



Bimanes and Related Heterocycles as Laser Dyes

FINAL REPORT

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position, policy, or decision, unless so d 12a. DISTRIBUTION/AVAILABILITY STATEMENT Approved for public release; distribution	unlimited.
3. ABSTRACT (Maximum 200 words)	530 nm were obtained for 37 pur himmers by reference to
cournarin 30 (RE 100). RE > 80 was observed for bimanes $1 - \frac{4}{3}$.	
$H_{3}C$	CH ₃ $H_{3}C$ X CH ₃ Y $N + N$ Y H ₃ C P F CH ₃
$\frac{1}{2} A = CH_2O_2CCH_3 \qquad \frac{3}{2} X = C(CO_2CH_3)_2 \frac{1}{2} A = CH_2(O)P(OCH_3)_2 \qquad \frac{3}{4} X = C(CO_2C_2H_5)_2 $	$\frac{5}{2} X = CH_3, Y = SO_3Na$ $\frac{6}{2} X = CH_3, Y = C_2H_5$
The relative efficiencies (RE) for laser activity in the spectral region 52 (P-BF ₂) by reference to rhodamine 6G (RE 100). The complexes 5 and most power efficient laser dyes known. Bimanes 1 and 3 and P-BF ₂ 5 Orleans, LA).	0-620 nm were obtained for over 20 pyrromethene-BF ₂ complexes $\underline{6}$ were the first dyes to surpass rhodamine 6G and are now the and $\underline{6}$ are now commercially available (DEKK-TEC, Inc., New
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Bimanes (1,5-Diazabicyclo[3.3.0]octadienediones): Laser Activity in *syn*-Bimanes

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ABSTRACT

The conversion of 3-methyl-4-benzyl-4-chloro-2-pyrazolin-5-one **10b** was catalyzed by a mixture of potassium fluoride and alumina to give syn-(methyl,benzyl) bimane **6** (62%) without detectable formation of the anti isomer A6 [a 1:1 mixture (87%) of the isomers 6 and A6 was obtained when the catalyst was potassium carbonate]. In a similar reaction syn-(methyl,carboethoxymethyl)bimane 7 (15%) with the anti isomer A7 (36%) was obtained from 3-methyl-4-carboethoxymethyl-4-chloro-2-pyrazolin-5-one 10c. syn-(Methyl, β -acetoxyethyl)bimane 8 (70%) was obtained from 3-methyl-4-B-acetoxyethyl-4-chloro-2pyrazolin-5-one 10d (potassium carbonate catalysis) and was converted by hydrolysis to syn-(methyl, β hydroxyethyl)bimane 9 (40%). Acetyl nitrate (nitric acid in acetic anhydride) converted anti-(amino,hydrogen) bimane 11 to anti-(amino, nitro) bimane 15 (91%), anti-(methyl,hydrogen)bimane 13 to anti-(methyl,nitro)(methyl,hydrogen)bimane 16 (57%), and degraded syn-(methyl, hydrogen) bimane 12 to an intractable mixture. Treatment with trimethyl phosphite converted syn-(bromomethyl,methyl)bimane 17 to syn-(dimethoxyphosphinylmethyl, methyl)bimane 18 (78%) that was further converted to syn-(styryl, methyl) bimane 19 (29%) in a condensation reaction with benzaldehyde. Treatment with acryloyl chloride converted syn-(hydroxymethyl,methyl)bimane 20 to its acrylate ester 21 (22%). Stoichiometric bromination of syn-(methyl, methyl) bimane 1 gave a monobromo derivative that was converted in situ by treatment with potassium acetate to syn-(acetoxymethyl, methyl) (methyl, methyl) bimane 47. N-Amino- μ -amino-syn-(methylene,methyl)bimane 24 (68%) was obtained from a reaction between the dibromide 17 and hydrazine. Derivatives of the hydrazine 24 included a perchlorate salt and a hydrazone 25 derived from acetone. Dehydrogenation of syn-(tetramethylene) bimane 26 by treatment with dichlorodicyanobenzoquinone (DDQ) gave syn-(benzo,tetrameth-ylene)bimane 27 (58%) and syn-(benzo)bimane 28 (29%). Bromination of the bimane 26 gave a dibromide 29 (92%) that was also converted by treatment with DDQ to syn-(benzo)bimane 28. Treatment with palladium (10%) on charcoal dehydrogenated 5,6,10,11-tetrahydro-7H,9H-benz [6,7] indazol [1,2a]benz[g]indazol-7,9-dione **35** to syn-(α -naphtho)bimane 36 (71%). The bimane 35 was prepared from 1,2,3,4-tetrahydro-1-oxo-2-naphthoate 37 by stepwise

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treatment with hydrazine to give 1,2,4,5-tetrahydro-3H-benz[g]indazol-3-one **38**, followed by chlorine to give 3a-chloro-2,3a,4,5-tetrahydro-3H-benz[g]indazol-3-one **39**, and base. Dehydrogenation over palladium converted the indazolone **34** to 1H-benz[g] indazol-3-ol **36**. Helicity for the hexacyclic syn-(α naphtho)bimane **36** was confirmed by an analysis based on molecular modeling.

The relative efficiencies (RE) for laser activity in the spectral region 500-530 nm were obtained for 37 syn-bimanes by reference to coumarin 30 (RE 100): RE > 80 for syn-bimanes 3, 5, 18, and μ -(dicarbomethoxy)methylene-syn-(methylene,methyl)bimane 22: RE 20-80: for syn-bimanes 1, 2, 4, 20, 24, 26, and μ -thia-syn-(methylene,methyl)bimane 50: and RE 0-20 for 26 syn-bimanes. The bimane dyes tended to be more photostable and more water-soluble than coumarin 30. The diphosphonate 18 in dioxane showed laser activity at 438 nm and in water at 514 nm. Presumably helicity, that was demonstrated by molecular modeling, brought about a low fluorescence intensity for syn-(α -naphtho)bimane **36**, $\Phi 0.1$, considerably lower than obtained for syn-(benzo)bi*mane* 28, Φ0.9.

INTRODUCTION

Following its discovery in 1966 the dye laser [1] depended on the availability of laser dyes to provide coherent light over the spectral region from ultraviolet (UV) to infrared (IR). This laser activity was obtained from cyanine, xanthene (including rhodamine and fluoroscein), triarylmethane, acridine, azine, and chlorophyll dyes; linear and condensed polybenzenoid molecules; and certain heterocycles that included coumarins, quinolones, oxazoles, pyrazolines, and furans. In 1984, over 600 laser dyes were listed [2].

Parameters for a laser dye included high quantum fluorescence yield, (generally $\Phi > 0.7$), minimal overlap of fluorescence with onset of absorption (S-S) and triplet-triplet (T-T) spectral regions, photostability, efficiency in power output, favorable solubility and interaction with the solvent, and availability [3]. Other factors also contributed

to the laser performance. Aqueous solutions of a dye (10⁻⁴ molar was generally desirable) offered the superior thermo-optic properties of water that often improved laser activity [5c]. Groups that enhanced intersystem crossing $(S_1 \rightarrow T_1)$ through the heavy atom effect could interfere with laser activity and were generally avoided [3]. It was sometimes assumed that somewhat less than expected laser power output was the result of (1) nonradiative transfer $(S_1 \rightarrow S_0)$, (2) loss of electronic excitation through reversible charge transfer with the chromophore, and/or (3) self-quenching through dye aggregation [3]. About 125 tunable laser dyes more or less satisfied these special conditions and became commercially available to cover the region from 300–1200 nm [4].

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Other investigations led us to examine synbimanes (1,5-diazabicyclo[3.3.0]octadiene-2,8-diones) as laser dyes. Kosower introduced a system of trivial nomenclature for the bimanes based on substitution types. Type I: syn-(A,B)bimanes, Type II: syn-(A,B)(A',B')bimanes, Type III: μ -Xsyn-(methylene,methyl)bimanes, Type IV: anti-(A,B)bimanes, and Type V: anti-(A,B)(A',B')bimanes were adopted for this report [6, 7].

Laser activity in the spectral region 500-530 nm from syn-(methyl,methyl)bimane 1 was reported in 1986 [5a]. The discovery of similar activity from syn-(methyl,chloro)bimane 2, syn-(acetoxymethyl,methyl)bimane 3, syn-(fluoromethyl,methyl)bimane 4, and μ -(dicarboethoxy) methylene-syn-(methylene,methyl)bimane 5 followed rapidly [5b-d]. In our ongoing search for laser dyes it became desirable to examine greater diversification in substitution patterns in syn-bimanes.

syn-BIMANE DYE PREPARATIONS AND PROPERTIES

Background Information

Variation in substitution patterns in *syn*-bimanes has remained limited. In the Kosower scheme for their synthesis chlorination of a pyrazolinone followed by treatment with a base (potassium carbonate or a tertiary amine) brought about the forma-



Type I: A,B = A',B'Type II: $A,B \neq A',B'$



Type III: X = C,N,S



Type IV: A,B = A',B'Type V: $A,B \neq A',B'$



tion of mixtures of syn- and anti-bimanes, eq. (1) [6-8]. Selected conversions afforded preparative amounts of syn-bimanes with a limited range of substituents. syn-Bimanes with strong electron donating or withdrawing substituents were not prepared by this method and remain largely unknown. The chemical reactivity needed for further conversion of a substituent, e.g., methyl to acetoxymethyl [8] was restricted to the short axis where substituents ran parallel with the NN bond.

Chemical reactivity, "normal" positions of nuclear magnetic resonance (NMR) signals, and the occurrence of planar and nonplanar molecules in the crystal were properties that supported the perception of syn- and anti-bimanes as examples of α,β -unsaturated amide systems with no implication of "aromatic character" [6]. The fluorescence, $\Phi > 0.7$, from many syn-bimanes was, nevertheless, assumed to be a property of aromaticity insofar as strong fluorescence from an organic compound that was not aromatic has remained virtually unknown [5b]. A weak fluorescence from anti-bimanes [6] was shared with other pyrazolinones [9], γ -pyridones [10], maleimides [11], and presumably other quasiaromatic cyclic amides and hydrazides. A strong phosphorescence was noted for anti- but not for syn-bimanes [6].





Long Axis (Perpendicular to the NN Bond) Substitution

syn-(Methyl, benzyl) bimane 6 was prepared from 3-methyl-4-benzyl-4-chloro-2-pyrazolin-5-one 10b (obtained from ethyl benzylacetoacetate by treatment with hydrazine followed by chlorination) under the influence of a novel catalyst [12] that was provided by a mixture of potassium fluoride and alumina. Formation of the anti-isomer A6 was not detected; however, a mixture (1:1) of the isomers **6** and A6 was obtained when potassium carbonate was the catalyst. In related conversions 3-methyl-4-carboethoxymethyl-4-chloro-2-pyrazolin-5-one 10c (from diethyl acetosuccinate) gave syn-(methyl,carboethoxymethyl)bimane 7 along with the anti isomer A7, and 3-methyl-4- β -acetoxyethyl-4chloro-2-pyrazolin-5-one 10d (from ethyl β -acetoxyethylacetoacetate) gave syn-(methyl, β -acetoxyethyl)bimane 8. Hydrolysis converted the latter to

syn-(methyl, β -hydroxyethyl)bimane 9. Attempts to obtain syn-(hydrogen, carboethyoxy)bimane from ethoxymethylenemalonic ester were unsuccessful. Treatment with hydrazine converted the ester to a pyrazolinone that underwent chlorination to a product thought to be the chloropyrazolinone 10e; however, the latter in the presence of base resisted conversion to a bimane.

To enhance bimane functionality an exploratory investigation of the aromatic nitration of anti-(amino, hydrogen) bimane 11 (the syn isomer is unknown) and syn- and anti-(methyl.hydrogen)bimanes 12 and 13 was undertaken. The anti-bimane 11 was obtained from N.N'-dicvanoacetohydrazide 14 [(NHCOCH₂CN)₂] by cyclization in the presence of sodium bicarbonate [13]. Acetyl nitrate (explosive above 50°C), prepared in situ from a mixture of nitric acid (90%) and acetic anhydride, converted the anti-bimane 11 to anti-(amino.nitro)bimane 15, a structure assignment supported by IR, ¹³C NMR, EI-MS, and elemental analysis. Similar treatment converted *anti*-(methyl.hydrogen)bimane **13** [5] to anti-(methyl,nitro)(methyl,hydrogen)bimane 16. syn-(Methyl, hydrogen) bimane 12 [5] was completely converted by similar treatment to an intractable mixture that contained no more than a trace amount of a solid thought to be a mononitro derivative on the basis of M^+ 209 in the EI-MS. These aromatic substitution reactions resembled nitrations of pyrazolinones, hydroxy-, and aminopyrazoles [14] and tended to support quasiaromaticity of the bimane ring systems (see above).



Attempts to oxidize amino groups in bimanes 11 and 15 to nitro groups were unsuccessful and led instead to intractable mixtures. An unidentified product isolated as a hydrated dipotassium salt $C_6N_4O_8K_2 \cdot 1.5 H_2O$ from a treatment of diaminodinitrobimane 15 with potassium superoxide represented the oxidation level of a dihydroxydinitrobimane, in which hydroxyl groups had replaced amino groups. A hydrated sodium salt of a dihydroxydinitro-bimane $C_6H_4O_8Na_2 \cdot 1.5 H_2O$, was previously obtained in an oxidation of the corresponding dioxime [15].

