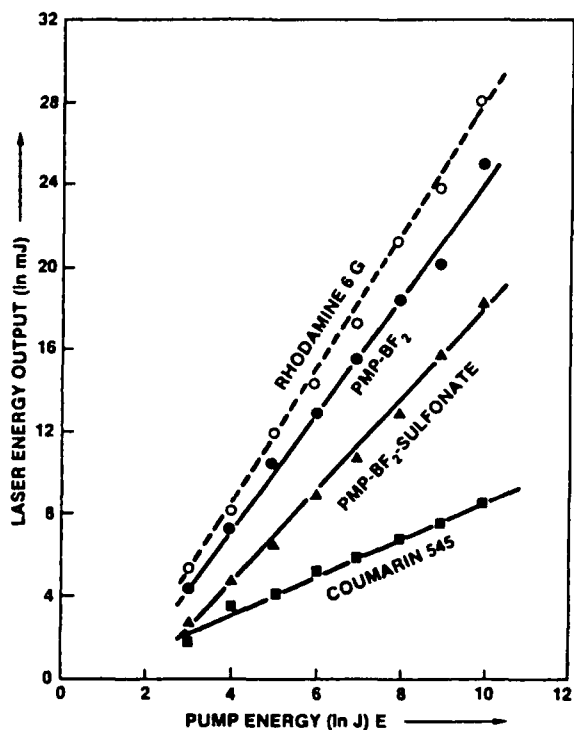


Figure 5. Absorption (S-S) and fluorescence FI spectra of pentamethylpyrromethene- $\text{BF}_2$  complex (PMP- $\text{BF}_2$ ) dissolved in ethanol. The T-T absorption spectrum was recorded at 77 K, employing a  $1 \times 10^{-4}$  molar solution of 2-methyltetrahydrofuran as a glassy solvent.

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