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Biimidazol-2-yl–BF_2 Complexes

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ABSTRACT

*Nonfluorescent 4,4′,5,5′-tetramethyl- and 4,5,4′,5′-bistetramethylene biimidazol-2-yls **5** and **6** combined with boron trifluoride to give the tetramethyl and bistetramethylenebiimidazol-2-yl–BF_2 complexes **9** and **10** isolated as strongly fluorescent BF_3 salts, λ_f (dichloromethane): 377 nm Φ 0.93 and 386 nm Φ 0.90. Similarly, fluorescent bibenzimidazol-2-yl **7**, λ_f (ethanol), 370 nm Φ 0.14, gave a BF_2 complex **11** isolated as a BF_3 salt λ_f (ethanol), 417 nm Φ 0.68.*

INTRODUCTION

Weak to strong fluorescence was cited for boron chelates derived from a small variety of bidentate ligands with oxygen and nitrogen atom termini [1]. In keeping with the generalization that luminescence of a chelate derived from a closed shell diamagnetic metal ion tends to resemble the spectrum for the free ligand [2], similar fluorescence spectra were obtained for pyrromethenes and the corresponding pyrromethene–BF_2 complexes (P–BF_2) **1**. Alkyl derivatives of P–BF_2 were noted for a thousandfold enhancement in the fluorescence due to chelation of the ligand. Very strong fluorescence, Φ 0.9 to 0.99, was characteristic of peralkylated P–BF_2 derivatives [1,3].

The rapid success achieved by derivatives of P–BF_2 as superior laser dyes [4–6], fluorescent probes for medical and biological research [7], and photodynamic therapeutic agents for cancer [8,9] revealed the need to evaluate other chelated heterocyclic systems as sources of fluorescent dyes, $\Phi >$ 0.7. Analogs of P–BF_2 were considered; however, attempts to prepare unknown BF_2 complexes **2** and **3** of pyrazomethenes and imidazomethenes and mixed pyrro-pyrazo-imidazo-methenes were unsuccessful.

Encouraging reports [10–12] on the coordination capacity of biimidazol-2-yls led to the selection of their hitherto unknown BF_2 complexes (*e.g.*, **8–11**) for examination; however, an expectation of fluorescence in the complexes was uncertain since fluorescence was not reported for biimidazol-2-yl **4** [12], the 4,4′,5,5′-tetramethyl derivative **5** [13] and the 4,5,4′,5′-bistetramethylene derivative **6** [13], and bibenzimidazol-2-yl **7** [14].

The complexes **8–11** described a new ring system: 7,7-difluoro-7-bora-3,4,6a,7a-tetraaza-6a,7-dihydro-4*H*-cyclopenta[a] pentalene.

DISCUSSION AND RESULTS

Known procedures were followed to obtain biimidazol-2-yl **4** [12], its tetramethyl **5** [13], and bistetramethylene derivative **6** [13] from condensations between glyoxal, ammonia, and a diketone as required. Bibenzimidazol-2-yl **7** [14] was prepared by a condensation between 1,2-diaminobenzene and oxamide. Each heterocycle **4–7** readily condensed with boron trifluoride. An excess of the latter facilitated formation of each BF_2 complex **8–11** as its BF_3 salt, whereas equimolar amounts led to intractable product mixtures. The unsubstituted complex **8** or its salt **8** · BF_3 shared an instability with the unsubstituted P–BF_2 dyes [1], and although it was presumably detected by fluorescence, the liberation of biimidazol-2-yl **4** precluded its isolation. Stabilization by alkyl substitution was shared with P–BF_2 [1,3] and led to the isolation of the tetramethyl- and the bistetramethylenebiimidazol-2-yl–BF_2 complexes **9** and **10** and the bibenzimidazol-2-yl–BF_2 complex **11**, each as its BF_3 salt.

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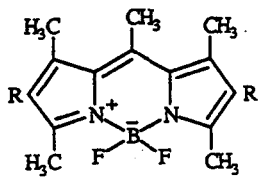

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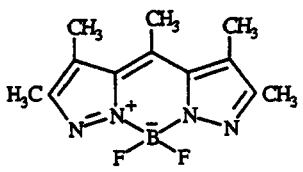

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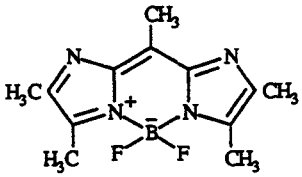

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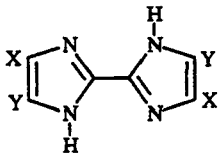

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5 X = Y = CH_3
6 XY = $(CH_2)_4$
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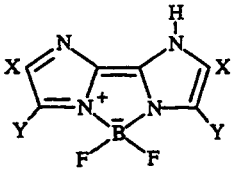

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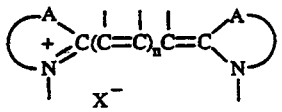

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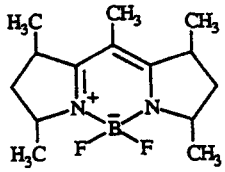
A = completion of heterocyclic ring



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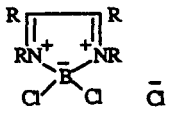

14

Attempts to liberate the BF_2 complexes from the salts **9** · BF_3, **10** · BF_3, and **11** · BF_3 were unsuccessful and led to intractable mixtures.