The accessibility of substituted *syn*-bimanes was restricted by degradation of the bimane structure when treated under mild conditions with either an oxidizing reagent or an acid and, as previously reported [6], by ring opening and conversion under alkaline conditions.

Short Axis (Parallel to the NN Bond) Substitution

Generally substituent variation proceeded from the nonfluorescent syn-(bromomethyl,methyl)bimane 17 [obtained from syn-(methyl, methyl)bimane 1 by bromination [7]. Conversion of the dibromide 17 to syn-(dimethoxyphosphinylmethyl,methyl)bimane 18 was brought about by treatment with trimethvlphosphite. A need for polymerizable syn-bimane monomers to be formulated into glassy polymer slugs led to the preparation of syn-(styryl, methyl) bimane 19 (from the diphosphonate 18 and benzaldehvde) and the acrylate ester 21 of syn-(hydroxymethyl.methyl)bimane 20 (from the dibromide 17 by treatment with alkali followed by esterification of the glycol 20 with acryloyl chloride). Laser activity from dyes in polymeric glasses [16] will be described elsewhere.

Stoichiometry controlled a monobromination of the bimane 1 [6, 8]. Without isolation the bromide was treated with potassium acetate to give syn-(acetoxymethyl,methyl)(methyl,methyl) bimane 47.

μ -Bridged syn-Bimanes

Ring closure between short axis methyl substituents by a one atom bridge afforded μ -bridged syn-bimanes [7]. These tricyclic heterocycles were generally obtained from the dibromide 17 in reactions with nucleophiles. We repeated Kosower's preparation of μ -(dicarboethoxy)methylene-syn-(methylene,methyl)bimane 5 from the dibromide 17 in a reaction with malonic ester [7], and similarly prepared the homologous dimethyl ester 22. The diester 5 was converted by hydrolysis with decarboxylation to the monocarboxylic acid 23 [7]. Our attempts to convert the acid to its sodium salt were unsuccessful; mild treatment with sodium hydroxide, sodium bicarbonate, sodium alkoxide, or



sodium hydride gave intractable mixtures, in agreement with a known instability of the bimane nucleus toward alkali [6].

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By replacing ammonia with hydrazine in Kosower's scheme for converting syn-(bromomethyl,methyl)bimane 17 to μ -amino-syn-(methylene, methyl)bimane 53 [7] the corresponding N-amino derivative 24 was obtained without competitive formation of the cyclic hydrazine isomer (with an eight-membered ring). The hydrazine 24 was characterized by conversion to its perchlorate salt and to the hydrazone derivative 25 obtained from acetone.

syn-(Benzo)- and syn-(α-naphtho)bimanes **28** and **36**

Dehydrogenation of the previously reported syn-(tetramethylene)bimane (26) [6] by treatment with dichlorodicyanobenzoquine (DDQ) afforded both syn-(benzo)bimane 28 and the intermediate syn-(benzo,tetramethylene)bimane 27. Attempted dehydrogenation of bimane 26 by treatment with either 1,4-chloranil or palladium (10%) on charcoal was unsuccessful.

Bromination converted the bimane 26 to a dibromide that was given the tentative assignment of 4,6-dibromo-1,2,3,4,6,7,8,9-octahydro-10H,12H-indazolo[1,2-a]indazol-10,12-dione 29. Treatment with an excess of DDQ converted the dibromide 29 to syn-(benzo)bimane 28. The formation of a bromo derivative of bimane 28 was not detected.

An alternative approach to the preparation of *syn*-(benzo)bimane **28** that called for dehydration with cyclization of N,N-di-o-carboxyphenylhydrazine **32** was abandoned when the corresponding nitrosamine precursor **31** was not obtained by the treatment of di-o-carboxyphenylamine **30** [17] with nitrosating agents. A related conversion of N,N'-dio-carboxyphenylhydrazine **33** [(o-HO₂CC₆H₄NH)₂] to *anti*-(benzo)bimane **34** was reported in 1916 [18].

syn-(α -Naphtho)bimane **36** was similarly obtained by a dehydrogenation of 5,6,10,-11-tetrahydro-7*H*,9*H*-benz[6,7]indazolo[1,2-*a*]benz[g]indazol-7,9-dione **35** by treatment with palladium (10%) on charcoal. The bimane **35** was prepared



from ethyl 1.2.3.4-tetrahydro-1-oxo-2-naphthoate **37** [19] by treatment with hydrazine to give 1.2.4.5tetrahydro-3*H*-benz[g]indazol-3-one **38** followed by chlorination to give 3a-chloro-2,3a,4,5-tetrahydro-3H-benz[g]indazol-3-one 39 and treatment with potassium carbonate. A structure confirmation of the indazolone 38 was provided by its dehydrogenation over palladium to give 1H-benz[g]indazol-3-ol 40. In the absence of an x-ray crystallographic analysis, precluded by inability to obtain a crystalline modification, helicity for bimane 36 was corroborated by an analysis based on molecular modeling. In contrast to the syn-(benzo)bimane 28 in which the carbon atoms attached to the axial substitution sites are calculated to lie in the molecular plane, the corresponding carbon atoms in the syn-(α -naphtho)bimane 36 are calculated to be displaced by 0.53 Å above and below the mean molecular plane.

syn-BIMANE LASER ACTIVITY

Background Information

In water syn-(methyl, hydrogen) bimane 12 [6] showed fluoroescence λ_{max} 430 nm ($\Phi = 0.7$), T-T absorption λ_{max} 490 nm with a shoulder at λ 420 nm, and no laser activity [20]. For comparison syn-(methyl, methyl) bimane 1 in water showed fluorescence λ_{max} 480 nm ($\Phi = 0.7$), the same T-T absorption curve, and broad-band laser activity at λ 504 nm [5a]. It was suggested that a long-axis methyl substituent introduced a red shift solvatochromic effect on the fluorescence of the bimane 1 in water that promoted its laser activity above 500 nm where T-T absorption had steeply declined in intensity [5a]. The lasing efficiency (about 40% as efficient as coumarin 30) [21] was low-presumably a consequence of declining fluorescence intensity in the same spectral region [5a]. An absence of detectable laser activity from the bimane 1 in ethanol or in p-dioxane was attributed to solvatochromic shifts in fluorescence λ_{max} to 460 and 420 nm, respectively, where T-T absorption was more intense [5a]. Laser activity for syn-(hydrogen, methyl)bimane Type I ($A = H, B = CH_3$), fluorescence λ_{max} 460 nm ($\Phi = 0.6$) [22], was not investigated; therefore a short-axis methyl substituent effect on laser activity was not directly established.

A study of the polarization of low energy electronic transitions (S-S and T-T) revealed the presence of two differently polarized T-T transitions in the spectral region of fluorescence for *syn*-bimanes. This increased the complexity of both long- and short-axis substituent effects on the T-T absorption and indirectly on the laser activity for *syn*-bimanes [20]. Investigations are planned to unravel these and other polarization effects in bimanes.

Angular endo-annelation was found in the laser active "boradiazinium salt" 41 [23] but was not



extended to test the possibility of a helical laser dye. That helicity could create an interference with luminescence was shown in an examination of a series of hydrocarbons in which progressive helicity correlated with diminished fluorescent intensity [24]. Presumably laser activity in coronene 42 [25] was enhanced by chromophore planarity. We have herein reported the angular *endo*-annelation of *syn*-bimane into four-ring and six-ring systems.



RESULTS AND DISCUSSION

syn-Bimane derivatives offered a promising new source of laser dyes for the spectral region 500-530 nm. An examination of 18 Type I, two Type II, 13 Type III, and four annelated syn-bimanes revealed significant laser activity in eight from Types I and II (Table 1) and five from Type III (Table 2). Relative efficiencies, RE (\pm 10%), in laser power output were determined by comparison with the performance shown by a 7.5×10^{-4} M solution in ethanol of coumarin 30 (RE arbitrarily 100). Bimanes 3, 5, 18, and 22 (Tables 1 and 2) gave RE > 80. Each of these four dyes offered a high quantum fluorescence yield ($\Phi > 0.7$), solvatochromic control of interference from absorption (S-S and T-T), superior photostability, and availability. In addition, dyes 3 and 18 were water soluble.

A replacement of the ester groups in dye 5 (or 22) with cyano groups offered the strongly fluorescent μ -dicyanomethylene-syn-(methylene,methyl) bimane 52 (RE 0). A complete inhibition of laser activity in 52 was attributed in part to an electronic interaction between the cyano groups and the nearby chromophore. (In other examples inhibition of luminescence was attributed to a similar interaction between nitro and chromophore

					Power Output, P ₁ and P ₂ (mJ)			
Compound ^{*,b}				RE°			RE	
No.	A	В	Solvent ^c	P1 ^d	(%)*	P_2'	(%)"	
1	CH ₃	CH3	HFI	2.45	41	5.27	43	
2	CH ₃	CI	TFE	1.75	29	5.15	42	
3	CH ₃ CO ₂ CH ₂	CH ₃	H2O	4.37	72	10.92	89	
4	FCH ₂	CH ₃	TFE ^{g,h}	0.31	5	3.0	24	
18	(CH ₃ O) ₂ P(O)CH ₂	CH ₃	H ₂ O ⁷	4.43	73	10.43	85	
20	HOCH2	CH ₃	H₂O	3.48	58	8.19	67	
No.	A,B	A'B'						
26	(CH ₂) ₄	(CH ₂) ₄	TFE	0.70	12	2.60	21	
46 ^{<i>K</i>}	$HOCH_2$, CH_3	CH_3 , CH_3	HFI ^m	0.23	4	2.39	19	
47	CH ₃ CO ₂ CH ₂ , CH ₃	CH₃, CH₃	H₂O″	0.7	15	4.98	56	

TABLE 1 syn-(A,B)Bimanes, Type I and syn(A,B)(A',B')Bimanes, Type II: Laser Activity in the Region 500-530 nm

[∎] 10⁻³ M.

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^b Fluorescence in the region 435–460 nm with Φ values in the range 0.6–0.9 was reported for compounds 1 [6], 2 [6], 3 [8], 4 [5c], 20 [8], 26 [6], and 46 [7]. See Experimental for compound 18.

^eHFI, hexafluoroisopropanol; TFE, trifluoroethanol.

^d Dye pumped to 5.0 J.

• Relative efficiency compared to 100 (arbitrary) for coumarin 30.

¹ Dye pumped to 10.0 J.

9 Mixed with water (10%).

^h Laser activity at 435 nm from bimane 4 in dioxane.

¹Laser activity at 438 nm from bimane 18 in dioxane.

¹ Mixed with water (10%).

* Rapid photodecomposition.

^m Concentration not determined.

" 20% HFI.

Compound ^{a,b}			Power Output, P ₁ and P ₂ (mJ)			
No.	x	Solvent°	P1 ^d	RE(%)*	P ₂ ^t	RE(%)*
5	C(CO ₂ C ₂ H ₅) ₂	HFI	4.76	79	10.00	82
22 ^h	C(CO ₂ CH ₃)2	TFE ⁹	5.85	97	13.13	107
24	NNH ₂	H ₂ O ⁷	2.17	36	6,27	51
50	S -	HFI	2.98	49	7.55	61
52	C(CN) ₂	H ₂ O/	0.17	3	0.4	3
53	NĤ ⁷	НĴО	0	0	1.22	9
55	NCOCF ₃	TĒE ⁹	0.33	5	1.6	13

TABLE 2 µ-X-syn-(Methylene, methyl)bimanes, Type III: Laser Activity in the Region 500-530 nm

■ 10⁻³ M.

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^b Fluorescence, λ (Φ): 426 (0.8) for compound 5 and 447 (0.8) for compound 50 were reported [7]. See Experimental for compounds 22, 24, and 55.

^e HFI, hexafluoroisopropanol; TFE, trifluoroethanol.

^d Dye pumped to 5.0 J.

* Relative efficiency compared to 100 (arbitrary) for coumarin 30.

⁴ Dye pumped to 10.0 J.

9 Mixed with water (10%).

[^] Ref. 7.

⁴ Contained perchloric acid. An aqueous solution of the perchlorate salt (Experimental) in water gave no laser activity when pumped to 5.0 J and 0.43 mJ (RE 3.5%) when pumped to 10.0 J.

/Mixed with 20% HFI.



FIGURE 1 Absorption (S-S and T-T), fluorescence (FL), and the center of broad-band laser activity at 438 nm for *syn*-(dimethoxyphosphinylmethyl,methyl)bimane **18** in *p*-dioxane. The T-T absorption spectrum was recorded at 77°K, employing a 2×10^{-4} molar solution of 2-methyltetrahydrofuran. The S-S and Fl (1×10^{-3} molar) spectra were recorded with *p*-dioxane as solvent.

groups. [3].) The conspicuous absence of a cyano derivative in current lists of dyes [2-4] was taken an an indication that the cyano group within the dye molecule generally quenched laser activity.

