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13 ABSTRACT (Maximum 200 words) <p>Pyrrromethene-BF<sub>2</sub> complexes (P-BF<sub>2</sub>) were obtained from <math>\alpha</math>-unsubstituted pyrroles by acylation and condensation to give intermediate pyrrromethene hydrohalides followed by treatment with boron trifluoride etherate. Conversion of ethyl <math>\alpha</math>-pyrrrocarboxylates to <math>\alpha</math>-unsubstituted pyrroles was brought about by thermolysis in phosphoric acid at 160°C, or by saponification followed by decarboxylation in ethanolamine at 180°C, or as unisolated intermediates in the conversion of esters to pyrrromethene hydrobromides by heating in a mixture of formic and hydrobromic acids. Addition of hydrogen cyanide followed by dehydrogenation by treatment with bromine converted 3,5,3',5'-tetramethyl-4,4'-diethylpyrrromethene hydrobromide to 3,5,-3',5'-tetramethyl-4,4'-diethyl-6-cyanopyrrromethene hydrobromide, confirmed by the further conversion to 1,3,5,7-tetramethyl-2,6-diethyl-8-cyanopyrrromethene-BF<sub>2</sub> complex on treatment with boron trifluoride etherate.</p> <p>An alternation effect in the relative efficiency (RE) of laser activity in 1,3,5,7,8-pentamethyl-2,6-di-n-alkylpyrrromethene-BF<sub>2</sub> dyes depended on the number of methylene units in the n-alkyl substituent, -(CH<sub>2</sub>)<sub>n</sub>H, to give RE <math>\approx</math> 100 when n = 0, 2, 4 and RE 65.85 when n = 1,3. (The RE 100 was arbitrarily assigned to the dye rhodamine 6G). The absence of fluorescence and laser activity in 1,3,5,7-tetramethyl-2,6-diethyl-8-isopropylpyrrromethene-BF<sub>2</sub> complex and a markedly diminished fluorescence quantum yield (<math>\Phi</math> 0.23) and lack of laser activity in 1,3,5,7-tetramethyl-2,6-diethyl-8-cyclohexylpyrrromethene-BF<sub>2</sub> complex were attributed to molecular nonplanarity brought about by the steric interference between each of the two bulky 8-substituents with the 1,7-dimethyl substituents. An atypically low RE 20 for a peralkylated dye without steric interference was observed for 1,2,6,7-bis(trimethylene)-3,5,8-trimethylpyrrromethene-BF<sub>2</sub> complex. Comparisons with peralkylated dyes revealed a major reduction in RE 0-40 for the six dyes lacking substitution at the 8-position.</p>			
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Low laser activity RE was brought about by functional group (polar) substitution in the 2,6-diphenyl derivative, RE 20, and the 2,6-diacetamido derivative, RE 5, of 1,3,5,7,8-pentamethylpyrromethene-BF<sub>2</sub> complex (PMP-BF<sub>2</sub>) and in 1,7-dimethoxy-2,3,5,6,8-pentamethylpyrromethene-BF<sub>2</sub> complex, RE 30. Diethyl 1,3,5,7-tetramethyl-8-cyanopyrromethene-2,6-dicarboxylate-BF<sub>2</sub> complex, and 1,3,5,7-tetramethyl-2,6-diethyl-8-cyanopyrromethene-BF<sub>2</sub> complex, offered examples of P-BF<sub>2</sub> dyes with electron withdrawing substituents at the 8-position. The dye,  $\lambda_{\text{las}}$  617 nm, showed nearly twice the power efficiency that was obtained from rhodamine B,  $\lambda_{\text{las}}$  611 nm.

# Pyrromethene-BF<sub>2</sub> Complexes as Laser Dyes: 2

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## ABSTRACT

Pyrromethene-BF<sub>2</sub> complexes (P-BF<sub>2</sub>) **7** were obtained from  $\alpha$ -unsubstituted pyrroles **5** by acylation and condensation to give intermediate pyrromethene hydrohalides **6** followed by treatment with boron trifluoride etherate. Conversion of ethyl  $\alpha$ -pyrrolocarboxylates **4** to  $\alpha$ -unsubstituted pyrroles **5** was brought about by thermolysis in phosphoric acid at 160°C, or by saponification followed by decarboxylation in ethanolamine at 180°C, or as unisolated intermediates in the conversion of esters **4** to pyrromethene hydrobromides **6** by heating in a mixture of formic and hydrobromic acids. Addition of hydrogen cyanide followed by dehydrogenation by treatment with bromine converted 3,5,3',5'-tetramethyl-4,4'-diethylpyrromethene hydrobromide **9** to 3,5,-3',5'-tetramethyl-4,4'-diethyl-6-cyanopyrromethene hydrobromide **6bb**, confirmed by the further conversion to 1,3,5,7-tetramethyl-2,6-diethyl-8-cyanopyrromethene-BF<sub>2</sub> complex **7bb** on treatment with boron trifluoride etherate.

An alternation effect in the relative efficiency (RE) of laser activity in 1,3,5,7,8-pentamethyl-2,6-di-*n*-alkylpyrromethene-BF<sub>2</sub> dyes depended on the number of methylene units in the *n*-alkyl substituent, -(CH<sub>2</sub>)<sub>*n*</sub>H, to give RE  $\geq$  100 when *n* = 0,2,4 and RE 65, 85 when *n* = 1,3. (The RE 100 was arbitrarily assigned to the dye rhodamine 6G). The absence of fluorescence and laser activity in 1,3,5,7-tetramethyl-2,6-diethyl-8-isopropylpyrromethene-BF<sub>2</sub> complex **7p** and a markedly diminished fluorescence quantum yield ( $\Phi$  0.23) and lack of laser activity in 1,3,5,7-tetramethyl-2,6-diethyl-8-cyclohexylpyrromethene-BF<sub>2</sub>

complex **7q** were attributed to molecular nonplanarity brought about by the steric interference between each of the two bulky 8-substituents with the 1,7-dimethyl substituents. An atypically low RE 20 for a peralkylated dye without steric interference was observed for 1,2,6,7-bistrimethylene-3,5,8-trimethylpyrromethene-BF<sub>2</sub> complex **7j**. Comparisons with peralkylated dyes revealed a major reduction in RE 0-40 for the six dyes **7u-z** lacking substitution at the 8-position.

Low laser activity RE was brought about by functional group (polar) substitution in the 2,6-diphenyl derivative **7l**, RE 20, and the 2,6-diacetamido derivative **7m**, RE 5, of 1,3,5,7,8-pentamethylpyrromethene-BF<sub>2</sub> complex (PMP-BF<sub>2</sub>) **7a** and in 1,7-dimethoxy-2,3,5,6,8-pentamethylpyrromethene-BF<sub>2</sub> complex **7n**, RE 30. Diethyl 1,3,5,7-tetramethyl-8-cyanopyrromethene-2,6-dicarboxylate-BF<sub>2</sub> complex, **7aa**, and 1,3,5,7-tetramethyl-2,6-diethyl-8-cyanopyrromethene-BF<sub>2</sub> complex, **7bb**, offered examples of P-BF<sub>2</sub> dyes with electron withdrawing substituents at the 8-position. The dye **7aa**,  $\lambda_{\text{las}}$  617 nm, showed nearly twice the power efficiency that was obtained from rhodamine B,  $\lambda_{\text{las}}$  611 nm.

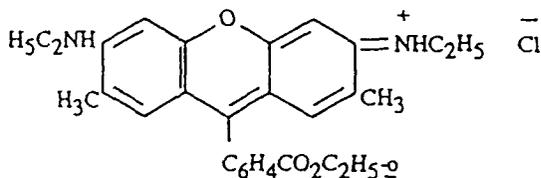
## INTRODUCTION

Along with identification of over 500 laser dyes for the spectral region, 300 to 1300 nm Maeda noted

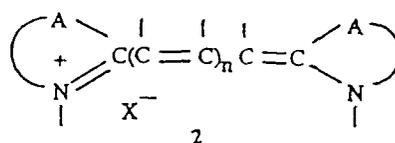
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special features in two groups of dye molecules. The group of fused linear 6,6,6-tricyclic ring systems contained the most important dyes and included rhodamine 6G (R - 6G) 1, the laser dye with the highest power efficiency from flash lamp pumping known at the time. In another group, the cyanine dyes 2 were recognized for the agility of their luminophors in providing laser activity in the longer wavelengths, particularly  $>800$  nm. A bath-

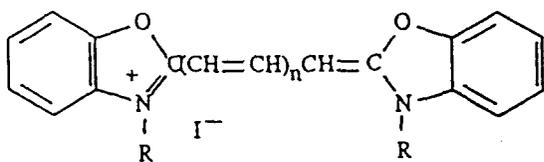
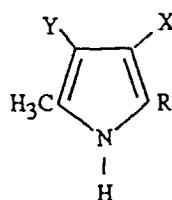
ochromic shift of about 100 nm with each unit increase in  $n$ , the number of conjugated ethylenic units in the odd numbered carbon chain connecting two heterocyclic nuclei in the monobasic salt, brought about a distribution of absorption, fluorescence, and laser activity over a wide spectral region. Structures 3a,  $\lambda_{\text{las}}$  541 nm, and 3b,  $\lambda_{\text{las}}$  800 nm, were seen as typical cyanine dyes [1].