The tetraalkyl dyes **9** and **10** shared strong fluorescence with peralkylated P–BF_2 compounds **1**, R = alkyl [1,3]. In dichloromethane, the complex salt **9** · BF_3 gave λ_f 377 nm, Φ 0.93, and the complex salt **10** · BF_3 gave λ_f 386 nm, Φ 0.90. Both imidazol-2-yl–and pyrromethene–BF_2 complexes bear some structural similarity with cyanine dyes **12** [15]; however, laser activity found in P–BF_2 and cyanine dyes has not been observed for the biimidazol-2-yl–BF_2 dyes, **9** · BF_3, **10** · BF_3, and **11** · BF_3. In sharp contrast to the thousandfold increase in fluorescence intensity brought about by the conversion of a pyrromethene, $\Phi \sim 10^{-4}$, to a P–BF_2 dye, Φ 0.3–0.99 [1,3], the chelation effect on fluorescence is more pronounced in the conversion of a biimidazol-2-yl with no detectable fluorescence to the BF_2 complex salts **9** · BF_3 and **10** · BF_3. A fivefold enhancement of fluorescence was brought about by converting bibenzimidazol-2-yl **7**, Φ 0.14, to its BF_2–complex salt **11** · BF_3, Φ 0.68.

A loss of fluorescence brought about by diminished conjugation was shared by P–BF_2, cyanine, and imidazol-2-yl–BF_2 derivatives. Catalytic hydrogenation of 1,3,5,7,8-pentamethylpyrromethene–BF_2 complex **1**, R = H, gave the nonfluorescent hexahydro derivative **13**. Cyanine dyes **12** became nonfluorescent when n = 0 [15], and the less conjugated BCl_2 complexes **14** were related to tetrahydro derivatives of the imidazol-2-yl–BF_2 complexes **8–10** but were not fluorescent [16].

EXPERIMENTAL

Spectral data were obtained from the following instruments: Sargent-Welch 3-200 IR, Varian EM 360A and Varian Gemini-300 NMR, Hewlett-Packard 5985 (70 eV) GC-MS, Cary 17 UV, and Perkin-Elmer LS-5B Luminescence Spectrometer. Elemental analyses were obtained from Galbraith Laboratories, Inc., Knoxville, TN, and Midwest Micro Lab, Indianapolis, IN. Melting points were obtained from a Laboratory Devices Mel-Temp II and were uncorrected. ^{1}H NMR spectra were run in $CDCl_3$ with $(CH_3)_4Si$ as an internal standard. Fluorescence quantum yields were determined with excitation at 300 nm by reference to 2,5-diphenyloxazole, Φ 1.00, for dyes **9** · BF_3 and **10** · BF_3 and to Coumarin 440, Φ 0.72, for dye **11** · BF_3. Column chromatography was performed on silica gel. Aqueous glyoxal (40%), purified boron trifluoride etherate, triethylamine, and 1,2-dichloroethane

(99%) were obtained from the Aldrich Chemical Company (Milwaukee-WI). Triethylamine was distilled and stored over potassium hydroxide; 1,2-dichloroethane was washed with water, dried ($CaCl_2$), distilled, and stored over molecular sieves.

Biimidazol-2-yl **4** [12], the 4,4',5,5'-tetramethyl- and the 4,5,4',5'-bistetramethylene derivatives **5** [13] and **6** [13], bibenzimidazol-2-yl **7** [14], and 1,3,5,7,8-pentamethylpyrromethene–BF_2 complex **1** (R = H) [1] were prepared by the methods cited. Fluorescence was not detected in the ligand molecules **4**, **5**, and **6**; bibenzimidazol-2-yl **7** showed λ_f (ethanol) 370 nm, Φ 0.14, with Coumarin 440 as a standard.