The diphosphonate 18 was noted for a solvatochromic effect that shifted its fluorescence maximum from 425 nm in dioxane to 460 nm in water without shifting T-T absorption at about 480 nm to afford laser activity at 438 nm in one and at 514 nm in the other solvent (Figures 1 and 2). In water the solubility of the diphosphonate 18 (0.2 M) surpassed coumarin 30 (less than 10⁻⁴ M) but was 20% less power efficient (Figure 3) when each was pumped to 4.5 J. The diphosphonate 18 showed good photostability; however, after exposure in methanol to irradiation at 250 nm for 1 week it was completely converted to unidentified material. Under similar prolonged irradiation syn-(methyl, methyl)bimane 1, a yellow solid, was converted to an unknown colorless powder.



Dyes that showed RE 20-80 included the bimanes 1 [5a], 2 [5b], 4 [5b], 20, and 26 (Table 1); and bimanes 24 and 50 (Table 2). A long-axis alkyl substituent effect that was discovered for the methyl group in bimane 1 [5a] was greatly diminished in syn-(tetramethylene)bimane 26 and was ineffective in bimanes 6-9 that were laser inactive. The performance (RE 42) that was characteristic of syn-(methyl,chloro)bimane 2, Φ 0.8 (Table 1) was not shared with syn-(carboethyoxy.chloro)bimane 45, Φ 0.1, (inactive) and syn-(phenyl,chloro)bimane 44, Φ 0.6, (inactive). Although these results are in line with the general requirement for the presence of strong fluorescence, the laser inactivity in the latter example was attributed in part to interference from an assumed T-T absorption (phenyl group).

The results obtained from syn-(hydroxymethyl,methyl)bimane **20**, Φ 0.60, (RE 67) and syn-(hydroxymethyl,methyl)(methyl,methyl)bimane **46**, Φ

FIGURE 2 Absorption (S-S and T-T), fluorescence (FL), and the center of broad-band laser activity at 514 nm for *syn*-(dimethoxyphosphinylmethyl,methyl)bimane **18**. The T-T absorption spectrum was recorded at 77°K, employing a 2×10^{-4} molar solution of 2-methyltetrahydrofuran. The S-S and FI (1 × 10^{-3}) spectra were recorded with water as a solvent.

FIGURE 3 Laser energy output (mJ) as a function of flashlamp pump energy (J) of (A) syn-(dimethoxyphosphinylmethyl,methyl)bimane **18**, 1×10^{-3} M in water and (B) coumarin 30, 7.5×10^{-4} M ethanol.



0.80, (RF 19) (Table 1) appeared to be in conflict; however, a decrease in the laser activity of the alcohol 46 was attributed to its rapid photodecomposition, a property not shared with the other bimanes in this report. Although a lower performance rating for the glycol 20 (RE 67), relative to its diacetate ester 3 (RE 89), could be attributed to self-quenching brought about by dye aggregation as a result of hydrogen bonding, a parallel improvement in the performance of the alcohol 46 (RE 19) on conversion to its acetate ester 47 (RE < 19) was not observed.

Our results indicated that bimane laser dyes with μ -heteroatom bridges did not afford superior performances. No laser activity was detected from μ -amino-syn-(methylene,methyl)bimane 53, its N- β -hydroxyethyl derivative 49, and its N-acetyl derivative 54. The N-trifluoroacetyl derivative 55 (RE 13) and the N-amino derivative 24 (RE 51) (Table 2) showed weak laser activity. There was some improvement shown by μ -thia-syn-(methylene,methyl)bimane 50 (RE 61); however, μ -sulfono-syn-(methylene,methyl)bimane 51 was laser inactive. Laser inhibition as a result of an electronic interaction between amino, thia, or sulfono bridges and the nearby chromophore was assumed.

Strong T-T absorption for *syn*-(benzo)bimane 28 was shown to interfere throughout the fluorescence spectral region [20] and presumably quenched laser activity. A similar quenching effect was assumed for the related bimanes 27 and 35. The absence of laser activity in bimanes 17, 29, 44, and 45 was partially attributed to the heavy atom effect. A low fluorescence quantum yield, Φ 0.1, for laser inactive *syn*-(α -naphtho)bimane 36 (compare Φ 0.9 for *syn*-(benzo)bimane 28) was attributed to further disruption in the planarity of the bimane chromophore that was presumably brought about by helicity.

EXPERIMENTAL

Spectral data were obtained from the following instruments: Pye-Unicam SP 200 IR, Varian A-60 and JEOL FX Q NMR, Hewlett-Packard 5985 (70 eV) (GC-MS), Beckman DU (UV), and a Perkin-Elmer LS-5B Luminescence Spectrometer. A dye laser was constructed at the Naval Ocean Systems Center [26]. It operated in the nonflowing (static) mode and had no tuning capability. The dye cell (2.5 mm diam., 50 mm long) had an elliptical cavity configuration of small eccentricity. The flashlamp pulser, EG & G model FX 139C-2, had a rise time of 200 ns, half-width length of 600 ns, and input energy of 2 J at 6.32 kV, 5 J at 10.00 kV, 7.2 J at 12.00 kV, and 10 J at 14.14 kV [5a]. Laser energy outputs were measured with an accuracy of $\pm 5\%$ by a Scientech 365 power and energy meter [5c]. Laser activities are described in Tables 1 and 2.

For each product the IR spectrum agreed with the literature data and/or supported the assigned structure. Each recorded UV absorption was restricted to the highest wavelength. H NMR (60 MHz) spectra were run in CDCl₃ with tetramethylsilane as an internal standard. ¹³C NMR were recorded at 22.5 MHz with the deuterated solvent as an internal reference. The central peak of the solvent multiplet signal was assigned: δ 77.00 (CDCl₃), 39.50 (CD₃)₂(SO). Fluorescence quantum yields were determined by reference to *syn*-(methyl, methyl)bimane **1**, Φ 0.72 [6], *syn*-(benzo)bimane **28**, Φ 0.9 [27], and/or quinine sulfate, Φ 0.55. The latter reference was abandoned for several determinations when it led to erratic results. The mass spectra were electron impact (70 eV). Melting points were determined on a Thomas Hoover melting point apparatus and are uncorrected. Elemental analyses were obtained from Midwest Micro Lab, Indianapolis, IN, and Galbraith Laboratories, Knoxville, TN. Solvents were removed by rotary evaporation under reduced pressure unless indicated otherwise. Column chromatography was performed on silica gel (various grades). Triplet extinction coefficients over the laser action spectral region of the dye were measured at the temperature of liquid nitrogen by equipment previously described [28] using McClure's method [29]. Molecular mechanics calculations were performed on a MicroVAX 2000 computer with Evans and Sutherland PS390 graphics display using the BIOGRAF [30] software package. The force field parameters were taken from the MM2 set [31].

Solvents, reagents, and starting materials that were obtained from the Aldrich Chemical Company, Milwaukee, WI included acetic anhydride, acetone, acetonitrile, acryloyl chloride, alumina, ammonium chloride, benzaldehyde, benzene, bromine, β -bromoethyl acetate, carbon tetrachloride, celite, cetyltrimethylammonium Bromide *m*chloroperbenzoic acid, chloroform-d, dichlorodicyanobenzoquinone (DDQ), dichloromethane, diethyl acetylsuccinate, diethyl carbonate, diethyl ethoxymethylenemalonate, N,N-disopropylethylamine, N,N-dimethylformamide (DMF), dimethyl sulfoxide-d₆ (DMSO-d₆), p-dioxane, 18-crown-6ether, ethanol, ethyl acetate, ethyl benzylacetoacetate, hexane, hexafluoroisopropanol, hydrazine hyiodobenzene diacetate. isopropanol. drate. methanol, α -methyltetrahydrofuran, nitric acid, palladium (10% on charcoal), perchloric acid, peroxytrifluoroacetic acid, petroleum ether, potassium bromide, potassium *tert*-butoxide, potassium carbonate, potassium fluoride, potassium superoxide, silica gel (230-400 mesh, 60 Å), sodium bicarbonate, sodium hydride, sodium hydroxide, sodium sulfate, tetrahydrofuran (THF), α -tetralone, *p*-toluenesulfonic acid, triethylamine, fluoroacetic anhydride, trifluoroethanol, and trimethyl phosphite. Coumarins 6, 30, 120, and 314, rhodamine 6G, sulforhodamine B and thin layer chromatography sheets were obtained from Eastman Kodak Co., Rochester, NY. Chlorine was obtained from Matheson Gas Products, Secaucus, NJ. Nitrogen was obtained from Air Products and Chemicals, Allentown, PA. Hydrogen peroxide (90%) was obtained from Shell Chemical Company, Houston, TX.

The following compounds were prepared according to the directions cited: bimanes type I: syn-(A,B)bimanes where (A,B) was (methyl,hydrogen) in 12 [6], (methyl,methyl) in 1 [6], (bromomethyl,methyl) in 17 [6, 8], (hydroxymethyl,methyl) in 20 [8], (tetramethylene) in 26 [6], (methyl,phenyl) in 43 [6], (phenyl,chloro) in 44 [6], and (carboethoxy,chloro) in **45** [22]; bimanes type II: syn-(hydroxymethyl,methyl)(methyl,methyl)bimane **46** [6]; bimanes type III: μ -X-syn-(methylene, methyl)bimanes where X was dicarboethoxymethylene in **5** [7], dicarbomethoxymethylene in **22** [7], carboxymethylene in **23** [7], thia in **50** [7], sulfono in **51** [7], dicyanomethylene in **52** [7], amino in **53** [7], and acetylamino in **54** [7]; bimanes type IV: anti-(methyl,hydrogen)bimane **13** [6] and anti-(amino,hydrogen)bimane **11** [13]; miscellaneous: 3-methyl-4-carboethoxymethyl-4-chloro-2pyrazolin-5-one **10c** [32], 4- β -acetoxyethylethyl-3methyl-2-pyrazolin-5-one [33], and ethyl 1,2,3,4tetrahydro-1-oxo-2-naphthoate **37** [19].

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4-Benzyl-4-chloro-3-methyl-2-pyrazolin-5-one **10b**

Hydrazine hydrate (10.5 g, 0.21 mol) in methanol (20 mL) was added slowly with stirring to ethyl benzylacetoacetate (44.0 g, 0.2 mol) in methanol (200 mL). The mixture was heated at 65°C for 1 h and cooled to bring about the precipitation of 3methyl-4-benzyl-2-pyrazolin-5-one that recrystallized from ethanol as a colorless solid, 32.0 g (85%), mp 230–231°C (lit. [34] 232°C); Η NMR (CDCl₃): δ 2.0 (s, 3 H, CH₃), 3.6 (s, 2 H, CH₂), and 7.2 (s, 5 H, C_6H_5). A solution of the pyrazolinone (32.0 g, 0.17 mol) in dichloromethane (300 mL) was treated with a stream of chlorine gas until the solid phase disappeared and the solution became yellow. Traces of chlorine were removed by purging with a stream of nitrogen. The solvent was removed to leave a yellow oil that recrystallized from benzene to give the chloropyrazolinone 10b as a yellow solid, 32.5 g (86%); mp 75–76°C; H NMR (CDCl₃): δ 2.1 (s, 3 H, CH₃), 3.3 (d, 2 H, CH₂), 7.2 (s, 5 H, C₆H₅), 8.9 (broad, 1 H, NH). Anal. calcd for C₉H₁₁N₂OCl: C, 59.32; H, 4.94; N, 12.58;. Cl, 15.95. Found: C, 59.26; H, 5.08; N, 12.79; Cl, 15.90.

syn-(Methyl,benzyl)bimane 6

The prepared mixture (10 g) of potassium fluoride and neutral alumina (2:3 by wt) was added to the chloropyrazolinone 10b (1.0 g, 5 mmol) in dichloromethane (100 mL) at 10°C and the mixture was stirred for 1 h. Filtration and concentration of the mother liquor left a residue that recrystallized from carbon tetrachloride to give the bimane 6 as a yellow crystalline solid, 0.5 g (62%); mp 124-125°C; H NMR (CDCl₃): δ 2.25 (s, 6 H, CH₃), 3.6 (s, 4 H, CH₂), 7.25 (s, 10 H, C₆H₅); ¹³C NMR (CDCl₃): δ 159.78 (CO); 145.99 (0=C-C=C); 138.58, 128.43, 128.04, and 126.22 (C_6H_5); 115.56 (0=C-C=C); 27.51 (CH₂); 11.71 (CH₃). UV (CH₃CN): λ (ε) 375 (7916); fluorescence (dioxane): λ (Φ) 417 (0.8); EI-MS: 344 (M⁺). Anal. calcd for C₂₂H₂₀N₂O₂: C, 76.74; H, 5.81; N, 8.13. Found: C, 76.52; H, 5.80; N, 8.25.