1

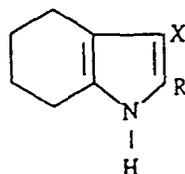
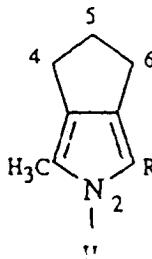


A = completion of heterocyclic ring

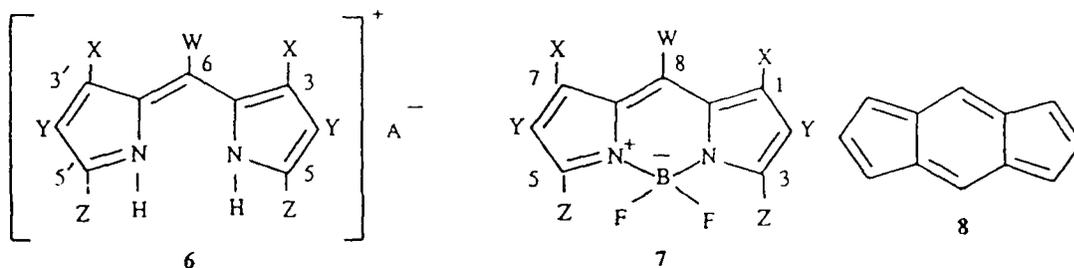
3a  $n=1$ ,  $R=C_2H_5$ 3b  $n=3$ ,  $R=CH_3$ 4  $R=CO_2CH_2CH_3$ 5  $R=H$ 

4, 5	X	Y
a	CH <sub>3</sub>	H
b	CH <sub>3</sub>	CH <sub>3</sub>
c	CH <sub>3</sub>	CH <sub>2</sub> CH <sub>3</sub>
d	CH <sub>3</sub>	(CH <sub>2</sub> ) <sub>2</sub> CH <sub>3</sub>
e	CH <sub>3</sub>	(CH <sub>2</sub> ) <sub>3</sub> CH <sub>3</sub>
f	CH <sub>3</sub>	CH(CH <sub>3</sub> ) <sub>2</sub>
g	CH <sub>3</sub>	C(CH <sub>3</sub> ) <sub>3</sub>
k	CH <sub>2</sub> CH <sub>3</sub>	CH <sub>2</sub> CH <sub>3</sub>
o	C <sub>6</sub> H <sub>5</sub>	CH <sub>2</sub> CH <sub>3</sub>
p	C <sub>6</sub> H <sub>5</sub>	C <sub>6</sub> H <sub>5</sub>
q	C <sub>6</sub> H <sub>5</sub>	COCH <sub>3</sub>

5	X	Y
l	CH <sub>3</sub>	C <sub>6</sub> H <sub>5</sub>
m	CH <sub>3</sub>	NHCOCH <sub>3</sub>
n	OCH <sub>3</sub>	CH <sub>3</sub>

4i  $X=CH_3$ ,  $R=CO_2C_2H_5$ 5b  $X=R=H$ 5i  $X=CH_3$ ,  $R=H$ 4j  $R=CO_2C_2H_5$ 5j  $R=H$ 

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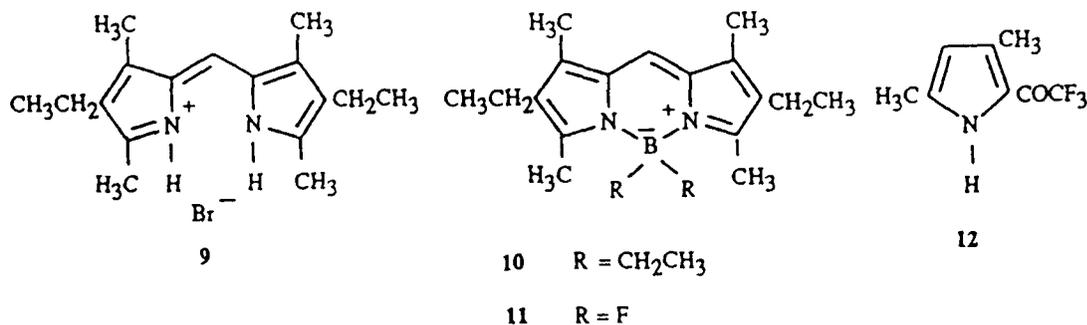


6,7	W	X	Y	Z	A
a	CH <sub>3</sub>	CH <sub>3</sub>	H	CH <sub>3</sub>	Cl
b	CH <sub>3</sub>	CH <sub>3</sub>	CH <sub>3</sub>	CH <sub>3</sub>	Cl
c	CH <sub>3</sub>	CH <sub>3</sub>	CH <sub>2</sub> CH <sub>3</sub>	CH <sub>3</sub>	Cl
d	CH <sub>3</sub>	CH <sub>3</sub>	(CH <sub>2</sub> ) <sub>2</sub> CH <sub>3</sub>	CH <sub>3</sub>	Cl
e	CH <sub>3</sub>	CH <sub>3</sub>	(CH <sub>2</sub> ) <sub>3</sub> CH <sub>3</sub>	CH <sub>3</sub>	Cl
f	CH <sub>3</sub>	CH <sub>3</sub>	CH(CH <sub>3</sub> ) <sub>2</sub>	CH <sub>3</sub>	Cl
g	CH <sub>3</sub>	CH <sub>3</sub>	C(CH <sub>3</sub> ) <sub>3</sub>	CH <sub>3</sub>	Cl
h	CH <sub>3</sub>	H	-(CH <sub>2</sub> ) <sub>4</sub> -		Cl
i	CH <sub>3</sub>	CH <sub>3</sub>	-(CH <sub>2</sub> ) <sub>4</sub> -		Cl
j	CH <sub>3</sub>		-(CH <sub>2</sub> ) <sub>3</sub> -	CH <sub>3</sub>	Cl
k	CH <sub>3</sub>	CH <sub>2</sub> CH <sub>3</sub>	CH <sub>2</sub> CH <sub>3</sub>	CH <sub>3</sub>	Cl
l	CH <sub>3</sub>	CH <sub>3</sub>	C <sub>6</sub> H <sub>5</sub>	CH <sub>3</sub>	Cl
m	CH <sub>3</sub>	CH <sub>3</sub>	NHCOCH <sub>3</sub>	CH <sub>3</sub>	Cl
n	CH <sub>3</sub>	OCH <sub>3</sub>	CH <sub>3</sub>	CH <sub>3</sub>	Cl
o	CH <sub>2</sub> CH <sub>3</sub>	CH <sub>3</sub>	CH <sub>2</sub> CH <sub>3</sub>	CH <sub>3</sub>	Cl
p	CH(CH <sub>3</sub> ) <sub>2</sub>	CH <sub>3</sub>	CH <sub>2</sub> CH <sub>3</sub>	CH <sub>3</sub>	Cl
q	<i>o</i> -C <sub>6</sub> H <sub>11</sub>	CH <sub>3</sub>	CH <sub>2</sub> CH <sub>3</sub>	CH <sub>3</sub>	Cl
r	CH <sub>2</sub> OCOCH <sub>3</sub>	CH <sub>3</sub>	CH <sub>2</sub> CH <sub>3</sub>	CH <sub>3</sub>	Cl
s	<i>p</i> -(CH <sub>3</sub> ) <sub>2</sub> NC <sub>6</sub> H <sub>5</sub>	CH <sub>3</sub>	CH <sub>2</sub> CH <sub>3</sub>	CH <sub>3</sub>	Cl
t	<i>p</i> -CH <sub>3</sub> OC <sub>6</sub> H <sub>5</sub>	CH <sub>3</sub>	H	CH <sub>3</sub>	Cl
u	H	C <sub>6</sub> H <sub>5</sub>	CH <sub>2</sub> CH <sub>3</sub>	CH <sub>3</sub>	Br
v	H	C <sub>6</sub> H <sub>5</sub>	C <sub>6</sub> H <sub>5</sub>	CH <sub>3</sub>	Br
w	H	C <sub>6</sub> H <sub>5</sub>	H	CH <sub>3</sub>	Br
x	H	CH <sub>3</sub>	C(CH <sub>3</sub> ) <sub>3</sub>	CH <sub>3</sub>	Br
y	H	CH <sub>2</sub> CH <sub>3</sub>	CH <sub>2</sub> CH <sub>3</sub>	CH <sub>3</sub>	Br
z	H	CH <sub>3</sub>	CH <sub>3</sub>	CH <sub>3</sub>	Br
aa	CN	CH <sub>3</sub>	CO <sub>2</sub> CH <sub>2</sub> CH <sub>3</sub>	CH <sub>3</sub>	Br
bb	CN	CH <sub>3</sub>	CH <sub>2</sub> CH <sub>3</sub>	CH <sub>3</sub>	Br

Recently, derivatives 7 of pyrromethene-BF<sub>2</sub> complex (P - BF<sub>2</sub>) were found to have laser activ-

ity. In a typical procedure, 2,3,4-trimethylpyrrole 5b, obtained from the corresponding  $\alpha$ -pyrrolecarboxylate ester 4b, was treated with acetyl chloride to bring about the formation of an unstable pyrromethene hydrochloride intermediate 6b, the product of a condensation between the pyrrole 5b and its  $\alpha$ -acyl derivative prepared *in situ*. The crude intermediate was treated with boron trifluoride etherate in the presence of a tertiary amine for conversion to the 1,2,3,5,6,7,8-heptamethyl derivative 7b [2]. In relative efficiency (RE) for laser activity 1,3,5,7,8-pentamethyl-2,6-diethylpyrromethene-BF<sub>2</sub> complex (PMDEP-BF<sub>2</sub>), 7c was outstandingly successful with RE 110 in comparison with RE 100 assigned to R-6G [2,3,4].

