Pyrromethene-BF₂ Complexes as Laser Dyes: 2

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Pyrromethene–BF₂ Complexes as Laser Dyes: 2

Pyrromethene–BF₂ complexes (P–BF₂) 7 were obtained from α-unsubstituted pyrroles 5 by acylation and condensation to give intermediate pyrromethene hydrohalides 6 followed by treatment with boron trifluoride etherate. Conversion of ethyl α-pyrrolecarboxylates 4 to α-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–BF₂ 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–BF₂ dyes depended on the number of methylene units in the n-alkyl substituent, –(CH₂)ₙH, to give RE ≥ 100 when n = 0, 2, 4 and RE 65, 85 when n = 1, 3. (RE 100 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–BF₂ complex 7p and a markedly diminished fluorescence quantum yield (Φ 0.23) and lack of laser activity in 1,3,5,7-tetramethyl-2,6-diethyl-8-cyclohexylpyrromethene–BF₂ 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–BF₂ complex 7j. Comparisons with peralkylated dyes revealed a major reduction in RE 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–BF₂ complex (PMP–BF₂) 7a and in 1,7-dimethoxy-2,3,5,6,8-pentamethylpyrromethene–BF₂ complex 7n, RE 30. Diethyl 1,3,5,7-tetramethyl-8-cyanopyrromethene-2,6-dicarboxylate–BF₂ complex 7aa, and 1,3,5,7-tetramethyl-2,6-diethyl-8-cyanopyrromethene–BF₂ complex 7bb, offered examples of P–BF₂ dyes with electron withdrawing substituents at the 8-position. The dye 7aa, λₘₐₓ 617 nm, showed nearly twice the power efficiency that was obtained from rhodamine B, λₘₐₓ 611 nm.
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