When the reaction was catalyzed by potassium

carbonate a mixture (1:1) (87%) of the bimane **6** and its *anti* isomer **A6** was obtained.

syn-(Methyl,carboethoxymethyl)bimane 7

To 3-methyl-4-carboethoxymethyl-4-chloro-2-pyrazolin-5-one (4.4 g, 20 mmol) in dichloromethane (200 mL) a prepared mixture (44 g) of potassium fluoride and neutral alumina (2:3 by wt) was added at 25°C with stirring that was continued for 1 h. After filtration the mother liquor was concentrated to leave a brown solid that was purified by flash chromatography from a column of silica gel (dichloromethane) to give anti-(methyl,carboethoxymethyl)bimane A7 as a colorless solid, 1.2 g (36%), mp 183–184°C (lit. [32] mp 180°C), followed by the syn isomer 7 as a pale-yellow solid, 0.5 g (15%); mp 146–147°C; H NMR (CDCl₃): δ 1.27 (t, 6 H, CH₃), 2.4 (s, 6 H, CH₃), 3.3 (s, 4 H, CH₂), 4.13 (q, 4 H, CH₂); UV (CH₃CN): λ (ε) 370 (7303); fluorescence (ethanol): λ (Φ) 420 (0.8); EI-MS: 336 (M⁺). Anal. calcd for C₁₆H₂₀N₂O₆: C, 57.14; H, 5.92; N, 8.33. Found: C, 56.91; H, 5.71; N, 8.58. When an attempt to repeat the preparation with potassium carbonate as the catalyst was made the starting material was partially converted to a mixture of bimanes 3 and A3 after 20 h at 25°C.

4-β-Acetoxyethyl-4-chloro-3-methyl-2-pyrazolin-5-one **10d**

Chlorine gas was bubbled into a suspension of $4-\beta$ acetoxyethyl-3-methyl-2-pyrazolin-5-one (15.0 g, 80 mmol) in dichloromethane (500 mL) until the suspension dissolved to give a yellow solution. The solution was stirred for an additional 30 minutes. Excess chlorine and the solvent were removed under reduced pressure to give a yellow residue, which was recrystallized from a mixture of hexane and carbon tetrachloride to give $4-\beta$ -acetoxyethyl-4-chloro-3-methyl-2-pyrazolin-5-one 10d as a colorless crystalline solid, 13.5 g (76%); mp 94-95°C; H NMR (CDCl₃): δ 2.00 (s, 3 H, CH₃), 2.14 (s, 3 H, CH₃), 2.47 (t, 2 H, CH₂), 4.05 (t, 2 H, CH₂), 9.35 (br, 1 H, NH). Anal. calcd for $C_8H_{11}N_2O_3Cl$: C, 43.95; H, 5.07; N, 12.81; Cl, 16.22. Found: C, 43.83; H, 5.04; N, 12.89; Cl, 16.66.

syn-(Methyl, β -acetoxyethyl)bimane **8**

4- β -Acetoxyethyl-4-chloro-3-methyl-2-pyrazolin-5one **10d** (5.0 g, 23 mmol), potassium carbonate (10.0 g, 72 mmol), and water (2 mL) were added to dichloromethane (300 mL). The resulting suspension was stirred vigorously for 4 h. The reaction was monitored with thin-layer chromatography (ethyl acetate). Celite 545 (10 g) was then added, and the resulting mixture was passed through a short silica gel column (dichloromethane, 100 mL). The solvent was removed to give a yellow residue which was recrystallized from ethyl acetate to give 2.7 g (70%) of the bimane **8**, mp 134–135°C; H NMR (CDCl₃): δ 2.03 (s, 3 H, CH₃), 2.37 (s, 3 H, CH₃), 2.62 (t, 2 H, CH₂), 4.15 (t, 2 H, CH₂); UV (H₂O): λ (ϵ) 384 (6048); fluorescence (dioxane): λ (Φ) 457 (0.8). Anal. calcd for C₁₆H₂₀N₂O₆: C, 57.13; H, 6.39; N, 11.10. Found: C, 57.08; H, 6.57; N, 10.99.

syn-(Methyl,2-hydroxyethyl)bimane 9

syn-(Methyl,acetoxyethyl)bimane **8** (1.0 g, 3 mmol) and toluenesulfonic acid (20 mg) was dissolved in methanol (50 mL). The solution was heated at 60°C for 2 days, and the reaction was monitored with thin-layer chromatography (ethyl acetate). The solvent was removed to give a yellow residue which recrystallized in acetonitrile and dimethylformamide to give 0.30 g (40%) of the bimane **9** mp 186.5–188°C; H NMR (CDCl₃-DMSO-d₆): δ 2.33 (t, 2 H, CH₂) 2.39 (s, 3 H, CH₃), 3.39 (t, 2 H, CH₂), 3.77 (br, 1 H, OH); UV (H₂O): λ (ϵ) 317 (23,048); fluorescence (dioxane): λ (Φ) 464 (0.5). Anal. calcd for C₁₂H₁₆N₂O₄: C, 57.13; H, 6.39; N, 11.10. Found: C, 57.08; H, 6.57; N, 10.99.

Ethyl 4-chloro-5-oxo-2-pyrazoline-4-carboxylate **10e**

Hydrazine hydrate (5.5 g, 0.1 mol) in ethanol (20 mL) was added with stirring to a solution of diethyl ethoxymethylenemalonate (21.6 g, 0.1 mol) in ethanol (200 mL). The mixture was heated at 80°C for 18 h and cooled. Ethyl 2-pyrazolin-5-one-4-carboxylate precipitated and recrystallized from ethanol as a colorless crystalline solid, 7.5 g (48%); mp 177-178°C (dec); H NMR (DMSO- d₆): δ 1.2 (t, 3 H, CH₃), 4.2 (q, 2 H, CH₂), 7.9 (s, 1 H, CH); EI-MS: 156 (M^+) . Anal. calcd for C₆H₈N₂O₃: C, 46.15; H, 5.12; N. 17.94. Found: C, 46.25; H, 5.13; N, 17.93. The pyrazolinone (5.0 g, 32 mmol) in dichloromethane (200 mL) was treated with a stream of chlorine gas at 25°C until the solid phase disappeared and the solution became yellow. Excess chlorine was purged with a stream of nitrogen. Removal of the solvent left the chloropyrazolinone **10e** or an isomer that recrystallized from benzene as a yellow solid, 5.5 g (90%); mp 103–105°C; H NMR (CDCl₃): δ 1.3 (t, 3 H, CH₃), 4.4 (q, 2 H, CH₂), 7.4 (s, 1 H, CH), and 9.6 (broad, 1 H, CH). Anal. calcd for C₆H₇N₂O₃Cl: C, 37.79; H, 3.79; N, 14.69; Cl, 18.68. Found: C, 37.87; H, 3.57; N, 14.63; Cl, 18.72. Attempts to convert the product 10e (or isomer) under the catalysis of either potassium carbonate, or N,N-diisopropylethylamine, or potassium fluoride on alumina, or sodium hydride in tetrahydrofuran to syn-(hydrogen, carboethoxy) bimane were unsuccessful.

anti-(Methyl,nitro)(methyl,hydrogen)bimane 16

After a mixture of nitric acid (90%, 0.20 mL) and acetic anhydride (0.75 mL) was stirred at 0°C for 15 m, *anti*-(methyl,hydrogen)bimane **13** (0.16 g, 1.0 mmol) was added slowly. The mixture was stirred at 0°C for 30 m and poured onto crushed ice to precipitate the nitrobimane **16** as an orange solid, 0.12 g (57%), mp 196°C (dec) (acetone). H NMR (CDCl₃): δ 2.6 (s, 3 H, CH₃), 3.0 (s, 3 H, CH₃), and 5.5 (s, 1 H, CH); EI-MS: 209 (M⁺). Anal. calcd for C₈H₇N₃O₄: C, 45.94; H, 3.37; N, 20.09. Found: C, 45.62; H, 3.19; N, 19.59.

Attempts to extend the nitration reaction to syn-(methyl,hydrogen)bimane 12 gave intractable mixtures. A trace amount of solid was thought to be a *syn*-isomer of bimane 16 since the mass spectrometric analysis showed EI-MS 209 (M⁺).

anti-(Amino, nitro) bimane 15

Following the above procedure *anti*-(amino,hydrogen)bimane **11** (0.4 g, 2.4 mmol) in a mixture of nitric acid (90%, 0.7 mL) and acetic anhydride (2.0 mL) at 0°C with stirring for 30 min gave the dinitrobimane **15** as a red orange solid, 0.56 g (91%), mp 318°C (dec) (acetone). ¹³C NMR (DMSO-d₆): δ 107.8, 151.3, and 153.7; EI-MS 256 (M⁺). Anal. calcd for C₆H₄N₆O₆: C, 28.13; H, 1.56; N, 32.81. Found: C, 28.07; H, 1.57; N, 32.07.

Oxidation of Aminobimanes

The diaminobimane 11 in a mixture of trifluoroacetic anhydride and hydrogen peroxide (90%) was converted to an intractable yellow gum. The diaminodinitrobimane 15 was unaffected by *m*-chloroperbenzoic acid, or peroxytrifluoroacetic acid, or iodobenzene diacetate.

A slurry of the diaminodinitrobimane 15 (0.8 g, 3.1 mmol), 18-crown-6 ether (0.15 g), and potassium superoxide (1.0 gm 14.1 mmol) in benzene was stirred for 17 h at 25°C under nitrogen. Addition of water gave a clear yellow aqueous layer that was acidified (dilute hydrochloric acid) to precipitate a trace amount of solid, mp > 300°C, that was discarded. Addition of ethanol to the filtrate caused the precipitation of a potassium salt as a colorless solid, 0.15 g (13%), mp 150°C (dec) (aqueous ethanol). Anal. calcd for C₆N₄O₈K₂ · 1.5 H₂O: C, 19.94; H, 0.83; N, 15.51. Found: C, 19.82; H, 0.71; N, 15.96.

syn-(Dimethoxyphosphinylmethyl,methyl) bimane **18**

A mixture of syn-(bromomethyl,methyl)bimane 17 (7.0 g, 0.2 mmol) and trimethyl phosphite (10 mL) was heated at 115° C for 30 m as it became homogeneous and solidified. After trituration with hexane (50 mL) the mixture was taken up in ethyl acetate.

The bimane **18** separated as a yellow crystalline solid, 6.3 g (78%); mp 224–225°C; H NMR (CDCl₃): δ 1.87 (d, 6 H, J = 4 Hz, CH₃), 3.72 (d, 4 H, J = 22 Hz, CH₂), 3.75 (d, 12 H, J = 10 Hz, OCH₃); ¹³C NMR (CDCl₃): δ 159.52 (CO), 140.40 and 139.95 (O=C-C=C), 114.91 and 114.58 (O=C-C), 53.52 and 53.19 (PO-CH₃), 26.34 and 20.09 (CH₂), and 6.83 (CH₃); UV (CH₃CN): λ (ϵ) 380 (6984); fluorescence (dioxane): λ (Φ) 417 (0.7); EI-MS: 408 (M⁺). Anal. calcd for C₁₄H₂₂N₂O₈P₂: C, 41.17; H, 5.39; N, 6.86; P, 15.19. Found: C, 40.95; H, 5.35; N, 6.80; P, 15.41.

syn-(Styryl, methyl) bimane 19

A mixture of the diphosphonate 18 (1.0 g, 2.5 mmol), potassium carbonate (1.4 g, 10 mmol), benzaldehyde (0.5 g, 5 mmol), and water (2 mL) was heated at 100°C for 4 h, cooled, combined with dichloromethane (200 mL), and washed with water $(2 \times 50 \text{ mL})$. The organic layer was dried (sodium sulfate) and concentrated to leave a brown solid that recrystallized from methanol to give the bimane 19 as a yellow crystalline solid, 0.3 g (29%); mp 214–215°C; H NMR (DMSO-d₆): δ 2.1 (s, 6 H, CH₃), 7.3–7.8 (m, 14 H, C₆H₅CH=CH); ¹³C NMR $(DMSO-d_6): \delta 161.36 (CO); 149.92 (O=C-C=C);$ 112.50 140.68 $(C_6H_5C==C),$ 114.67 and $(C_6H_5C=C-C=C-C=0); 135.09, 129.68, 128.72,$ and 127.42 (C₆H₅); 8.02 (CH₃); UV (CH₃CN): λ (ϵ) 400 (2530); fluorescence (dioxane): λ (Φ) 428 (0.2); EI-MS: 368 (M⁺). Anal. calcd for C₂₄H₂₀N₂O₂: C, 78.24; H, 5.47; N, 7.60. Found: C, 78.01; H, 5.52; N, 7.53.