The P-BF<sub>2</sub> molecules 7 uniquely blended the structural features of a cyanine dye 2,  $n = 3$ , and a planar fused tricyclic ring system and introduced laser dyes with a linear 5,6,5-tricyclic ring system. The parent linear 5,6,5-tricyclic antiaromatic (4me) hydrocarbon, *s*-indacene C<sub>12</sub>H<sub>8</sub> 8, [5] was a red solid but was not described as fluorescent. In contrast, the parent 6,6,6-tricyclic aromatic (4m + 2e) hydrocarbon, anthracene C<sub>14</sub>H<sub>10</sub>, showed  $\lambda_f$  400 nm [6]. Laser activity in fluorescent dyes showed a dependence on  $\pi$  electron distribution as described by a simple rule found by Drexhage [7]. The rule states that "in a dye where the  $\pi$ -electrons of the chromophore can make a loop when oscillating between the end groups, the trip



10 R = CH<sub>2</sub>CH<sub>3</sub>

11 R = F

12

let yield will be higher than in a related compound [e.g., R-6G and P-BF<sub>2</sub>] where this loop is blocked. It may be said that the circulating electrons create an orbital magnetic moment which couples with the spin of the electron. This increased spin-orbit coupling then enhances the rate of intersystem crossing, thus giving rise to a higher triplet yield." According to Sorokin [8], an accumulation of molecules in the triplet state was partially attributed to a slow rise-time of the flash lamp and brought about significant reduction in laser activity as triplet-triplet (T-T) absorption overlapped with the fluorescence spectral region.

Although pyromethene salts also met the structural requirement of a cyanine dye with  $n = 3$ , they were weakly fluorescent, e.g., 3,3',5,5'-tetramethyl-4,4'-diethylpyromethene hydrobromide **9** showed  $\Phi_f 4.3 \times 10^{-4}$  [9]. Conversion to boron complexes, such as 1,3,5,7-tetramethyl-2,6-diethylpyromethene-B(C<sub>2</sub>H<sub>5</sub>)<sub>2</sub> complex **10** ( $\Phi_f$  0.31) and the corresponding BF<sub>2</sub> complex **11** ( $\Phi_f$  0.81), raised the fluorescence quantum yield by a thousandfold [9]. In addition, laser activity 550 to 570 nm became a characteristic property of P-BF<sub>2</sub> **7** [2,3]. This property qualified P-BF<sub>2</sub> compounds as bridged cyanine dyes,  $n = 3$ , with the particular feature of a hypsochromic shift of over 200 nm from  $\lambda_{\text{las}}$  800 nm observed for a linear cyanine dye **3b**,  $n = 3$ .

In this report, we wish to offer further characterization of P-BF<sub>2</sub> laser dyes, including observations on substituent effects in the 1,2,6,7, and 8-positions.

## RESULTS AND DISCUSSION

### Synthesis

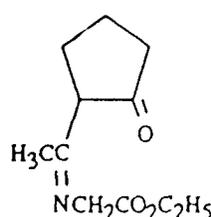
**Pyroles.** A Knorr cyclization between ethyl  $\alpha$ -aminoacetoacetate (prepared *in situ*) and a 3-alkyl-2,4-pentandione was selected for the preparation of ethyl alkylpyrrole-2-carboxylate derivatives **4b-f**, **i**. After attempts to obtain ethyl 3,5-dimethyl-4-*tert*-butylpyrrole-2-carboxylate **4g** by a Knorr cyclization were unsuccessful, it was prepared from ethyl 3,5-dimethylpyrrole-2-carboxylate **4a** in an alkylation with *tert*-butyl acetate. In a modifica-

tion of a Knoevenagel condensation of ethyl N-(3-oxo-1-alkenyl)aminoacetates to ethyl pyrrole-2-carboxylates [10] ethyl 3-methyl-2,4,5,6-tetrahydrocyclopenta[*c*]pyrrolecarboxylate, **4j** was obtained by a base catalyzed cyclization of an unsaturated enamine **13**, in turn obtained from a condensation between glycine ethyl ester and  $\alpha$ -acetylcyclopentanone.

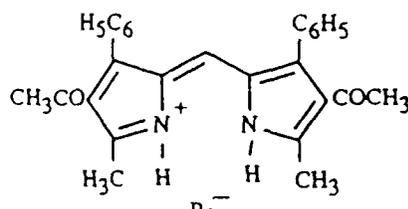
Conversion of  $\alpha$ -pyrrolecarboxylate esters to  $\alpha$ -unsubstituted pyrroles by treatment with phosphoric acid provided a convenient preparation of pyrrole **5b** [2] and was extended to 3-*n*-propyl, 3-*n*-butyl, and 3-isopropyl derivatives **5d-f** of 2,4-dimethylpyrrole **5a**. A similar conversion afforded 3-methyl-4,5,6,7-tetrahydroindole **5i** from its 2-carboxylate ester derivative **4i**. Unsuccessful attempts to extend the method to the preparation of 2,4-dimethyl-3-*tert*-butylpyrrole **5g** led instead to the replacement of both the carboethoxy and *tert*-butyl groups with hydrogen to give 2,4-dimethylpyrrole **5a**. The pyrroles **5g, j, k** were obtained from ethyl 3,5-dimethyl-4-*tert*-butylpyrrole-2-carboxylate **4g**, ethyl 3-methyl-2,4,5,6-tetrahydrocyclopenta[*c*]pyrrolecarboxylate **4j** [10], and ethyl 3,4-diethyl-5-methylpyrrole-2-carboxylate **4k** [11] by saponification with potassium hydroxide followed by decarboxylation of the free acids in ethanolamine at 180°C.

### Pyromethene-BF<sub>2</sub> Complexes (P-BF<sub>2</sub>)

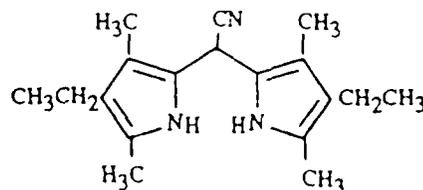
Treatment with an acyl chloride converted pyrroles **5** to P-BF<sub>2</sub>**7** via unstable and generally unisolated pyromethene hydrochlorides **6**. Kryptopyrrole **5c** and acetyl chloride gave the isolated but unstable 3,5,3',5',6-pentamethyl-4,4'-diethylpyromethene hydrochloride **6c** [2]. It was subsequently determined that conversion of the unstable intermediate **6c** without isolation to PMDEP-BF<sub>2</sub> **7c** by treatment with boron trifluoride etherate was recommended and became the basis for a general procedure for conversions of other pyrroles to P-BF<sub>2</sub>. Derivatives of 2,4-dimethylpyrrole with 3-substituents (*n*-propyl **5d**, *n*-butyl **5e**, isopropyl **5f**, *tert*-butyl **5g**, phenyl **5l**, and acetamido **5m**) gave the corresponding 2,6-disubstituted derivatives **7d-g, l, m** of 1,3,5,7,8-pentamethylpyromethene-BF<sub>2</sub> complex (PMP-BF<sub>2</sub>) **7a**. Similar treatment with



13



14



15

acetyl chloride converted tetrahydroindole **5h**, 3-methyltetrahydroindole **5i**, 3-methyl-2,4,5,6-tetrahydrocyclopenta[*c*]pyrrole **5j**, and 3,4-diethyl-5-methylpyrrole **5k** [11] to 2,3,6,7-bistetramethylene-8-methylpyrromethene-BF<sub>2</sub> complex **7h**, its 1,7-dimethyl derivative **7i**, 1,2,6,7-bistrimethylene-3,5,8-trimethylpyrromethene-BF<sub>2</sub> complex **7j**, and 1,2,6,7-tetraethyl-3,5,8-trimethylpyrromethene-BF<sub>2</sub> complex **7k** and converted 2,3-dimethyl-4-methoxypyrrole **5n** to 1,7-dimethoxy-2,3,5,6,8-pentamethylpyrromethene-BF<sub>2</sub> complex **7n**.

