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BORON PHOTOCHEMISTRY

XVI *. BASE STABILIZATION OF DIMESITYLBORYL-CONTAINING DYES AND RELATED ^{11}B NMR STUDIES

M.E. GLOGOWSKI, N. ZUMBULYADIS, and J.L.R. WILLIAMS
Research Laboratories, Eastman Kodak Company, Rochester, New York 14650 (U.S.A.)

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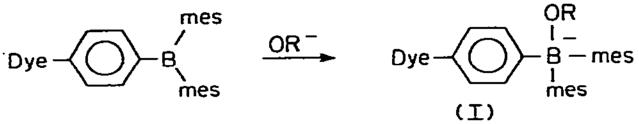
Summary

The UV-visible spectral shifts observed from *p*-dimesitylboryl-containing dyes in alcohol/sodium hydroxide solutions are caused by attack of the base on the boron atom. This attack produces the light-sensitive, tetravalent, "ate" structure. Dyes have been synthesized with 6 methyl groups *ortho* to the boron. These dyes are stable to base. The ^{11}B NMR spectra of a number of dyes and model compounds containing the dimesitylborylphenyl moiety reveal evidence of adduct formation in donor solvents. No adduct formation occurs when 5 or 6 methyl groups surround the boron atom.

Introduction

The inductive and mesomeric electronic effects of the dimesitylboryl group were previously described [1]. Both acidic and basic aprotic, nondonor solvent solutions of azonaphthol dyes containing this group gave UV-visible absorption spectra nearly identical with the spectra of solutions of the corresponding nitro dyes [2,3]. When the absorption spectra of *p*-dimesitylborylphenylazonaphthol dyes were measured in methanol or basic methanol, an anomalous 60 nm hypsochromic shift was observed. As a result of the ^{11}B NMR and light stability measurements reported here, we now attribute this hypsochromic shift to the formation of the "ate" structure (I) in base.



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[*] For part XV see ref. 1.

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Results and discussion

The photodecomposition rates of 4-(4-nitrophenylazo)-1-naphthol (II) in acidic and basic media, when exposed to a G.E. model 200 par 46/3 photoflood lamp, were nearly identical. When acetone solutions of II and 4-(4-dimesitylborylphenylazo)-1-naphthol (III) were prepared with an excess of sodium hydroxide, strong absorption peaks were observed at 648 nm, ϵ 38,000, and 585 nm, ϵ 32,000, respectively. Upon irradiation of solutions of equal optical density, the absorption at λ_{max} of III decreased at an initial rate 12 times greater than the λ_{max} absorption of II. However, under acidic conditions, i.e.,