To a slurry of potassium t-butoxide (0.8 g, 7.8 mmol) in N,N-dimethylformamide (DMF) (100 mL) the diphosphonate **18** (1.0 g, 2.5 mmol) in DMF (25 mL) was added with stirring under nitrogen at 25°C over a period of 2 h, heated at 70°C for 3 h, cooled, and treated with saturated aqueous ammonium chloride (10 mL). DMF was removed by distillation. The residue was treated with dichloromethane (200 mL), washed with water (2×50 mL), dried (sodium sulfate), and concentrated to give a brown solid that afforded the bimane **19** as a yellow crystalline solid, 0.22 g (25%), mp 214–215°C, after purification from methanol.

syn-(Acryloxymethylene,methyl)bimanc 21

Triethylamine (3.6 g, 36 mmol) and acryloyl chloride (3.4 g, 36 mmol) were added separately to syn-(hydroxymethyl,methyl)bimane **20** (2.0 g, 9 mmol) in DMF (50 mL) with stirring at 25°C over a period of 48 h. The mixture was combined with water (200 mL), extracted with chloroform (3×100 mL), washed with aqueous sodium bicarbonate (5%) (30 mL), dried (sodium sulfate), and concentrated to leave a dark brown solid. Purification by flash chromatographic separation from a column of silica gel (80 g, chloroform) gave the bimane **21** as a yellow .

solid, 0.65 g (22%); mp 121–122°C; H NMR (CDCl₃): δ 1.9 (s, 6 H, CH₃), 5.2 (s, 4 H, OCH₂), and 5.8–6.6 (m, 6 H, CH₂==CH); UV (CH₃CN): λ (ϵ) 385 (7552); fluorescence (dioxane): λ (Φ) 432 (0.6); EI-MS: 332 (M⁺). Anal. calcd for C₁₆H₁₆N₂O₆: C, 57.83; H, 4.81; N, 8.43. Found: C, 57.38; H, 4.79; N, 8.07.

syn-(Acetoxymethyl,methyl)(methyl,methyl) bimane 47

Bromine (1.25 g, 7.8 mmol) in dichloromethane (25 mL) was added dropwise to syn-(methyl, methyl)bimane (1.5 g, 7.8 mmol) in dichloromethane (50 mL) at 25°C over a period of 1 h. The solution was stirred for 30 min, and the solvent was removed to leave a red residue that was dissolved in dichloromethane (40 mL). The solution was mixed with aqueous potassium acetate (2 M, 30 mL) that contained cetyltrimethylammonium bromide (300 mg) and stirred for 18 h in the dark. The organic layer was separated, washed with water, and dried (anhydrous sodium sulfate). The solvent was then removed, and the yellow residue gave 0.78 g (40%) of syn-(acetoxymethyl,methyl)(methyl,methyl)bimane as a yellow crystalline solid: mp 185–186.5°C (ethyl acetate); H NMR (CDCl₃) δ 1.82 (s, 3 H, CH₃), 1.94 (s, 3 H, CH₃), 2.14 (s, 3 H, CH₃), 2.33 (s, 3 H, CH₃), 5.04 (s, 2 H, CH₂); UV (dioxane): λ (ϵ) 373 (6836). Anal. calcd for C₁₂H₁₄N₂O₄: C, 57.59; H, 5.64; N, 11.19. Found: C, 57.31; H, 5.63; N, 11.38.

μ-Aminoimino-syn(methylene,methyl)bimane **24**

Hydrazine hydrate (0.5 g, 10 mmol) in acetonitrile (10 mL) was added to a solution of syn-(bromomethyl, methyl) bimane 17 (0.7 g, 2 mmol) in acetonitrile (25 mL) with stirring at 25°C. The reaction mixture contained a colorless precipitate after 10 m that was collected by filtration after the mixture was diluted with water. The precipitate was triturated with acetonitrile and dried and recrystallized from DMF to give the hydrazine 24 as a yellow solid, 0.3 g (68%); mp 220-221°C (dec); H NMR (trifluoroacetic acid): δ 1.8 (s, 6 H, CH₃), 4.5 (s, 4 H, CH₂); ¹³C NMR (trifluoroacetic acid): δ 165.70 (CO), 148.50 (O=CC=C), 116.6 (O=C-C=C), 48.3 (CH₂), 5.4 (CH₃); UV (CH₃CN): λ (ϵ) 335 (5700); fluorescence(dioxane): λ (Φ): 419 (0.1); EI-MS: 220 (M⁺). Anal. calcd for $C_{10}H_{12}N_4O_2$: C, 54.54; H, 5.45, N, 25.45. Found: C, 54.33; H, 5.48; N, 25.33. The monoperchlorate derivative was prepared in ethanol as a yellow solid, 85%, mp 182-183°C (dec); H NMR (D_2O): δ 1.8 (s, 6 H, CH₃), 4.03 (s, 4 H, CH₂); UV (H₂O): λ (ϵ) 339 (4611); fluorescence (water): λ (Φ) 460 (0.1); EI-MS: 220 (M⁺-HClO₄). Anal. calcd for $C_{10}H_{13}N_4O_6Cl \cdot 1.5 H_2O$: C, 34.53; H, 3.74; N, 16.14; Cl, 10.21. Found: C, 34.59; H, 4.28; N, 16.28; Cl, 10.41.

The hydrazine **24** combined with acetone to give the hydrazone **25** (85%); mp 182–183°C; H NMR (CDCl₃): δ 1.8 (s, 6 H, CH₃), 2.0 [d, 6 H, C(CH₃)₂], 3.8 (s, 4 H, CH₂); UV (CH₃CN): λ (ϵ) 339 (6932); fluorescence (dioxane): λ (Φ): 420 (0.15); EI-MS: 260 (M⁺). Anal. calcd for C₁₃H₁₆N₄O₂: C, 60.00; H, 6.15; N, 21.53. Found: C, 59.85; H, 6.09; N, 21.46.

N-Trifluoroacetyl

μ -amino-syn-(methylene,methyl)bimane 55

A suspension of μ -amino-syn-(methylene,methyl) bimane 53 (0.50 g, 2.4 mmol) in trifluoroacetic anhydride (7 mL) was stirred at 25°C for 2 h as a pale vellow precipitate appeared. The solvent was removed and the yellow residue recrystallized from a mixture of ethyl acetate and acetonitrile (1:1, 10 mL) to give the amide 55 as a colorless crystalline solid (0.30 g, 42%): mp 173-174°C; H NMR (CDCl₃) δ 1.86 (s, 3 H, CH₃), 4.78 (s, 2 H, CH₂); UV (CH₃CN): 331 nm (ε 6309); fluorescence (dioxane): λ (Φ) 418 (0.8): EI-MS: 301 (M⁺). Anal. calcd for C₁₂H₁₀N₃O₃F₃: C, 47.85; H, 3.35; N, 13.95; F, 18.92. Found: C, 47.74; H, 3.34; N, 13.89; F, 18.73.

syn-Benzobimane 28

A solution of syn-(tetramethylene)bimane 26 (1.2 g, 5.0 mmol) in dioxane (50 mL) was treated with DDQ (2.3 g, 10.0 mmol). The solution was heated at 100°C for 24 h as the reaction was monitored with thin-layer chromatography (dichloromethane). After cooling a yellow precipitate was removed by filtration and the solvent was concentrated to give a dark brown residue which was redissolved in a minimal amount of dichloromethane and purified by chromatography (silica gel column, dichloromethane). The first fraction contained syn-(benzo) bimane 28 as a yellow solid (0.25 g, 29%), mp 308-310°C; H NMR (CDCl₃): δ 7.3–8.0 (m); UV (CH₃CN): λ (ε) 420 (6910); fluorescence (50% aqueous ethanol): λ (Φ) 428 (0.9) (reference quinine sulfate Φ 0.55) [27]; EI-MS: 236 (M⁺). Anal. calcd for $C_{14}H_8N_2O_2$: C, 71.18; H, 3.41; N, 11.86. Found: C, 71.11: H, 3.41: N. 11.79. The following fraction contained syn-(ben_o)(tetramethylene)bimane 27 (0.51 g, 58%) as a yellow solid, mp 226-227°C; H NMR (CDCl₃): δ 1.88 (m, 4 H), 2.32 (m, 2 H), 2.80 (m, 2 H), 7.10–7.90 (m, 4 H); UV (CH₃CN): λ (ε) 390 (8400); fluorescence (dioxane): λ (Φ) 435 (0.4); EI-MS: 240 (M⁺). Anal. calcd for $C_{14}H_{12}N_2O_2$: C, 69.99; H, 5.03; N, 11.66. Found: C, 69.87; H, 4.92; N, 11.56. syn-(Tetramethylene)bimane 26 (0.30 g) was recovered in the final fraction. When five equivalents of DDQ were employed all of the starting material was converted: syn-(benzo)bimane 28 (0.85 g, 72%) was obtained and only a trace amount of syn-(benzo) (tetramethylene)bimane 27 was detected by thinlayer chromatography.

4,6-Dibromo-1,2,3,4,6,7,8,9-octahydro-10H, 12H-indazolo[1,2-a]indazol-10,12-dione **29**

A solution of bromine (1.6 g, 10.0 mmol) in dichloromethane (20 mL) was added dropwise in the dark to a solution of *syn*-(tetramethylene)bimane **26** (1.2 g, 5.0 mmol) in dichloromethane (30 mL). The reaction mixture was stirred for 15 h as a deep-red solution gradually changed to orange. The solution was washed (aqueous sodium bicarbonate), dried (magnesium sulfate), concentrated, and the residue recrystallized from acetonitrile to give the dibromoindazoloindazoldione **29** as a yellow crystalline solid, 1.85 g (92%); mp 142–143°C; H NMR (CDCl₃): δ 1.85–2.67 (m, 12 H), 5.57 (m, 2 H); EI-MS: 402 (M⁺). Anal. calcd for C₁₄H₁₄N₂O₂Br₂: C, 41.82; H, 3.51; N, 6.97; Br, 39.74. Found: C, 41.57; H, 3.43, N, 6.87; Br, 39.66.

DDQ (1.1 g, 5.0 mmol) and the indazoloindazoldione **29** (0.4 g, 1.0 mmol) were dissolved in dioxane (50 mL). The solution was heated at reflux for 24 h as the reaction was monitored with thin-layer chromatography (dichloromethane) until the starting material **29** was consumed. *syn*-(Benzo)bimane **28**, the major product, was detected by thin layer chromatography.

1,2,4,5-Tetrahydro-3H-benz[g]indazol-3-one 38

Hydrazine monohydrate (10.0 g, 0.2 mol) was added dropwise to a solution of ethyl 1,2,3,4-tetrahydro-1-oxo-2-naphthoate **37** (43.6 g, 0.2 mol) in methanol (100 mL). After an exothermic reaction subsided the solution was heated at reflux for 2 h, and cooled to give a colorless precipitate that was isolated and recrystallized from hot methanol to give the indazolone **38**, 23.2 g (62%), mp 214–215°C; H NMR (DMSO-d₆): δ 2.70 (q, 4 H, CH₂), 7.13–7.63 (m, 4 H, aromatic); EI-MS: 186 (M⁺). Anal. calcd for C₁₁H₁₀N₂O: C, 70.95; H, 5.41; N, 15.03. Found: C, 70.70; H, 5.46; N, 15.14.

1H-Benz[g]indazol-3-ol 40

A sample of palladium (10% on charcoal) was added to a solution of the indazolone **38** in 1,2dichlorobenzene (5 mL). The mixture was heated at reflux for 2 days as the reaction was monitored with thin-layer chromatography (dichloromethane). The catalyst was isolated, the solvent was removed, and an ivory solid residue was recrystallized from isopropanol to give the benzindazole **40**, 0.39 g (78%), mp 245–247°C (dec.); H NMR (DMSOd₆): δ 3.70. Anal. calcd for C₁₁H₈N₂O: C, 71.73; H, 4.38; N, 15.21. Found: C, 71.58; H, 4.40; N, 14.83.

3a-Chloro-2,3a,4,5-tetrahydro-3Hbenz[g]indazol-3-one **39**

Chlorine gas was slowly passed into a suspension of the indazolone **38** (20.0 g, 0.1 mol) in dichloro-

methane (250 mL) as the solid gradually dissolved. The yellow solution was stirred for 30 min and the solvent was removed to give a solid that recrystallized from a mixture c. benzene and petroleum ether to give the chloroindazolone **39**, 17.6 g (74%), 200-205°C (dec); H NMR (CDCl₃-DMSO-d₆): δ 2.30 (m, 2 H, CH₂), 3.10 (m, 2 H, CH₂), 7.20-7.90 (m, 4 H, aromatic, 11.72 (s, 1 H, NH). Anal. calcd for C₁₁H₉N₂OCl: C, 59.88; H, 4.11; N, 12.70; Cl, 16.33. Found: C, 59.62; H, 4.08; N, 12.45; Cl, 16.07.

5,6,10,11-Tetrahydro-7H,9H-benz[6,7]indazolo [1,2-a]benz[g]indazol-7,9-dione **35**

Potassium carbonate sesquihydrate (22.0 g, 0.13 mol) was added in one portion to a solution of the chloroindazolone **39** (11.0 g, 0.05 mol) in dichloromethane (100 mL). The mixture was stirred at room temperature as the reaction was monitored with thin-layer chromatography (dichloromethane). After the reaction was completed (16 h) the mixture was chromatographed (silica gel column, dichloromethane) to give an orange solid that was purified from a mixture of isopropanol and acetonitrile as the bimane **35**, 4.5 g (53%), mp 265–267°C; H NMR ((CDCl₃): δ 2.58 (t, 4 H, CH₂), 2.99 (t, 4 H, CH₂), 7.03–7.38 (m, 8 H, aromatic); UV (CH₃CN): λ (c) 419 (3137); EI-MS: 340 (M⁺). Anal. calcd for C₂₂H₁₆N₂O₂: C, 77.63; H, 4.74; N, 8.27%. Found: C, 77.66; H, 4.83; N, 8.28%.

syn-(α -Naphtho)bimane **36**

A sample of palladium (10% on charcoal) (0.1 g)was added to a solution of the bimane 35 (3.4 g, 0.01 mol) in 1,2-dichlorobenzene (10 mL). The mixture was heated at reflux temperature for 2 days as the reaction was monitored with thin-laver chromatography (dichloromethane). Removal of the catalyst and solvent left a red residue that was purified (reprecipitated) from a mixture of hexafloropropan-2-ol and methanol, as syn-(α -naphtho)bimane 36 as a yellow powder, 2.4 g (71%); mp $313-315^{\circ}$ C; H NMR (CDCl₃): δ 7.30–7.90 (m); UV (CH₃CN): λ (ε) 460 (10,201); fluorescence (CH₂Cl₂): λ (Φ) 492 (0.1); EI-MS: 336 (M⁺). Anal. calcd for C₂₂H₁₂N₂O₂: C, 78.56; H, 3.60; N, 8.33. Found: C, 78.35; H, 3.66; N, 8.10. In the absence of a crystalline form an x-ray crystallographic analysis for the bimane 36 was not determined.