Kryptopyrrole **5c** condensed with propionyl chloride, isobutyryl chloride, cyclohexanecarbonyl chloride, acetoxyacetyl chloride, and *p*-dimethylaminobenzoyl chloride to produce the 8-ethyl, 8-isopropyl, 8-cyclohexyl, 8-acetoxymethyl, and 8-dimethylaminophenyl derivatives **7o-s** of 1,3,5,7-tetramethyl-2,6-diethylpyrromethene-BF<sub>2</sub> complex. A straightforward extension of the procedure was found in the reaction between 2,4-dimethylpyrrole **5a** and *p*-anisoyl chloride to give 1,3,5,7-tetramethyl-8-*p*-methoxyphenylpyrromethene-BF<sub>2</sub> complex **7t** via the intermediacy of the otherwise uncharacterized pyrromethene hydrochloride **6t**. Attempts to convert 2-trifluoroacetyl-3,5-dimethylpyrrole **12** to a derivative of 8-trifluoromethylpyrromethene-BF<sub>2</sub> complex were unsuccessful.

Treatment with hydrobromic acid in formic acid brought about the conversion of  $\alpha$ -pyrrole-carboxylate esters **4** to pyrromethene hydrobromides **6** via the presumed intermediacy of  $\alpha$ -unsubstituted pyrroles **5** followed by condensations with  $\alpha$ -formyl derivatives formed *in situ*. Thus, the esters **4k**, **o**, and **p** afforded the pyrromethene salts **6y**, **6u**, and **6v**, respectively. Straightforward treatment with boron trifluoride etherate converted these crude pyrromethene hydrobromides to 1,2,6,7-tetraethyl-3,5-dimethylpyrromethene-BF<sub>2</sub> complex **7y** and the 1,7-diphenyl-2,6-diethyl-3,5-dimethyl and 1,2,6,7-tetraphenyl-3,5-dimethylpyrromethene-BF<sub>2</sub> derivatives **7u**, **v**.

Similar treatment converted 3,3'-diphenyl-4,4'-diacetyl-5,5'-dimethylpyrromethene hydrobromide **14** (from ethyl 3-phenyl-4-acetyl-5-methylpyrrole-2-carboxylate **4q**) after an initial deacetylation to 1,7-diphenyl-3,5-dimethylpyrromethene-BF<sub>2</sub> complex **7w**. An assumed unisolated pyrromethene hydrobromide intermediate **6x** from the pyrrole-carboxylate ester **4g** was converted to 1,3,5,7-tetramethyl-2,6-di-*tert*-butylpyrromethene-BF<sub>2</sub> complex **7x**.

Addition of hydrogen cyanide to the pyrromethene hydrobromide **9** [12] presumably brought about the formation of 3,5,3',5'-tetramethyl-4,4'-diethyl-6-cyanopyrromethane **15**. Dehydrogenation by bromine followed by treatment with boron trifluoride etherate converted the pyrromethane **15** to 1,3,5,7-tetramethyl-2,6-diethyl-8-cyanopyrromethene-BF<sub>2</sub> complex **7bb** via the corresponding pyrromethene hydrobromide **6bb**.

TABLE 1 Pyrromethene-BF<sub>2</sub> Laser Dyes 7

7	$\lambda_{\max}^a$ (nm)	log $\epsilon$	$\lambda_l^b$ (nm)	$\Phi_l$	$\lambda_{\text{las}}^b$ (nm)	RE <sup>c</sup>
a <sup>d</sup>	493	4.90	519	0.99	542	100
b <sup>d</sup>	518	4.67	546	0.70	573	65
c <sup>d</sup>	517	4.81	546	0.83	570	110
d	517	4.89	549	0.99	578	85
e	518	4.92	550	0.90	580	100
f	516	4.85	548	0.67	577	45
g	525	4.83	567	0.77	597	50
h	535	4.93	560	0.84	589	75
i	522	4.91	552	0.80	582	90
j	512	4.82	535	0.81	560	20
k	521	4.89	554	0.75	582	75
l	519	4.90	559	0.43	582	20
m	498 <sup>e</sup>	4.63	542 <sup>f</sup>	0.17	566 <sup>f</sup>	5
n	485	4.85	522	0.84	540	30
o	520	4.92	546	0.84	571	75
p	527	4.84	562	0.07 <sup>g</sup>	<sup>h</sup>	—
q	516	4.81	526	0.23	<sup>h</sup>	—
r	543	4.89	575	0.74	605	30
s	519	4.95	575	0.04	<sup>h</sup>	—
t	497	4.86	521	0.63	547	50
u	540	5.00	564	0.60	582	10
v	552	4.91	590	0.69	<sup>h</sup>	—
w	521	4.92	551	0.61	580	5
x	527	4.93	554	0.84	580	30
y	529	4.89	554	0.70	580	40
z	528	4.84	552	0.56	570	30
aa	556 <sup>i</sup>	4.98	589 <sup>j</sup>	0.82	617 <sup>i</sup>	55
bb	580 <sup>i</sup>	4.72	620 <sup>i</sup>	0.55	670 <sup>ij</sup>	<sup>k</sup>

<sup>a</sup>  $5 \times 10^{-6}$  M in ethanol except where noted otherwise. <sup>b</sup>  $2 \times 10^{-4}$  M in ethanol, except where noted otherwise. <sup>c</sup> Relative efficiency 100 assigned to R-6G. <sup>d</sup> Ref. [2]. <sup>e</sup>  $5 \times 10^{-6}$  M in trifluoroethanol. <sup>f</sup>  $2 \times 10^{-4}$  M in trifluoroethanol. <sup>g</sup> With reference to R-6G  $\Phi$  0.90 (K. H. Drexhage, *J. Res. Nat. Bur. Std.*, **80A**, 1976, 421). <sup>h</sup> No laser activity detected. <sup>i</sup>  $2 \times 10^{-4}$  M in *p*-dioxan. <sup>j</sup> Obtained from a Phase-R DL-1100 dye laser with DL-5Y coaxial flashlamp. <sup>k</sup> RE not determined.

### Laser Activity

Variation in similar pairs of 2,6-dialkyl substituents in derivatives **7b-g** of PMP-BF<sub>2</sub> **7a** was carried out in a search for dyes competitive with PMDEP-BF<sub>2</sub> **7c** in laser activity. As the pairs of similar 2,6-disubstituents changed from hydrogen to methyl, ethyl, *n*-propyl, *n*-butyl, and isopropyl in dyes **7a-f**, the electronic absorption shifted as expected from  $\lambda_{\max}$  493 nm to  $517 \pm 1$  nm with a nearly constant log  $\epsilon$   $4.8 \pm 0.1$ . A significantly larger bathochromic shift led to  $\lambda_{\max}$  525, log  $\epsilon$  4.83, for the 2,6-di-*tert*-butyl derivative **7g** (Table 1).

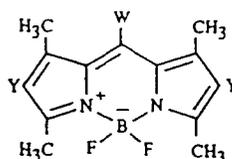
Laser activity  $\lambda_{\text{las}}$  was previously reported for PMP-BF<sub>2</sub> **7a** at 542 nm and for PMDEP-BF<sub>2</sub> **7c** at 570 nm [2]. Similar activity was found in the 2,6-dimethyl, 2,6-di-*n*-propyl, 2,6-di-*n*-butyl, and 2,6-diisopropyl derivatives **7b**, **d-f** at 573, 578, 580, and 577 nm and in the 2,6-di-*tert*-butyl derivative **7g** at 597 nm. In partial fulfillment of the factors contributing to laser activity, each of these seven dyes showed high extinction coefficients log  $\epsilon$  4.8 to 4.9

and high fluorescence quantum yields  $\Phi_f$  0.67 to 0.99. PMP-BF<sub>2</sub> 7a, PMDEP-BF<sub>2</sub> 7c, and the 2,6-di-*n*-butyl derivative 7e were superior to the other four 2,6-dialkyl derivatives in laser activity RE. The data revealed an alternation in RE as the 2,6-di-*n*-alkyl substituents contained an odd number of carbon atoms 7b, d (RE 65, 85) or zero and an even number of carbon atoms 7a, c, e, RE  $\geq$  100 (Table 1). Although the bistetramethylene dyes 7h, i and the bistrimethylene dye 7j gave nearly identical  $\lambda_{\max}$  with high extinction coefficients,  $\log \epsilon > 4.8$ , and shared strong fluorescence  $\Phi_f \geq 0.8$ , they differed significantly in laser activity with RE  $\geq 75$  for the bistetramethylene dyes and RE 20 for the bistrimethylene dye (Table 1). The structure for the dye 7j was confirmed by an X-ray crystallographic analysis to have chromophore planarity with negligible strain [13].