Tetramethylbiimidazol-2-yl–BF_2 Complex, BF_3 Salt **9** · BF_3

Triethylamine (1.7 mL, 17.1 mmol) was added via a syringe to a stirred mixture of tetramethyl-biimidiazol-2-yl **5** (0.5 g, 2.5 mmol) in 1,2-dichloroethane (110 mL), at 25°C. After 10 minutes, boron trifluoride etherate (3.3 mL, 26.8 mmol) was added slowly. The solution was heated at 85°C for 1 hour, cooled to 30°C, washed with water (3 × 30 mL), and dried over potassium carbonate. The solution was concentrated, slurried with silica gel (30 g), and purified by column chromatography (petroleum ether followed by dichloromethane). Blue fluorescent fractions were combined to give the complex salt **9** · BF_3 as a colorless adduct, 0.25 g (30%), mp 226–228°C (dec). ^{1}H NMR ($CDCl_3$/TMS): δ 2.31 (s, 6H), 2.28 (s, 6H). EI-MS (*m/z*) (%): 287 (7), 286 (5), 285 (2), 238 (70), 237 (100), 236 (24). Anal. calcd for $C_{10}H_{13}N_4B_2F_5$: C, 39.26; H, 4.28; N, 18.32; F, 31.05. Found: C, 39.32; H, 4.37; N, 17.90; F, 30.60. UV absorption (dichloromethane): λ_{max} 334 nm, log ϵ 4.26. Fluorescence (dichloromethane): λ_{max} 377 nm, Φ 0.93.

By the same method, bistetramethylenebiimidazol-2-yl **6** was converted to the complex salt **10** · BF_3 as a colorless adduct, 42%, mp 355–360°C (dec). ^{1}H NMR ($CDCl_3$/TMS): δ 1.90 (t, 8H), 2.79 (m, 8H). EI-MS (*m/z*) (%): 339 (4), 290 (81), 289 (32), 262 (100), 261 (31). Anal. calcd for $C_{14}H_{17}N_4B_2F_5$: C, 46.98; H, 4.79; N, 15.65; F, 26.54. Found: C, 46.42; H, 4.92; N, 15.24; F, 25.96. UV absorption (dichloromethane): λ_{max} 339 nm, log ϵ 4.30. Fluorescence (dichloromethane): λ_{max} 386 nm, Φ 0.90.

Bibenzimidazol-2-yl–BF_2 Complex, BF_3 Salt **11** · BF_3

A solution of methyllithium (0.46 g, 21 mmol) in diethyl ether (15 mL) was added to a stirred solution of bibenzimidazol-2-yl [14] **7** (0.94 g, 4 mmol) in dry tetrahydrofuran. After 30 minutes, boron trifluoride etherate (3.5 g, 25 mmol) was added and the reaction mixture was heated at 65°C for 1 hour, cooled to room temperature, and concentrated at reduced pressure. The crude residue was dissolved in dichloromethane (100 mL), washed with water (3 × 15 mL), dried (potassium carbonate), and concentrated. Purification by column chromatography (dichloromethane) gave the complex salt **11** · BF_3 as a yellow amorphous solid adduct, 0.15 g (11%), mp 268–271°C (dec). ^{1}H NMR (DMSO-d_6): δ 7.25 (m, 4H), 7.65 (m, 4H). EI-MS (*m/z*) (%): 331 (5), 282 (70), 281 (100), 254 (25), 253 (12). Anal. calcd for $C_{14}H_9N_4B_2F_5$: C, 48.00; H, 2.57; N, 16.00; F, 27.14. Found: C, 48.12; H, 2.42; N, 16.15; F, 26.98. UV absorption (ethanol): λ_{max} 355 nm, log ϵ 4.41. Fluorescence (ethanol): λ_{max} 417 nm, Φ 0.68.

1,2,3,5,6,7-Hexahydro-1,3,5,7,8-pentamethylpyrromethene–BF_2 Complex **13**

Following a procedure of Treibs and Kreuzer [17], a 500 mL pressure bottle was charged with 1,3,5,7,8-pentamethylpyrromethene–BF_2 complex **1**, R = H (0.60 g, 2.3 mmol), ethanol (95%, 200 mL), and Pd/C (5%, 0.3 g). The bottle was attached to a Parr hydrogenation apparatus, evacuated, filled three times with hydrogen, and shaken under a pressure of about 50 psi for 12 hours as the solution lost fluorescence. The mixture was filtered to remove the catalyst, and the solution was concentrated by rotary evaporation (50°C). The suspension was filtered and the precipitate was dried overnight (ca. 65°C/<1 torr) to give the hexahydro compound **13**, 0.46 g, as light beige microcrystals. The crude product was recrystallized from pentane with decolorizing carbon and then recrystallized again from ethanol and water to give 0.36 g (58%) of colorless platelets, mp 129.5–130°C. UV absorption (95% ethanol): λ_{max} 334 nm (log ϵ 4.28). Anal. calcd for $C_{14}H_{23}N_2BF_2$: C, 62.70; H, 8.64; N, 10.45; B, 4.03; F, 14.17. Found: C, 62.81 ; H, 8.61; N, 10.41; B, 3.44; F, 14.02.

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