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Pyrromethene–BF₂ Complexes as Laser Dyes:1.

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ABSTRACT

Condensations between 3-X-2, 4-dimethylpyrroles (X = H, CH_3, C_2H_5 , and $CO_2C_2H_5$) and acyl chlorides gave derivatives of 3,5,3',5'-tetramethylpyrromethene (isolated as their hydrochloride salts): 6-methyl, 6-ethyl, 4,4',6-trimethyl, 4,4'-diethyl-6-methyl, and 4,4'-dicarboethoxy-6-ethyl derivatives for conversion on treatment with boron trifluoride to 1,3,5,7-tetramethylpyrromethene- BF_2 complex (TMP- BF_2) and its 2,6,8-trimethyl 8-methyl $(PMP-BF_2), 8-ethyl,$ (HMP-BF2),2,6-diethyl-8-methyl (PMDEP-BF2), and 2,6-dicarboethoxy-8-ethyl derivatives. Chlorosulfonation converted 1,3,5,7,8-pentamethylpyrromethene-BF₂ complex to its 2,6-disulfonic acid isolated as the lithium, sodium (PMPDS–BF2), potassium, rubidium, cesium, ammonium, and tetramethylammonium disulfonate salts and the methyl disulfonate ester. Sodium 1,3,5,7-tetramethyl-8-ethylpyrromethene-2,6-disulfonate-BF2 complex was obtained from the 8-ethyl derivative of TMP-BF2. Nitration and bromination converted PMP-BF₂ to its 2,6-dinitro-(PMDNP-BF₂) and 2,6-dibromo- derivatives. The time required for loss of fluorescence by irradiation from a sunlamp showed the following order for $P-BF_2$ compounds (10⁻³ to 10⁻⁴ M) in ethanol: PMPDS-BF₂, 7 weeks; PMP-BF₂, 5 days; PMDNP-BF₂, 72 h; HMP-BF2, 70 h; and PMDEP-BF2, 65 h. Under similar irradiation PMPDS-BF₂ in water lost fluorescence after 55 h. The dibromo derivative was inactive, but each of the other pyrromethene-BF₂ complexes under flashlamp excitation showed broadband laser activity in the region λ 530-580 nm. In methanol PMPDS-BF₂ was six times more resistant to degradation by flashlamp pulses than was observed for Rhodamine-6G (R-6G). An improvement (up to 66%) in the laser power efficiency of PMPDS-BF₂ (10⁻⁴ M in methanol) in the presence of caffeine (a filter for light <300 nm) was dependent on flashlamp pulse width (2.0 to 7.0 µsec).

INTRODUCTION

In 1984, less than two decades after its discovery, a review described the dye laser as one of the most useful and practical of tunable coherent sources; it became serviceable over the spectral region 300 to 1300 nm by the frequency agility of over 600 laser dyes, including cyanine, xanthene (e.g., rhodamine and fluoroscein), triarylmethane, acridine, azine, chlorophyll, polybenzenoid, coumarin, quinolone, oxazole, pyrazoline, and furan derivatives. Rhodamine dyes, for example, R-6G, gave !aser activity over the spectral range 530–710 nm and were cited as the most important and most efficient group of all laser materials [1]. Laser dye activity was presumed to reflect a causal relationship with various ancillary properties, including photostability, solubility and other interactions with solvent, fluorescence quantum yield, molar extinction

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of absorption, and minimal overlap of fluorescence with onset of absorption spectral regions (S-S) and triplet-triplet (T-T) [1,2]. Bathochromic and hyperchromic shifts were introduced by the substitution of auxochromic and antiauxochromic groups, but this benefit was often offset by the ability of certain groups, for example, nitro, cyano, and heavy atoms, to quench laser activity [1-3]. Since the known dyes, were each deficient in one or more properties the search for new stuctures to offer superior performance standards was undertaken.

A recognition that the family of syn-bimanes A offered examples fulfilling many of the auxiliary conditions led to our discovery of their laser activity at 500-530 nm. Four bimanes A1-4 were as efficient (80-100%) as coumarin 30 (coumarin 515) (laser activity in the same range) and showed improvements in photostability and solvent effects, and diminished overlap between fluorescence and absorption spectral regions (S-S and T-T) [3]. More recently the properties of certain pyrromethene-BF2 complexes 10 and 11 also afforded candidates for laser dyes. We discovered laser activity at 533 nm from 1,3,5,7-tetramethylpyrromethene-BF₂ complex (TMP-BF₂) 10a in methanol in 1988 [4]. Superior activity was rapidly discovered in 1,3,5,7,8-pentamethylpyrromethene-BF2 complex (PMP-BF₂) and its 2,6-dimethyl (HMP-BF₂), 2,6-diethyl (PMDEP-BF₂), and 2,6-disulfonic acid (isolated as the disodium salt PMPDS-BF2) derivatives [5,6]. Modest laser activity in the 2,6-dinitro derivative (PMDNP-BF₂) was exceptional [6] insofar as similar activity was not known for other dyes containing a nitro substituent. We report here on the synthesis of pyrromethene–BF₂ complexes and further discovery and development of them as laser dyes.

BACKGROUND INFORMATION

A generally efficient condensation between an α acylpyrrole and a pyrrole unsubstituted at an α position was developed as a classical synthesis of the pyrromethene precursors to porphyrins [7]. More recently the condensation reaction accommodated investigations on the pyrromethene chromophore and fluorophore in tailored derivatives that included P-BF₂ compounds [4, 5, 8, 9]. When expressed in a simplified version [R₂N(CR=CR)_n CR=NR₂]⁺ the cationic chromophore of a cyanine dye [1] included the pyrromethene cation (n = 4); however, the role of the latter has been limited to P-BF₂ compounds for laser activity [4-6], fluorescent probes for medical and biological research [10], and photodynamic therapy for cancer [11].

The unsubstituted pyrromethene B1 was unstable above -30° C and gave a yellow solution (λ_{max} 400 nm) in *n*-pentane moistened with methanol at -60° C [12]. Extensive alkylation brought about a bathochromic shift from 400 nm (log ϵ 4.35) for 3,5dimethylpyrromethene B2 in pentane [12] to 447 nm (log ϵ 4.53) for 3,5,3',5'-tetramethyl-4,4'-diethylpyrromethene B3 in ethanol [13]. Further bathochromic and hyperchromic shifts to 488 nm (log ϵ 5.00) and 528 nm (log ϵ 4.71) revealed related cationic pyrromethene chromophores for the hydrobromide and BF₂-complex derivatives C and D of the pyrromethene B3 [10, 14, 15]. The band near 440 nm was shown to be polarized parallel to the long axis of the chromophore, whereas shorter wavelength bands were shown to be perpendicular to the long axis [16].

The nearly identical fluorescence quantum yields $\Phi 2.6 \times 10^{-4}$ and 4.3×10^{-4} in ethanol, were descriptive of comparable fluorophores for 3,5,3',5'-tetramethyl-4,4'-diethylpyrromethene B3 and its hydrobromide C [17]. To account for these low quantum yields fluorescence quenching in a pyrromethene was variously correlated with proton tunneling [9], proton exchange between nitrogen atoms in the Z syn conformation, and photoisomerization at the exocyclic double bond [18, 19]; however, a deactivation of a pyrromethene S₁ state via exciplex formation, a process well known for polyamines [20], was not incompatible with the available information.

Chelation of boron difluoride by a pyrromethene bidentate anion was achieved by a treatment of a pyrromethene with boron trifluoride. Characterization of various pyrromethene-BF₂ (P-BF₂) derivatives included large extinction coefficients log $\epsilon \sim 5$ (comparable to the extinction coefficient shown for unchelated pyrromethene cations) and fluorescence quantum yields Φ 0.33 to 0.81 [14, 17]. A similar value Φ 0.31 was obtained for the corresponding $B(C_2H_5)_2$ complex E [17]. This thousandfold enhancement in fluorescence that was brought about by boron chelation with the pyrromethene bidentate ligand was reminiscent of a similar fluorescence enhancement that was recently attributed to the chelation of zinc dichloride by the diamino moieties in the nonfluorescent 9,10-bis(((2-(dimethylamino)ethyl)methylamino)methyl)anthracene F; fluorescence quenching in the tetramine F was attributed to exciplex formation [21].

Strong fluorescence in a bidentate BF₂ complex with nitrogen and/or oxygen atoms as ligand termini was afforded by P-BF₂ derivatives 10 and 11 (Scheme 1) and by the recently patented dicarbonyl chelates G (laser activity range 455-635 nm) [22]. Although fluorescence was noted for BF₂ complexes H [23] and J [24] from 1-amino-7-imino-1,3,5-cycloheptatrienes and 8-amino- and 8-hydroxyquinoline these complexes were not examined for laser activity. BF₂ complexes with less unsaturation, for example, the hexahydropyrromethene-BF₂ complex K with λ_{max} (C₂H₅OH) 320 nm (log ϵ 4.4) [25], were not examined for fluorescence (<400 nm) and laser activity. The hypsochromic shift ~120 nm relating P-BF₂ derivatives (λ max ~440 nm) and the

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partially reduced structure K was typical of other cyanine dyes [1]. The structure assignment for PMP-BF₂ 10b was supported by an X-ray crystallographic analysis [26].

Chelation of aluminum dichloride by a pyrromethene bidentate ligand gave an unstable orange solid; light absorption and emission data were not reported [25]. A different type of pyrromethene (P)-metal (M) chelate (P_2M) afforded by tetracoordinate zinc, nickel, and copper showed weak fluorescence above 500 nm ($\Phi \sim 10^{-3}$) [16, 18]. Pyrazoboles (dimeric 1-borylpyrazole chelates of dialkylboron (BR₂)) and the BF₂ complexes of 1,2,3,4tetrahydro-1,10-phenanthroline were not fluorescent [27, 28].

Laser activity was reported for a "boratriazinium" salt L and a "boradiazinium" salt M; however, preparations and structure characterizations for these molecules have not appeared in the literature [29].



R-6G-HCl



A1	$X = CH_2O_2CCH_3$
A2	$X = CH_2 P(O)(OCH_3)_2$
A3	$XX = CH_2C(CO_2C_2H_5)_2CH_2$
A4	$XX = CH_2C(CO_2CH_3)_2CH_2$



B1 X = Y = Z = H**B2** $X = Y = H, Z = CH_3$

B3 $X = Z = CH_3, Y = C_2H_5$





 $H_{5}C_{2} \xrightarrow{CH_{3}} CH_{3} \xrightarrow{CH_{3}} CL_{3} \xrightarrow{CH_{3}} B \xrightarrow{CH_{3}} CH_{3} \xrightarrow{H_{5}C_{2}} H_{5}C_{2} \xrightarrow{H_{5}} H_{5}C_{2} \xrightarrow{H_{5}} N \xrightarrow{B} Z \xrightarrow{CH_{3}} CH_{3} \xrightarrow{H_{5}C_{2}} H_{5}C_{2} \xrightarrow{H_{5}} N \xrightarrow{H_{5}} C_{2}H_{5} \xrightarrow{H_{5}} C_{2}$

С















RESULTS AND DISCUSSION

Synthesis

A general pathway shown in Scheme 1 was followed for the conversion of pyrroles 1-4 to P-BF₂ 10b-f. Kryptopyrrole 3 was commercially available; the pyrroles 1, 2, and 4 were obtained by adapting reported procedures for the hydrolysis and decarboxylation of diethyl 3,5-dimethylpyrrole-2,4-dicarboxylate 5 [30, 31] and ethyl 3,4,5-trimethylpyrrole-2-carboxylate 6[32,33] and the thermolysis of *tert*-butyl 3,5-dimethyl-4-carboethoxypyrrole-2carboxylate 7 [34]. In reactions with appropriate acyl chlorides pyrroles 1-4 afforded the unstable intermediate pyrromethene derivatives 9b-f. These intermediates were isolated as hydrochloride salts and immediately converted, sometimes without purification, to their P-BF₂ derivatives 10b-f. As Csubstitution increased the pyrromethene hydrochlorides became more stable and more amenable to isolation and characterization. According to a previously reported procedure 2-formyl-3,5-dimethylpyrrole 8 and 2,4-dimethylpyrrole 1 gave unisolated 3,5,3',5'-tetramethylpyrromethene 9a [14].