Alkyl and other group substituent effects at the 8-position in 1,3,5,7-tetramethyl-2,6-dialkylpyrromethene-BF<sub>2</sub> complex structures were examined. In comparison with peralkylated structures (7b, g, k), corresponding examples lacking a substituent at the 8-position (7z, x, y) showed a slight bathochromic shift in absorption, an erratic effect on fluorescence, and a marked decrease in laser activity RE (Table 1). Presumably, nonplanarity for 1,3,5,7-tetramethyl-2,6-diethyl-8-isopropylpyrromethene-BF<sub>2</sub> complex 7p was brought about by a steric interaction between the isopropyl group and the 1,7-dimethyl substituents and led to the large reduction in fluorescence and the loss of laser activity. A similar steric effect was introduced by the replacement of the 8-ethyl substituent in 1,3,5,7-tetramethyl-2,6,8-triethylpyrromethene-BF<sub>2</sub> complex 7o  $\Phi$  0.84 with 8-cyclohexyl to bring about reduction in the fluorescence quantum yield to  $\Phi$  0.23 and no laser activity for the dye 1,3,5,7-tetramethyl-2,6-diethyl-8-cyclohexylpyrromethene-BF<sub>2</sub> complex 7q. Insofar as laser dyes with cyano substituents were rarely encountered (Maeda listed four) [1], the laser activity in diethyl 1,3,5,7-tetramethyl-8-cyanopyrromethene-2,6-dicarboxylate-BF<sub>2</sub> complex 7aa and 1,3,5,7-tetramethyl-2,6-diethyl-8-cyanopyrromethene-BF<sub>2</sub> complex 7bb was of exceptional interest.

Pairs of similar functional group (polar) substituents in the 2,6-positions of P-BF<sub>2</sub> dyes brought about erratic results in RE. As expected, fluorescence and laser activity were drastically reduced in a P-BF<sub>2</sub> dye by a nitro substituent and quenched by a bromo substituent [2]. Metal and ammonium salts of 1,3,5,7,8-pentamethylpyrromethene-2,6-disulfonic acid-BF<sub>2</sub> complex 16 were exceptionally powerful dyes with RE 95, but the sodium salt of 1,3,5,7-tetramethyl-8-ethylpyrromethene-2,6-disulfonic acid-BF<sub>2</sub> complex 17 showed RE 50 [2]. Low values were also obtained for the disulfonate ester 18 RE 35 [2], the dicarboxylate ester 19 RE 50 [2], the 2,6-diacetamido derivative 7m RE 5, and

the 2,6-diphenyl derivative 7l RE 20. The singular example of 1,7-dimethoxy-2,3,5,6,8-pentamethylpyrromethene-BF<sub>2</sub> complex 7n RE 30 suggested that laser activity was diminished by electron donating substituents at the 1,7-positions. Poor lasing activity resulted from the introduction of phenyl substituents in the 1- and 2-positions in dyes 7l, 7u, and 7w, and the absence of lasing activity was noted for 1,2,6,7-tetraphenyl-3,5-dimethylpyrromethene-BF<sub>2</sub> complex 7v.



- 16 W = CH<sub>3</sub>, Y = SO<sub>3</sub><sup>-</sup> M<sup>+</sup>  
 M = Na, K, Rb, Cs, NH<sub>4</sub>, (CH<sub>3</sub>)<sub>4</sub>N<sup>+</sup>  
 17 W = CH<sub>2</sub>CH<sub>3</sub>, Y = SO<sub>3</sub><sup>-</sup> Na<sup>+</sup>  
 18 W = CH<sub>3</sub>, Y = SO<sub>3</sub>CH<sub>3</sub>  
 19 W = CH<sub>2</sub>CH<sub>3</sub>, Y = CO<sub>2</sub>CH<sub>2</sub>CH<sub>3</sub>

## EXPERIMENTAL

Instruments for spectroscopic measurements included the following: Perkin-Elmer 1600 FTIR, Varian Gemini 300 NMR, Hewlett-Packard 5985 (70 eV) GC-MS, Cary 17 (UV), and Perkin-Elmer LS-5B Luminescence spectrometer. A dye laser was constructed at the Naval Ocean Systems Center. It operated in the nonflowing (static) mode and had no tuning capability. The dye cell (2.5 mm diameter, 50 mm long) had an elliptical 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 [14,15]. Laser energy outputs were measured with an accuracy of  $\pm 5\%$  by a Scientech 365 power and energy meter [16].

Light absorption, luminescence, and laser activity properties for the dyes 7 are described in Table 1. Each recorded UV absorption was restricted to the highest wave length. Fluorescence quantum yields of the dyes were determined for ethanol solutions with excitation at 450 and 460 nm by reference to acridine orange,  $\Phi$  0.46 [17], in ethanol; for the dye 7p, the reference was R-6G,  $\Phi$  0.90. Table 2 lists yield, mp, <sup>1</sup>H NMR, and elemental analysis for the laser dyes 7. Melting points were obtained from a Mel-Temp II device and were uncorrected. The solvent for <sup>1</sup>H NMR spectra was chloroform *d* with tetramethylsilane as an internal standard. Elemental analyses were obtained from Midwest Micro Lab, Indianapolis, IN and Galbraith Laboratories, Inc., Knoxville, TN. Solvents were removed by rotary evaporation under reduced pressure unless indicated otherwise. Column chromatography was performed on silica gel. Molecular weights were confirmed by EI-MS for the pyrrole 4j 193 and for laser dyes 7d 346, 7e