×



In a typical chelation the hydrochloride salt of 3,5,3',5'-tetramethylpyrromethene 9a gave TMP-BF₂ 10a by treatment with boron trifluoride in the pres-











10a-f

 $i = YCOCl; ii = BF_3 \cdot O(C_2H_5)_2, R_3N$

1 X = H; 2 X = CH_3 ; 3 X = C_2H_5 ; 4 X = $CO_2C_2H_5$

a X = Y = H; **b** X = H, $Y = CH_3$; **c** X = H, $Y = C_2H_5$;

11k, m
$$\stackrel{iv}{\leftarrow}$$
 10b $\stackrel{iii}{\longrightarrow}$ 11a-j
iii = ClSO₃H, base; iv = HNO₃ (k); Br₂ (m)





a-e $X = SO_3M$, M = H (a), Li (b), Na (c), K (d), Rb (e), Cs (f);

g X = SO₃ NH₄; h X = SO₃ N(CH₃)₄; j X = SO₃CH₃; k X = NO₂; m X = Br; n X = SO₃Na, Y = C₂H₅

SCHEME 1

ence of triethylamine [14], or diisopropylethylamine (preferred) [16]. A similar conversion of the pyrrole derivative 4 afforded diethyl 1,3,5,7-tetramethyl-8-ethylpyrromethene-2,6-dicarboxylate-BF₂ complex 10f [25]. To extend the method to the preparation of PMP-BF₂ 10b, the precursor 3,5,3',5',6pentamethylpyrromethene 9b was obtained directly from the treatment of 2,4-dimethylpyrrole 1 with acetyl chloride. A similar preparation afforded the 8-ethyl- derivative 10c from the precursor 3,5,3',5'-tetramethyl-6-ethylpyrromethene 9c, which was in turn obtained from 2,4-dimethylpyrrole 1 and propionyl chloride. Complete C-substitution in a pyrromethene and its BF₂-complex was rarely encountered. In addition to the complex 10f other examples were found in chelations affording 1,2,3,5,6,7,8-heptamethyl- and 1,3,5,7,8-pentamethyl-2,6-diethyl-pyrromethene-BF2 complexes (HMP-BF₂ and PMDEP-BF₂) 10d, 10e.

Electrophilic sulfonation in the 2- and 6- positions was reported for the complex 10a [15]. A similar substitution was initially useful in the preparation of the disodium (PMPDS-BF₂) and dimethyl 1,3,5,7,8-pentamethylpyrromethene-2,6-disulfonate-BF2 complexes 11c and 11j. Straightforward modifications led to the formation of other dimetal (Li, K, Rb, and Cs) salts 11b and 11d-f and the diammonium and the bistetramethylammonium 1,3,5,7,8-pentamethylpyrromethene-2,6-disulfonate-BF₂ complexes 11g and 11h. Other examples of complete C-substitution were discovered in electrophilic nitration and bromination to give the 2,6dinitro (PMDNP-BF2) and 2,6-dibromo derivatives 11k and 11m. These substitution reactions were considered to be supportive of quasiaromaticity for the pyrromethene-BF₂ complexes (cf., D). This property is characteristic of various metal chelates [35, 36] and is further supported by proton nmr signals a 6.00 to 7.62 for unsubstituted ring positions in P-BF₂ derivatives [13].

Laser Activity

Laser activity for P-BF₂ complexes (Table 1) gave RE from 0 to 100. Presumably a heavy atom effect brought about inactivity (RE 0) for 2,6-dibromo-1,3,5,7,8-pentamethylpyrromethane-BF₂ complex 11m. Each of the P-BF2 complexes 10a-f and 11a-n showed high molecular extinction coefficients (log ϵ_s 4 to 5) and high fluorescence quantum yields Φ 0.3 to 1.0) (Table 1). Minimal T-T absorption in or near the fluorescence spectral region was determined for TMP-BF₂ 10a [4], PMP-BF₂ 10b [5] and PMPDS-BF₂ 11c (Figure 1). A value ϵ_T (567) = 1.5 × 10³ L/mole cm for PMDEP-BF₂ 10e was exceptionally low in comparison with $\epsilon_{\rm T}$ (570) = 7.9 × 10³ L/mol cm and $\epsilon_{\rm T}$ (580) = 6.6 × 10³ L/mole cm for rhodamine dyes 560 and 575 [6]. To avoid selfquenching through aggregation a dye concentration of about 10⁻⁴ M was generally sought. A hypsochromic shift in fluorescence from 534 to 509 nm for PMPDS-BF₂ 11c in water was brought about by dilution from 10^{-3} to 10^{-8} M and attributed to diminished aggregation as dilution increased [37]. Although methanol (preferred), ethanol, or water were solvents of choice for laser activity from many P-BF₂, other satisfactory solvents in certain instances included acetonitrile, chloroform, dimethylsulfoxide, N,N-dimethylformamide, dichloromethane, dioxane, ethyl acetate, ethylene glycol, and hexafluoroisopropanol. Since the use of water minimized problems of storage and disposal or recovery of large amounts of organic solvents, water soluble dyes were sought. Aqueous solutions also offered thermooptic properties of water that often improved laser activity [2].

Just as a reaction between a P-BF₂ complex and methanolic potassium hydroxide was attributed to the initial nucleophilic attack at the 8-position that led to destruction of the chromophore [25], a similar reaction was assumed to account in part for the loss of fluorescence from PMP-BF₂ 10b in ethanol solution after exposure to sunlamp irradiation for 5 days. In contrast, the loss of fluorescence from the complex 10b in dichloromethane required a similar exposure to irradiation for 21 days. A greater photolability was demonstrated in the loss of fluorescence from other $P-BF_2$ derivatives (10⁻⁴ M in ethanol): PMDNP-BF2 10k after 72 h, HMP-BF2 10d after 70 h, and PMDEP-BF₂ 10e after 65 h; and from PMPDS-BF₂ 11c (10⁻⁴ M in water) after 55 h. In methanol PMPDS-BF₂ 11c was markedly more stable; the loss of fluorescence in a similar experiment required 7 weeks. When photostability was determined by the number of flashlamp pulses required to lower laser power efficiency by 50% the complex 11c in methanol or ethanol was discovered to be much more photostable than other known laser dyes (including other P-BF₂ derivatives) for the spectral region 530-560 nm [38, 39]. In one laboratory, when methanol solutions were examined the complex 11c was six times more photostable than the dye R-6G (9000 pulses vs. 1500 pulses) [40].

A comparison of laser energy output as a function of flashlamp pump energy showed PMPDS-BF2 11c in ethanol offered three times the power efficiency from coumarin 545 and was comparable in efficiency to R-6G [5]. Because of its exceptional photostability in methanol, PMPDS-BF₂ 11c was selected for further examination. From flashlamp excitation (pulsewidth 2 μ sec, risetime 0.7 μ sec) with pump energy at 300 J in conjunction with an LFDL-8 laser, a 30% improvement in power efficiency for PMPDS-BF₂ 11c over R-6G (each 10⁻⁴ M in methanol) was realized [41, 42]. In the presence of caffeine (a filter for light <300 nm) PMPDS-BF₂ (10⁻⁴ M in methanol) gave an improvement (28% to 66%) in laser efficiency that was dependent on flashlamp pulse width (2.0 to 7.0 μ sec) [38, 39]. In contrast with an enhancement in laser activity from 10^{-3} M aqueous solutions of R-6G and other xanthene dyes brought about by the presence of β cyclodextrin (10⁻² M), the fluorescence of PNPDS- BF_2 (10⁻³ to 10⁻⁸ M) in water was unaffected by similar treatment [37]. An interest in the effect on laser activity by the formation of a salt between R-6G (the free base) and 1,3,5,7,8-pentamethylpyrromethene-2,6-disulfonic acid 11a was thwarted by the failure to obtain a tractable product from their interaction. There was no improvement in laser ac-

TABLE 1 Pyrromethene-BF₂ Complexes^{*}

No.	λ _{max} nm	log ¢	λ _{FI} nm	Φ	λ _{las} nm	RE [®] %
10a	505	4.92	516	0.80	533	30
10b	493	4.90	519	0.99	542	100
10c	495	4.99	517	1.0	546	90
10d	518	4.67	543	0.70°	570	75
10e	517	4.81	546	0.83°	570	100
10f	493°	4.97 ^d	531	0.38°	556	50
11b	497	4.96	533	0.62°	554	65
11c	492	4.86	533	0.73°	560	90
11d	498	4.96	534	0.78°	556	100
11e	497	4.91	533	0.88*	553	95
11f	497	4.91	531	0.81*	553	95
11g	496	4.92	533	0.90*	557	95
11ĥ	497	4.97	535	0.89*	556	95
11	483'	4.82	520'	0.829	554'	35
11k	493	4.62	533	h	h	h
11m	516'	4.81	546′	0.45 ^g		
11n	498	4.90	530	0.44 ^c	555	50

^aMethanol was used as solvent except where noted otherwise. ^bRelative Efficiency in laser power output. RE 100 assigned to PMP-BF₂ 10b. RE 30 observed for Coumarin 545 [5].

^cin ethanol,

^dλ_{max} 495 nm (log ε 5.26) [23].

In water.

'In a mixture (9:1) of methanol and dichloromethane.

⁹In dichloromethane.

"Due to photoinstability the data was not reproducible.

No.	Yield %	mp °C	Formula	Calculated, % Found, %
10b	66	254-257	C ₁₄ H ₁₇ N ₂ F ₂ B	C, 64.15; H, 6.53; N, 10.74
10c	45	dec 214–216	$C_{15}H_{19}N_2F_2B$	C, 64.34; H, 6.71; N, 10.84 C, 65.24; H, 6.92; N, 10.15 C, 64.97; H, 6.88; N, 10.05
10d	34	286–287 dec	$C_{16}H_{21}N_2F_2B$	C, 66.20; H, 7.24; N, 9.65 C, 66.23; H, 7.35; N, 9.57
10e	34	207-208	C ₁₈ H ₂₅ N ₂ F ₂ B	C, 67.92; H, 7.86; N, 8.80 C, 67.88; H, 8.06; N, 8.79
11b	. 84	>280	$C_{14}H_{25}N_2O_6F_2BS_2Li \cdot 2H_2O$	C, 35.74; H, 3.19; N, 5.95 C, 36.16; H, 3.50; N, 5.97
11c	75	> 300	$C_{14}H_{15}N_2O_6F_2BS_2Na_2$	C, 36.07; H, 3.24; N, 6.01 C, 36.42; H, 3.35; N, 6.14
11d	82	>280	$C_{14}H_{15}N_2O_6F_2BS_2K_2$	C, 33.79; H, 3.01; N, 5.62 C, 33.91; H, 3.02; N, 5.62
11e	62	>280	$C_{14}H_{15}N_2O_6F_2BS_2Rb_2$	C, 28.42; H, 2.53; N, 4.73 C, 28.36; H, 2.45; N, 4.69
11f	57	>280	$C_{14}H_{15}N_2O_6F_2BS_2Cs_2$	C, 24.49; H, 2.18; N, 4.08 C, 24.58; H, 2.18; N, 4.08
11g	60	>300	$C_{14}H_{23}N_4O_6F_2BS_2$	C, 36.85; H, 5.08; N, 12.28 C, 36.91; H, 5.02; N, 12.20
11h	78	281–282 dec	$C_{22}H_{39}N_4O_6F_2BS_2\cdotH_2O$	C, 45.05; H, 7.05; N, 9.55 C, 45.29; H, 6.73; N, 9.50
11j	40	218-222 dec	$C_{16}H_{21}N_2O_6F_2BS_2$	C, 42.67; H, 4.70; N, 6.22 C, 42.54; H, 4.70; N, 6.22
11k	71	279–281 dec	$C_{14}H_{15}N_4O_4F_2B$	C, 47.70; H, 4.26; N, 15.90 C, 48.18; H, 4.46; N, 15.94
11m	50	300-302 dec	$C_{14}H_{15}N_2Br_2F_2B$	C, 40.00; H, 3.57; N, 6.66 C, 40.13; H, 3.67; N, 6.69
11n	69	>260	$C_{15}H_{17}N_2O_6F_2BS_2Na_2$	C, 37.52; H, 3.57; N, 5.84 C, 38.20; H, 3.79; N, 5.75

 TABLE 2
 Pyrromethene-BF₂ Complexes

tivity from an equimolar mixture of the two dyes R-6G (as the hydrochloride salt) and PMPDS-BF₂ 11c, in methanol.

EXPERIMENTAL

Spectral data was obtained from the following instruments: Pye-Unicam SP 200 and Sargent-Welch 3-200 IR, Varian EM 360A, and IBM AF200 NMR [43], Hewlett-Packard 5985 (70 eV) (GC-MS), Cary 17 (UV), and Perkin-Elmer LS-5B Luminescence Spectrometers. A dye laser was constructed at the Naval Ocean Systems Center [44]. It operated in the non-flowing (static) mode and had no tuning capability. The dye cell (2.5 mm diameter, 50 mm long) had an eliptical cavity configuration of small eccentricity. The flashlamp EG & G model FX 139C-2, produced a pulse that had a rise time of 200 ns, half-width length of 600 ns, and input energy of 2 J at 6.32 kV, 5 J at 10.00 kV, 7.2 J at 12.00 kV, and 10 J at 14.14 kV [44, 45]. Laser energy outputs were measured with an accuracy of $\pm 5\%$ by a Scientech 365 power and energy meter [46]. Light absorption, luminescence, and laser activity properties are described in Table 1.