TABLE 2 Pyrromethene-BF<sub>2</sub> Laser Dyes 7

No.	Yield, (%)	mp °C	<sup>1</sup> H NMR (CDCl <sub>3</sub> ) δ	Formula Calculated % Found %
7d	21	193-194	2.57 (s, 3H), 2.46 (s, 6H), 2.33 (t, 4H), 2.29 (s, 6H), 1.42 (m, 4H), 0.91 (t, 6H)	C <sub>20</sub> H <sub>29</sub> N <sub>2</sub> BF <sub>2</sub> C, 68.86; H, 8.32; N, 8.03 C, 69.46; H, 8.25; N, 8.04
7e	18	185-186	2.58 (s, 3H), 2.47 (s, 6H), 2.35 (t, 4H), 2.30 (s, 6H), 1.35 (m, 8H), 0.91 (t, 6H)	C <sub>22</sub> H <sub>33</sub> N <sub>2</sub> BF <sub>2</sub> C, 70.62; H, 8.83; N, 7.49 C, 69.91; H, 8.81; N, 7.39
7f	15	186 dec	2.5 (s, 3H), 2.3 (s, 6H), 2.1 (s, 6H), 1.9-2.0 (m, 2H), 0.9-1.0 (d, 12H)	C <sub>20</sub> H <sub>29</sub> N <sub>2</sub> BF <sub>2</sub> C, 69.36; H, 8.38; N, 8.09; F, 10.98 C, 69.40; H, 8.29; N, 8.13; F, 11.10
7g	15	246-247	2.67 (s, 6H), 2.59 (s, 3H), 2.46 (s, 6H), 1.39 (s, 18H)	C <sub>22</sub> H <sub>33</sub> N <sub>2</sub> BF <sub>2</sub> C, 70.62; H, 8.83; N, 7.49 C, 71.09; H, 9.01; N, 7.34
7h	19	191-192	6.8 (s, 2H), 3.03 (s, 3H), 2.5 (t, 8H), 1.77 (t, 8H)	C <sub>18</sub> H <sub>21</sub> N <sub>2</sub> BF <sub>2</sub> C, 68.78; H, 6.68; N, 8.91 C, 68.57; H, 6.72; N, 8.75
7i	32	265-267	2.96 (t, 4H), 2.56 (s, 3H), 2.40 (t, 4H), 2.26 (s, 6H), 1.76 (m, 8H)	C <sub>20</sub> H <sub>25</sub> N <sub>2</sub> BF <sub>2</sub> C, 70.21; H, 7.31; N, 8.19 C, 70.99; H, 7.49; N, 8.26
7j	14	268-269 dec	2.68 (t, 4H), 2.53 (t, 4H), 2.46 (s, 6H), 2.40 (m, 4H), 2.34 (s, 3H)	C <sub>18</sub> H <sub>21</sub> N <sub>2</sub> BF <sub>2</sub> C, 68.83; H, 6.69; N, 8.92; C, 68.99; H, 6.72; N, 8.76
7k	40	120	2.74-2.79 (q, 4H), 2.68 (s, 3H), 2.49 (s, 6H), 2.35-2.40, (q, 4H), 1.16-1.21 (t, 6H), 1.04-1.09 (t, 6H)	C <sub>20</sub> H <sub>29</sub> N <sub>2</sub> BF <sub>2</sub> C, 69.36; H, 8.38; N, 8.09; F, 10.98 C, 69.09; H, 8.43; N, 8.05; F, 10.74
7l	45	234-236 dec	7.2-7.4 (s, 10H), 2.6 (s, 3H), 2.45 (s, 6H), 2.3 (s, 6H)	C <sub>26</sub> H <sub>25</sub> N <sub>2</sub> BF <sub>2</sub> C, 75.54; H, 6.05; N, 6.77; F, 9.20 C, 75.78; H, 6.34; N, 6.64; F, 9.41
7m	19	340-343 dec	9.27 (s, NH), 2.66 (s, 3H), 2.29 (s, 6H), 2.25 (s, 6H), 2.06 (s, 6H)	C <sub>18</sub> H <sub>23</sub> N <sub>4</sub> O <sub>2</sub> BF <sub>2</sub> C, 57.29; H, 6.36; N, 14.85 C, 57.06; H, 6.18; N, 14.36
7n	31	210-211	3.9 (s, 6H), 2.65 (s, 3H), 2.47 (s, 6H), 2.0 (s, 6H)	C <sub>16</sub> H <sub>21</sub> N <sub>2</sub> O <sub>2</sub> BF <sub>2</sub> C, 59.62; H, 6.52; N, 8.69 C, 59.71; H, 6.68; N, 8.77
7o	60	150-152	3.07 (q, 2H), 2.52 (s, 6H), 2.42 (q, 4H), 2.38 (s, 6H), 1.34 (t, 3H), 1.07 (t, 6H)	C <sub>19</sub> H <sub>27</sub> N <sub>2</sub> BF <sub>2</sub> C, 68.69; H, 8.19; N, 8.43 C, 68.80; H, 8.14; N, 8.40
7p	29	127-128	2.5 (m, 17H), 1.5 (d, 6H), 1.07 (t, 6H)	C <sub>20</sub> H <sub>29</sub> N <sub>2</sub> BF <sub>2</sub> C, 69.36; H, 8.38; N, 8.09 C, 69.37; H, 8.44; N, 8.10
7q	45	185 dec	2.40-2.60 (m, 16H), 1.35-2.30 (m, 11H), 1.03-1.08 (t, 6H)	C <sub>23</sub> H <sub>33</sub> N <sub>2</sub> BF <sub>2</sub> C, 71.50; H, 8.54; N, 7.25 C, 71.86; H, 8.57; N, 7.42
7r	18	181-182	5.3 (s, 2H), 2.5 (m, 19H), 1.05 (t, 6H)	C <sub>20</sub> H <sub>27</sub> N <sub>2</sub> O <sub>2</sub> BF <sub>2</sub> C, 63.82; H, 7.18; N, 7.44; C, 63.69; H, 7.20; N, 7.41
7s	32	330-332 dec	6.7-7.1 (m, 4H), 3.1 (s, 6H), 2.5 (s, 6H), 2.2-2.3 (q, 4H), 1.3 (s, 6H), 1.1 (t, 6H)	C <sub>25</sub> H <sub>32</sub> N <sub>2</sub> BF <sub>2</sub> C, 70.92; H, 7.56; N, 9.92; F, 8.98 C, 71.09; H, 7.82; N, 9.55; F, 8.49
7t	42	212-214 dec	7.1-7.3 (m, 4H) 6.1 (s, 2H), 3.8 (s, 3H), 2.3 (s, 6H), 1.3 (s, 6H)	C <sub>20</sub> H <sub>21</sub> N <sub>2</sub> OBF <sub>2</sub> C, 67.80; H, 5.93; N, 7.91; F, 10.74 C, 67.75; H, 6.01; N, 7.88; F, 10.75
7u	52	230-232 dec	7.33 (s, 10H), 6.3 (s, 1H), 2.44-2.65 (m, 10H), 1.04 (t, 6H)	C <sub>27</sub> H <sub>27</sub> N <sub>2</sub> BF <sub>2</sub> C, 75.73; H, 6.31; N, 6.54; F, 8.88 C, 75.65; H, 6.37; N, 6.28; F, 8.76
7v	42	308-310 dec	7.1-7.4 (m, 21H), 2.6 (s, 6H)	C <sub>35</sub> H <sub>27</sub> N <sub>2</sub> BF <sub>2</sub> C, 80.18; H, 5.15; N, 5.34; F, 7.25 C, 79.85; H, 5.24; N, 5.26; F, 7.36
7w	40	225 dec	7.2-7.5 (m, 12H), 6.39 (s, 1H), 2.66 (s, 6H)	C <sub>23</sub> H <sub>19</sub> N <sub>2</sub> BF <sub>2</sub> C, 74.19; H, 5.10; N, 7.52; F, 10.21 C, 74.21; H, 5.10; N, 7.38; F, 9.93
7x	9	235-236	6.98 (s, 1H), 2.66 (s, 6H), 2.29 (s, 6H), 1.36 (s, 18H)	C <sub>21</sub> H <sub>31</sub> N <sub>2</sub> BF <sub>2</sub> C, 70.00; H, 8.61; N, 7.77 C, 69.51; H, 8.78; N, 7.45
7y	57	116-117	6.93 (s, 1H), 2.5 (m, 14H), 1.1 (m, 12H)	C <sub>19</sub> H <sub>27</sub> N <sub>2</sub> BF <sub>2</sub> C, 68.67; H, 8.13; N, 8.43 C, 68.70; H, 8.21; N, 8.34
7z	52	275 dec	6.94 (s, 1H), 2.47 (s, 6H), 2.14 (s, 6H), 1.97 (s, 6H)	C <sub>15</sub> H <sub>19</sub> N <sub>2</sub> BF <sub>2</sub> C, 65.45; H, 6.90; N, 10.18; F, 13.81 C, 65.26; H, 6.85; N, 10.16; F, 13.90
7bb	9	155-156	2.4 (m, 16H), 1.05 (t, 6H)	C <sub>18</sub> H <sub>22</sub> N <sub>3</sub> BF <sub>2</sub> C, 65.65; H, 6.68; N, 12.76 C, 65.46; H, 6.63; N, 12.63

374, 7g 374, 7i 342, 7j 314, and 7x 360. IR absorption data satisfactorily supported structure assignments for the laser dyes 7.

Commercially available pyrroles included ethyl 3,5-dimethylpyrrole-2-carboxylate 4a, ethyl 3,4-

diethyl-5-methylpyrrole-2-carboxylate 4k, 2,4-dimethyl-3-ethylpyrrole 5c (kryptopyrrole), and 4,5,6,7-tetrahydroindole 5h.

The following pyrroles and pyrromethene derivatives were prepared by the methods cited: ethyl

3,5-dimethyl-4-ethylpyrrole-2-carboxylate **4c** [18], ethyl 3,4-diethyl-5-methylpyrrole-2-carboxylate **4k** [11], ethyl 3-phenyl-4-ethyl-5-methylpyrrole-2-carboxylate **4o** [19,20], ethyl 3,4-diphenyl-5-methylpyrrole-2-carboxylate **4p** [20], ethyl 3-phenyl-4-acetyl-5-methylpyrrole-2-carboxylate **4q** [20], 2,4-dimethylpyrrole **5a** [21], 2,4-dimethyl-3-phenylpyrrole, **5l** [20], 3-acetamido-2,4-dimethylpyrrole **5m** [22], 3-methoxy-4,5-dimethylpyrrole **5n** [23], 1,2,3,5,6,7-hexamethylpyrromethene-BF<sub>2</sub> complex **7z** [17], diethyl 1,3,5,7-tetramethyl-8-cyanopyrromethene-2,6-dicarboxylate-BF<sub>2</sub> complex **7aa** [24], and 3,5,3',5'-tetramethyl-4,4'-diethylpyrromethene hydrobromide **9** [12].

**3-*n*-Propyl-2,4-pentanedione.** A procedure [25] for the methylation of acetylacetone was adapted. A mixture of iodopropane (317 g, 1.87 mol), 2,4-pentanedione (146 g, 1.51 mol), and anhydrous potassium carbonate (200 g) in dry acetone (300 ml) was heated at 60°C for 20 hours, cooled, combined with petroleum ether (300 ml), and filtered. The filtrate was washed with a mixture (1:1, 200 ml) of petroleum ether and acetone. Solvent removal left 3-*n*-propyl-2,4-pentanedione as a light yellow oil, 53 g (25%), bp 195°C (Ref. [26] bp 73°C/11 mm). In a similar procedure, (a) iodobutane and 2,4-pentanedione gave 3-*n*-butyl-2,4-pentanedione as a light yellow oil, 28%, bp 208°C (Ref. [27] bp 104–106°C/20 mm) and (b) isopropyl iodide and 2,4-pentanedione gave 3-isopropyl-2,4-pentanedione as a light yellow oil, 40%, bp 182°C (Ref. [28] bp 94°C/45 mm).