For each product the IR and EI-MS data agreed

with the literature data and/or supported the assigned structure. Each recorded UV absorption was restricted to the highest wave length. ¹H NMR spectra were run in CDCl₃ with tetramethylsilane as an internal standard. ¹³C NMR were recorded at 22.5 MHz with the deuterated solvent as an internal reference; the central peak of the solvent multiplet signal was assigned: ∂ 77.00 (CDCl₃), 39.50 (CD₃)₂(SO). Poor solubility precluded NMR analyses in many instances. Fluorescence quantum yields of the dyes were determined for methanol solutions with excitation at 450 and 460 nm by reference to acridine orange, φ 0.46 [14], in ethanol. Melting points were determined on a Thomas Hoover melting point apparatus and were uncorrected. Elemental analyses were obtained from Midwest Micro Lab, Indianapolis, Indiana and Galbraith Laboratories, Inc., Knoxville, Tenn. Solvents were removed by rotary evaporation under reduced pressure unless indicated otherwise. Column chromatography was performed on silica gel (various grades). Triplet extinction coefficients over the laser action spectral region of the dye were measured at the temperature of liquid nitrogen by equipment previously described [47] using McClure's method [48].

Solvents, reagents, and starting materials that

Shah et al.



were obtained from the Aldrich Chemical Company, Milwaukee, WI included acetic anhydride, acetone, acetonitrile, acetyl chlcride, alumina, ammonium carbonate, ammonium chloride, benzene, boron trifluoride etherate, bromine, carbon tetrachloride, celite, cesium carbonate, chloroform-d, chlorosulfonic acid, deuterium oxide, dichloromethane, N,N-disopropylethylamine, N,N-dimethylformamide (DMF), dimethyl sulfoxide-d₆ (DMSO d_6), p-dioxane, ethanol, ethyl acetate, hexane, hexafluoroisopropanol, hydrazine hydrate, lithium carbonate, isopropanol, isopropyl ether, kryptopyrrole (2,4-dimethyl-3-ethylpyrrole 3), magnemethanol, nitric sium sulfate. acid. 2-methyltetrahydrofuran, petroleum ether, phosphoric acid, potassium bromide, potassium carbonate, potassium fluoride, propionyl chloride, rubidium carbonate, silica gel (230–400 mesh, 60 Å), sodium bicarbonate, sodium hydroxide, sodium sulfate, tetrahydrofuran (THF), tetramethylammonium carbonate, toluene, triethylamine, and trifluoroethanol. Rhodamine 6G and thin layer chromatography sheets were obtained from Eastman Kodak Co., Rochester, NY. Chlorine was obtained from Matheson Gas Products, Secaccus, NJ. Nitrogen was obtained from Air Products and Chemicals, Inc., Allentown, PA.

The following compounds were prepared according to the directions cited: ethyl 2,4-dimethylpyrrole-3-carboxylate 4 [34]; diethyl 3,5-dimethylpyrrole-2,4-dicarboxylate 5 [30, 31]; ethyl 3,4,5trimethylpyrrole-2-carboxylate 6 [32]; tert-butyl 3,5dimethyl4-carboethoxypyrrole-2-carboxylate 7 [34]; 2-formyl-3,5-dimethylpyrrole 8 [12]; 3,5,3',5'-tetramethylpyrromethene 9a (modified for isolation as its hydrochloride salt) [14]; 1,3,5,7-tetramethylpyrromethene-BF₂ complex 10a (modified procedure) [14]; and 4.4'-dicarboethoxy-6-ethyl-3,5,3',5'-tetramethylpyrromethene 9g (modified for isolation as the hydrochloride derivative, mp 227-232°C (dec), EI-MS (relative abundance): 373 (100, M⁺ - Cl)) [34].

2,4-Dimethylpyrrole 1

In an adaptation of a procedure [30], diethyl 3,5dimethylpyrrole-2,4-dicarboxylate 5 (160.0 g, 0.66 mol) as a melt at 140°C was treated with phosphoric acid (85%, 320 mL). The mixture was heated at 180°C for 30 min and poured into aqueous sodium

396

hydroxide (3.5 M, 3.5 L). Codistillation gave 3 L that was extracted with isopropyl ether (3 \times 500 mL). The organic phase was dried (potassium carbonate) and concentrated to give a dark brown oil that distilled, 70-80°C (10 mm), to give 2,4-dimethylpyrrole 1 as a colorless oil, 40.00 g (64%); bp 162-165°C (lit. [30] 160-165°C), 'H NMR (CDCl₃): ∂ 2.07 (s, 3H), 2.16 (s, 3H), 5.72 (s, 1H) 6.31 (s, 1H), 7.20-7.87 (br s, 1H). Similarly, ethyl 3,4,5-trimethyl-2-carboxylate 6 was converted to 2,3,4-trimethylpyrrole 2 as a colorless solid (67%), mp 37-38°C (lit. [32] mp 36-38°C).

3,5,3',5',6-Pentamethylpyrromethene Hydrochloride **9b**

Acetyl chloride (35 mL, 0.49 mol) was added dropwise with stirring over a period of 15 min to a solution of 2,4-dimethylpyrrole 1 (20.0 g, 0.21 mol) in dichloromethane (150 mL). The reaction mixture was heated at 40°C for 1 h, cooled to room temperature, diluted with petroleum ether (1.5 L), and triturated for 12 h to bring about the separation of 3,5,3',5',6-pentamethylpyrromethene hydrochloride 9b. It was isolated by vacuum filtration as a red-brown powder, 24.0 g (91%), mp 180–185°C (dec); EI-MS (relative abundance): 214 (51.8) M⁺ – HCl); ¹H NMR (CDCl₃); ∂ 2.02 (s, 6H); 2.20 (s, 6H); 2.49 (s, 3H); 6.20 (s, 2H) [43]. Instability precluded elemental analysis.

Similarly, the hydrochloride salts of derivatives of 3,5,3',5'-tetramethylpyrromethene were obtained. The pyrrole 1 and propionyl chloride gave the 6-ethyl- derivative 9c, 81%, mp 192–195°C (dec). Anal. Calcd. for C₁₅H₂₁N₂Cl: C, 68.04; H, 7.99; N, 10.58. Found: C, 67.47; H, 7.80; N, 10.17. The pyrrole 2 and acetyl chloride gave the 4,4',6-trimethyl derivative 9d, 80%, mp 210-212°C (dec); 'H NMR (CDCl₃): ∂ 1.90 (s, 6H), 2.00 (s, 6H), 2.45 (s, 6H), 2.75 (s, 3H) [33]. Anal. Calcd. for $C_{16}H_{23}N_2Cl$: C, 68.94; H, 8.25; N, 10.05; Cl, 12.74. Found: C, 69.41; H, 7.72; N, 10.21; Cl, 12.97. The pyrrole 3 and acetyl chloride gave the 4,4'-diethyl-6-methyl derivative 9e, 77%, mp 185–186°C (dec); 'H NMR (CDCl₃): ∂ 1.01 (t, 6H), 2.07 (s, 6H), 2.35 (q, 4H), 2.46 (s, 6H), 2.76 (s, 3H) [43]. Anal. Calcd. for C₁₈H₂₇N₂Cl: C, 70.47; H, 8.80; N, 9.13; Cl, 11.58. Found: C, 70.67; H, 9.00; N, 9.15; Cl, 11.73.

1,3,5,7,8-Pentamethylpyrromethene-BF₂ Complex (PMP-BF₂) 10b

Triethylamine (15 mL, 113 mmol) was added at room temperature to a suspension of 3,5,3',5',6pentamethylpyrromethene hydrochloride 9b (6.0 g, 24 mmol) in toluene (600 mL) and the mixture was stirred for 15 min. Boron trifluoride etherate (20 mL, 163 mmol) was added dropwise with stirring as a green fluorescence developed. The reaction mixture was heated (80°C) for 15 min, cooled to

40°C, washed with warm water $(3 \times 100 \text{ mL})$, dried (magnesium sulfate), and concentrated to give a dark brown solid. Flash chromatographic [49] separation of a solid mixture (silica gel, 250 g, 230-400 mesh, 60 Å, a mixture (80:20) of toluene and hexane), followed by concentration of the intense greenyellow fluorescent fractions, gave PMP-BF2 10b. It recrystallized from ethyl acetate as an orange crystalline solid, 4.1 g (66%) (see Tables 1 and 2 for other properties). In reactions with boron trifluof, ride the hydrochlorides of pyrromethenes 9c-f gave the corresponding P-BF2 derivatives 10c-f (Table 1). ¹H NMR [43]: HMP-BF₂ 10d (CDCl₃): ∂ 1.91 (s, 6H), 2.29 (s, 6H), 2.46 (s, 6H), and 2.57 (s, 3H); PMDEP-BF₂ 10e (CDCl₃): ∂ 1.01 (t, 6H), 2.30 (s, 6H), 2.37 (q, 4H), 2.47 (s, 6H), and 2.57 (s, 3H).

Disodium 1,3,5,7,8-pentamethylpyrromethene-2,6-disulfonate-BF₂ Complex (PMPDS-BF₂) 11c

A solution of chlorosulfonic acid (3.26 g, 28 mmol) in dichloromethane (20 mL) was added dropwise to a suspension of PMP-BF₂ 10b (3.65 g, 14 mmol) in dichloromethane (50 mL) at -50°C. A yellow solid separated as the reaction mixture warmed slowly to room temperature. The disulfonic acid 11a was isolated by vacuum filtration and treated with water (600 mL). The aqueous solution was neutralized with sodium bicarbonate (2.52 g, 30 mmol). The solution was concentrated to 75 mL and treated with ethanol (400 mL) to bring about the separation of the salt 11c. It was isolated by vacuum filtration, recrystallized from aqueous ethanol (80%), and dried in air to give a yellow-orange powder, 5.0 g (75%) (Table 1). The dilithium, dipotassium, dirubidium, dicesium, diammonium, and the bistetramethylammonium salts 11b, 11d-h (Tables 1 and 2) were prepared in straightforward reactions. A similar conversion of 1,3,5,7-tetramethyl-8-ethylpyrromethene-BF2 complex 10c gave disodium 1,3,5,7tetramethyl-8-ethylpyrromethene-2,6-disulfonate-BF₂ complex 11n (Tables 1 and 2).

Dimethyl 1,3,5,7,8-pentamethylpyrromethene-2,6-disulfonate-BF₂ Complex 11j

A solution of chlorosulfonic acid (3.6 g, 30 mmol) in dichloromethane (20 mL) was added dropwise to a cooled suspension of 1,3,5,7,8-pentamethylpyrromethene-BF₂ complex 10b (2.0 g, 7.6 mmol) in dichloromethane (30 mL) at -50° C. A brown oil separated as the clear yellow solution warmed to room temperature. It was treated with methanol (10 mL), stirred for 0.5 h at room temperature, concentrated to a brown viscous oil, treated with methanol (40 mL), and stirred to bring about the separation of a yellow-brown solid that was isolated by vacuum filtration, treated with methanol (100 mL), and heated (60°C) for 0.5 h to complete an esteri÷ è

fication. The solid ester 11j, 1.4 g (40%), was isolated and purified from methanol to give an orangeyellow powder (Tables 1 and 2).

1,3,5,7,8-Pentamethyl-2,6dinitropyrromethene-BF₂ complex (PMDNP-BF₂) **11k**

After PMP-BF₂ 10b (3.0 g, 11.5 mmol) was added to nitric acid (50 mL, 70%) at 0°C, the orange-red mixture was stirred at 0°C for 1.5 h and poured into ice water (200 mL) to precipitate the 2,6-dinitro derivative 11k as an orange solid, isolated by filtration and washed with water. It recrystallized from ethyl acetate as an orange powder (2.9 g) (Tables 1 and 2).

1,3,5,7,8-Pentamethyl-2,6dibromopyrromethene-BF₂ Complex 11m

Bromine (16.0 g, 100 mmol) in dichloromethane (50 mL) was added dropwise to PMP-BF₂ 10b (2.0 g, 7.6 mmol) in dichloromethane (150 mL) over a period of 10 min at 25°C with stirring. An orange precipitate was separated, triturated with dichloromethane (150 mL), and dried to give the dibromo derivative 11m as an orange crystalline solid, 1.6 g (Tables 1 and 2); ¹H NMR [43] (CDCl₃): ∂ 2.41 (s, 6H), 2.55 (s, 6H), and 2.60 (s, 3H).

Pyrromethene-BF₂ Complexes Photostability

A solution of 1,3,5,7,8-pentamethylpyrromethene-BF₂ complex (PMP-BF₂) 10b (0.10 g, 0.3 mmol) in ethanol (250 mL) was irradiated by a sunlamp (GE 275W) at a distance of 30 cm. Fluorescence at 500 nm became undetectable after 5 days. In similar experiments other P-BF₂ derivatives (10⁻⁴ M in ethanol) also lost fluorescence: PMDNP-BF2 11k after 72 h, HMP-BF2 10d after 70 h, and PMDEP-BF2 10e after 65 h. Disodium 1,3,5,7,8-pentamethylpyrromethene-2,6-disulfonate-BF2 complex (PMPDS-BF₂) 11c (2.0 mg) in water (50 mL) lost its fluorescence at 492 nm after 55 h of similar irradiation; when water was replaced with methanol the duration of fluorescence was 7 weeks. In brown bottles all P-BF₂ compounds were indefinitely stable to storage at 25°C.

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