**Ethyl 3,5-dimethyl-4-*n*-propylpyrrole-2-carboxylate 4d.** A solution of sodium nitrite (28.2 g, 0.41 mol) in water (100 ml) was added to a stirred cold solution of ethyl acetoacetate (49.4 g, 0.38 mol) in acetic acid as the temperature was held below 15°C. After the solution was stirred and stored overnight at 25°C, 3-*n*-propyl-2,4-pentanedione (53.7 g, 0.38 mol) and zinc (53 g) were sequentially added and the mixture was stored at 60°C for 1 hour. Dilution with water brought about the precipitation of ethyl 3,5-dimethyl-4-*n*-propylpyrrole-2-carboxylate **4d** as a yellow solid, 22.4 g (29%), mp 98–99°C (Ref. [29] mp 99–99.5°C) after recrystallization from ethanol; <sup>1</sup>H NMR (CDCl<sub>3</sub>): δ 9.3 (s, 1H), 4.25 (q, 2H), 2.55 (t, 2H), 2.24 (s, 3H), 2.18 (s, 3H), 1.41 (m, 2H), 1.30 (t, 3H), 0.90 (t, 3H). The procedure was extended to the conversions of: (a) 3-*n*-butyl-2,4-pentanedione to ethyl 3,5-dimethyl-4-*n*-butylpyrrole-2-carboxylate **4e**, a yellow solid, 32%, mp 99–100°C (Ref. [30] mp 99°C); <sup>1</sup>H NMR (CDCl<sub>3</sub>): δ 9.35 (s, 1H), 4.27 (q, 2H), 2.50 (t, 2H), 2.25 (s, 3H), 2.15 (s, 3H), 1.40 (m, 4H), 1.31 (t, 3H), 0.91 (t, 3H); (b) 3-isopropyl-2,4-pentanedione to ethyl 3,5-dimethyl-4-isopropylpyrrole-2-carboxylate **4f**, 20%, mp 104–106°C (Ref. [29] mp 105–106.5°C); and (c) 2-acetylcyclohexanone to ethyl 3-methyl-4,5,6,7-tetrahydroindole-2-carboxylate **4i**, 50%, mp 111–113°C (Ref. [31] 110°C); <sup>1</sup>H NMR

(CDCl<sub>3</sub>): δ 9.03 (s, 1H), 4.25 (q, 2H), 2.41 (m, 4H), 2.21 (s, 3H), 1.65 (m, 4H), 1.30 (t, 3H)

**Ethyl 3,5-dimethyl-4-*tert*-butylpyrrole-2-carboxylate 4g.** A solution of acetic acid (5.0 ml), sulfuric acid (1.2 ml), ethyl 3,5-dimethylpyrrole-2-carboxylate **5a** (5.0 g, 0.03 mol), and *tert*-butyl acetate (3.5 g, 0.03 mol) was heated at 75°C for 2 hours and combined with sodium carbonate (8 g) in ice water (100 ml) to bring about the precipitation of ethyl 3,5-dimethyl-4-*tert*-butylpyrrole-2-carboxylate **4g** as a colorless solid, mp 108–110°C (Ref. [21] 107–109°C), 3.1 g (47%); <sup>1</sup>H NMR (CDCl<sub>3</sub>): δ 9.80 (s, 1H), 4.28 (q, 2H), 2.43 (s, 3H), 2.39 (s, 3H), 1.35 (s, 9H), 1.33 (t, 3H).

**Ethyl 3-methyl-2,4,5,6-tetrahydrocyclopenta[c]pyrrolecarboxylate 4j.** A procedure [10] for the synthesis of pyrroles via N-(3-oxo-1-alkenyl)glycine ester was adapted. Ethyl aminoacetate hydrochloride (28 g, 0.20 mol) and triethylamine (20.1 g, 0.20 mol) were added to a solution of 2-acetylcyclopentanone (25.0 g, 0.20 mol) in ethanol (400 ml). The solution was stirred at room temperature for 15 hours and concentrated. The residue was combined with water (250 ml) and extracted with methylene chloride (4 × 100 ml). The combined extract was washed with water (100 ml), dried (sodium sulfate), and concentrated to leave a light brown oil. The oil was added with stirring at 50°C to a solution of sodium ethoxide (14 g, 0.20 mol) in absolute ethanol (400 ml). The mixture was heated at 80°C for 3 hours and poured into water (500 ml) to precipitate a light yellow solid. Recrystallization from ethanol gave ethyl 3-methyl-2,4,5,6-tetrahydrocyclopenta[c]pyrrolecarboxylate **4j**, 9.1 g (24%) as a pale yellow solid, mp 166–167°C; <sup>1</sup>H NMR (CDCl<sub>3</sub>): δ 8.38 (s, 1H), 4.24 (q, 2H), 2.78 (t, 2H), 2.52 (t, 2H), 2.30 (m, 2H), 2.18 (s, 3H), 1.30 (t, 3H). Anal. calcd. for C<sub>11</sub>H<sub>15</sub>NO<sub>2</sub>: C, 68.39; H, 7.77; N, 7.25. Found: C, 68.40; H, 7.85; N, 7.15.

**2-Trifluoroacetyl-3,5-dimethylpyrrole 12.** Trifluoroacetic anhydride (15.8 g, 75 mmol) was added dropwise with stirring to a solution of 2,4-dimethylpyrrole **5a** (9.6 g, 50 mmol) in benzene (140 ml) at 0°C. The mixture was stored at 0°C for 3 hours and washed with water (25 ml). The separated organic layer was dried (magnesium sulfate), concentrated, and chromatographed (silica gel, hexane/ethyl acetate, 3/1) to give 2-trifluoroacetyl-3,5-dimethylpyrrole **12** as a colorless solid, mp 80°C, 10.6 g (55%); IR (KBr): ν 3309, 1630, 1563, 1500, 1443, 1227, 800; <sup>1</sup>H NMR (CDCl<sub>3</sub>): δ 5.9 (s, 1H), 2.35 (bs, 6H). Anal. calcd. for C<sub>8</sub>H<sub>8</sub>NOF<sub>3</sub>: C, 50.26; H, 4.18; N, 7.32; F, 29.84. Found: C, 50.27; H, 4.28; N, 7.16; F, 29.92.

**Phosphoric acid method for the conversion of ethyl pyrrole-2-carboxylates to α-unsubstituted pyrroles. 2,4**

**Dimethyl 3-isopropylpyrrole 5f.** A general procedure developed by Treibs [21] was followed. Ethyl 3,5-dimethyl-4-isopropylpyrrole-2-carboxylate 4f (8.4 g, 40 mmol) as a melt at 100°C was treated with phosphoric acid (85%, 20 ml). The mixture was heated at 160°C for 30 minutes and combined with aqueous sodium hydroxide (200 ml, 200 mmol). Distillation gave 175 ml that was extracted with diethyl ether (3 × 100 ml). The organic phase was dried (magnesium sulfate) and concentrated to give a dark brown oil. Distillation gave 2,4-dimethyl-3-isopropylpyrrole 5f as a colorless oil, 1.6 g (30%), bp 65–66°C (10 mm). IR (KBr):  $\nu$  2296, 1684, 1591, 1448, 1094; <sup>1</sup>H NMR (CDCl<sub>3</sub>):  $\delta$  6.4 (s, 1H), 2.3 (s, 3H), 2.2 (s, 3H), 1.9 (m, 1H), 1.0 (d, 6H). Anal. calcd. for C<sub>9</sub>H<sub>15</sub>N: C, 78.83; H, 10.94; N, 10.21. Found: C, 78.69; H, 10.87; N, 10.12.

Similar reactions with phosphoric acid: (a) ethyl 3,5-dimethyl-4-*n*-propylpyrrole-2-carboxylate 4d converted to 2,4-dimethyl-3-*n*-propylpyrrole 5d, 54%, as a semi-solid, (Ref. [32] mp 13.5°C); <sup>1</sup>H NMR (CDCl<sub>3</sub>):  $\delta$  7.30 (s, 1H), 6.25 (s, 1H), 2.40 (t, 2H), 2.15 (s, 3H), 2.00 (s, 3H), 1.30 (m, 2H), 0.90 (t, 3H); (b) ethyl 3,5-dimethyl-4-*n*-butylpyrrole-2-carboxylate 4e to 2,4-dimethyl-3-*n*-butylpyrrole 5e as an oil [30] 48%; <sup>1</sup>H NMR (CDCl<sub>3</sub>):  $\delta$  7.45 (s, 1H), 6.30 (s, 1H), 2.30 (t, 2H), 2.15 (s, 3H), 2.01 (s, 3H), 1.40 (m, 4H), 0.90 (t, 3H); and (c) ethyl 3-methyl-4,5,6,7-tetrahydroindole-2-carboxylate 4i to 3-methyl-4,5,6,7-tetrahydroindole 5i, 53%, mp 55–57°C (Ref. [33] 58°C); <sup>1</sup>H NMR (CDCl<sub>3</sub>):  $\delta$  7.30 (s, 1H), 6.31 (s, 1H), 2.47 (m, 4H), 2.05 (s, 3H), 1.82 (m, 4H).

**2,4-Dimethyl-3-*tert*-butylpyrrole 5g.** A procedure reported for the decarboxylation of derivatives of pyrrole-3-carboxylic acid [34] was adapted. A solution of ethyl 3,5-dimethyl-4-*tert*-butylpyrrole-2-carboxylate 4g (3.0 g, 0.01 mol) and potassium hydroxide (6.0 g, 0.11 mol) in ethanol (50 ml) was heated at 80°C for 4 hours, combined with ice water (200 ml), and made slightly acidic by the addition of acetic acid to bring about the precipitation of crude 3,5-dimethyl-4-*tert*-butylpyrrole-2-carboxylic acid 4 (W = CH<sub>3</sub>, X = C(CH<sub>3</sub>)<sub>3</sub>, R = CO<sub>2</sub>H). The crude acid was combined with ethanolamine (5 g), heated at 180°C for 1 hour, and diluted with ice water (100 ml) to bring about the precipitation of 2,4-dimethyl-3-*tert*-butylpyrrole 5g as a colorless solid, 1.6 g (79%), mp 70–71°C (Ref. [21] 69–71°C) after drying in a vacuum for 24 hours; <sup>1</sup>H NMR (CDCl<sub>3</sub>):  $\delta$  7.60 (br, 1H), 6.30 (s, 1H), 2.25 (s, 3H), 2.15 (s, 3H), 1.28 (s, 9H). By the phosphoric acid method, the pyrrole ester 4g was converted to 2,4-dimethylpyrrole 5a [21].

**3-Methyl-2,4,5,6-tetrahydrocyclopenta[c]pyrrole 5j.** A solution of ethyl 3-methyl-2,4,5,6-tetrahydrocyclopenta[c]pyrrolecarboxylate 4j (9.1 g, 0.04 mol) and potassium hydroxide (26 g, 0.47 mol) in ethanol (200 ml) was heated at 80°C for 4 hours

and concentrated. The residue was combined with ice water (400 ml) and made slightly acidic by the addition of acetic acid to bring about the precipitation of crude 3-methyl-2,4,5,6-tetrahydrocyclopenta[c]pyrrolecarboxylic acid. The crude acid was combined with ethanolamine (5 g), heated at 180°C for 1 hour, and diluted with ice water (100 ml). Extraction by methylene chloride (3 × 100 ml) followed by solvent removal and distillation of a residual oil, bp 110–111°C (20 mm) gave 3-methyl-2,4,5,6-tetrahydrocyclopenta[c]pyrrole 5j, 3.6 g (64%) as a colorless oil; <sup>1</sup>H NMR (CDCl<sub>3</sub>):  $\delta$  7.57 (s, 1H), 6.33 (s, 1H), 2.67 (t, 2H), 2.59 (t, 2H), 2.35 (m, 2H), 2.22 (s, 3H). Anal. calcd. for C<sub>8</sub>H<sub>11</sub>N: C, 79.34; H, 9.09; N, 11.59. Found: C, 79.12; H, 9.29; N, 11.60.

**2,6-Di-*n*-propyl-1,3,5,7,8-pentamethylpyromethene-BF<sub>2</sub> complex 7d.** According to a procedure previously described [2], acetyl chloride (8.0 ml, 0.11 mol) was added dropwise over a period of 5 minutes to a solution of 2,4-dimethyl-3-*n*-propylpyrrole 5d (7.0 g, 0.05 mol) in dichloromethane (5 ml). The reaction mixture was heated at 40°C for 1 hour, cooled to 25°C, diluted with hexane (250 ml), triturated, and decanted. The residue, presumed to be crude 3,5,3',5',6-pentamethyl-4,4'-di-*n*-propylpyromethene hydrochloride 6d, was treated without further purification with ethyldiisopropyl amine (45 g) (triethyl amine was also effective) in toluene (300 ml) and stirred 15 minutes. After boron trifluoride etherate (40.8 ml, 0.33 mol) was added dropwise with stirring, the solution was heated at 40°C for 1 hour, washed with water (200 ml), dried over magnesium sulfate, and concentrated to give a dark brown solid. Flash chromatographic purification (twice, silica gel, 300–400 mesh, 60 Å, toluene) followed by concentration of the green-yellow fluorescent fraction gave the P-BF<sub>2</sub> 7d as a solid, 1.8 g. Further characterization and examples of similar conversions of pyrroles 5e–5n to P-BF<sub>2</sub> derivatives 7e–7n are described in Tables 1 and 2.

When acetyl chloride was replaced with propionyl chloride, isobutyryl chloride, cyclohexanecarbonyl chloride, acetoxyacetyl chloride, and *p*-dimethylaminobenzoyl chloride, similar reaction sequences converted kryptopyrrole 5c to 8-ethyl, 8-isopropyl, 8-cyclohexyl, 8-acetoxymethyl, and 8-dimethylaminophenyl derivatives 7o–s of 1,3,5,7-tetramethyl-2,6-diethylpyromethene-BF<sub>2</sub> complex 7 (X = Z = CH<sub>3</sub>, Y = CH<sub>2</sub>CH<sub>3</sub>). Treatment with *p*-anisoyl chloride followed by boron trifluoride etherate converted 2,4-dimethylpyrrole 5a to 1,3,5,7-tetramethyl-8-*p*-methoxyphenyl-pyromethene-BF<sub>2</sub> complex 7t. The products 7o–t are described in Tables 1 and 2.

**Pyromethene Hydrobromides and BF<sub>2</sub> Complexes.** Crude pyromethene hydrobromides 6 were obtained from  $\alpha$ -pyrrole carboxylate esters 4 [18]

and converted without purification to P-BF<sub>2</sub> dyes 7. A mixture of ethyl 3-phenyl-4-ethyl-5-methylpyrrole-2-carboxylate **4o** (2.57 g, 10 mmol), hydrobromic acid (3 ml, 48%), and formic acid (3.5 g) was heated at 100°C for 4 hours. The reaction mixture was cooled to 0°C to bring about the separation of crude 3,3'-diphenyl-4,4'-diethyl-5,5'-dimethylpyrromethene hydrobromide **6u** 1.3 g (55%) mp 235°C (dec); ethyl 3,4-diphenyl-5-methylpyrrole-2-carboxylate **4p** gave crude 3,4,3',4'-tetraphenyl-5,5'-dimethylpyrromethene hydrobromide **6v** (75%) mp 280°C (dec) (Ref. [20] mp 280°C (dec)); and ethyl-3-phenyl-4-acetyl-5-methylpyrrole-2-carboxylate **4q** gave crude 3,3'-diphenyl-4,4'-diacetyl-5,5'-dimethylpyrromethene hydrobromide **14** (50%) mp 230°C (dec). In similar conversions, 3,5-dimethyl-4-tert-butylpyrrole-2-carboxylate **4g** gave crude 3,5,3',5'-tetramethyl-4,4'-di-tert-butylpyrromethene hydrobromide **6x** and ethyl 3,4-diethyl-5-methylpyrrole-2-carboxylate **4k** gave crude 3,4,3',4'-tetraethyl-5,5'-dimethylpyrromethene hydrobromide **6y**.

Each salt **6u**, **v**, **x**, **y** and **14** was converted by treatment with boron trifluoride etherate, as described above, to the corresponding P-BF<sub>2</sub> dye **7u**, **v**, **x**, **y**, and **7w** (see Tables 1 and 2). Treatment of the pyrromethene hydrobromide **14** by boron trifluoride etherate also brought about deacylation. This may have occurred initially to give 3,3'-diphenyl-5,5'-dimethylpyrromethene hydrobromide **6w** as the precursor to the P-BF<sub>2</sub> derivatives **7w** or after an initial formation of undetected 1,7-diphenyl-2,6-di-acetyl-3,5-dimethylpyrromethene-BF<sub>2</sub> complex **7** (X = C<sub>6</sub>H<sub>5</sub>, Y = COCH<sub>3</sub>, W = H, Z = CH<sub>3</sub>).

**1,3,5,7-Tetramethyl-2,6-diethyl-8-cyanopyrromethene-BF<sub>2</sub> complex 7bb.** A procedure for a similar conversion was followed [35]. Ethyl 3,5-dimethyl-4-ethyl-pyrrole-2-carboxylate **4c** was converted to 3,5,3',5'-tetramethyl-4,4'-diethylpyrromethene hydrobromide **9**, mp 230–246°C (dec) by the process described above [12,17]. A mixture of the pyrromethene hydrobromide **9** (7.75 g, 0.02 mol) and potassium cyanide (5.6 g, 0.084 mol) in ethanol (85%, 70 ml) was heated at 80°C with stirring for 45 minutes cooled to 40°C, and diluted with water (80 ml) to bring about the precipitation of a pale brown solid. Flash chromatography on silica gel (300 g, 230–400 mesh, 60 Å, dichloromethane) gave an impure sample of 3,5,3',5'-tetramethyl-4,4'-diethyl-6-cyanopyrromethane **15**, 2.5 g, 44%, mp 110–114°C; IR (KBr):  $\nu$  2238 (CN). The impure pyrromethane **15** in chloroform was treated dropwise with an equimolar amount of bromine in chloroform at 25°C over a period of 5 minutes. Removal of solvent left 3,5,3',5'-tetramethyl-4,4'-diethyl-6-cyanopyrromethene hydrobromide **6bb**. Without purification, it was treated with boron trifluoride etherate (general procedure above) for conversion

to 1,3,5,7-tetramethyl-2,6-diethyl-8-cyanopyrromethene-BF<sub>2</sub> complex **7bb** (Tables 1 and 2).

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