TABLE 1

STRUCTURE OF BORYL-CONTAINING DYES

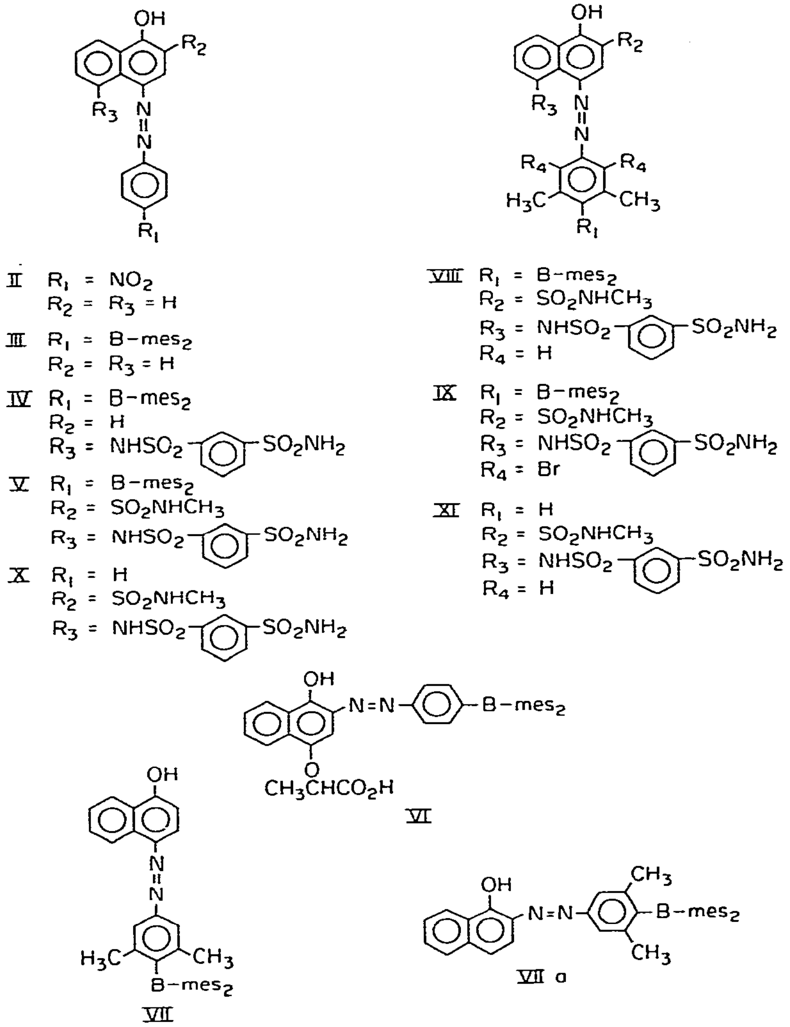


TABLE 2

ABSORPTION λ_{max} OF AZO DYES CONTAINING THE DIMESITYLBORYL GROUP

	λ_{max} (MeOH, NaOH) (nm)	λ_{max} (acetone, HCl) (nm)	λ_{max} (acetone, NaOH) (nm)
II	592	553 [a]	648
III	535	572 [a]	608
IV	—	595	595
V	—	575	~645 [b]
VI	540 [b]	—	635 [b]
VII	542 [c]	575	578
VIIa	532	585	553
VIII	530	500	555
IX	628	628 (580)	628
X	505	—	533
XI	505	475	523

[a] λ_{max} (MeOH/HCl). [b] Compound decomposed rapidly. [c] λ_{max} (MeOH).

acetone solution containing a drop of conc. HCl, the decomposition rate of III was less than one-third that of II. Rapid photodegradation was observed in methanolic and basic solutions of other *p*-dimesitylborylphenyl-containing azo dyes (IV—VI, Table 1).

Four highly hindered boryl-containing dyes were synthesized: 4-(4-dimesitylboryl-3,5-dimethylphenylazo)-1-naphthol (VII), 2-(4-dimesitylboryl-3,5-dimethylphenylazo)-1-naphthol (VIIa) isolated as a side product, *N*-[5-hydroxy-6-methylsulfamyl-8-(4-dimesitylboryl-3,5-dimethylphenylazo)naphthyl]-1,3-benzenedisulfonamide (VIII), and *N*-[5-hydroxy-6-methylsulfamyl-8-(4-dimesitylboryl-2,6-dibromo-3,5-dimethylphenylazo)naphthyl]-1,3-benzenedisulfonamide (IX). Two non-boron-containing dyes were synthesized for comparison: *N*-(5-hydroxy-6-methylsulfamyl-8-phenylazonaphthyl)-1,3-benzenedisulfonamide (X) and *N*-[5-hydroxy-6-methylsulfamyl-8-(3,5-dimethylphenylazo)naphthyl]-1,3-benzenedisulfonamide (XI).

Even in the acetone/NaOH solutions the expected bathochromic, pH-dependent spectral shift was not observed for the highly hindered boryl compound VII (Table 2). The isomer VIIa showed a hypsochromic spectral shift upon going from an acidic to a basic medium. When the spectra of these compounds, as well as those of VIII, are compared with spectra of the parent compound XI, the shifts agree with those predicted if the Hammett sigma value $\sigma_H = 0.42$ is used rather than $\sigma_{UV,H} = 0.67$ or $\sigma_{UV,K} = 0.58$ obtained earlier [1]. This observation can be accounted for if the steric requirements of the two additional methyl groups in VII, VIIa, and VIII caused the dimesitylboryl group to twist and thus prevent conjugation through the ring to boron. Despite the hypsochromic shift in base, compared to compounds II, III, IV, V, and IX, compounds VII, VIIa, and VIII did show increased photolytic stability over the 4-dimesitylborylphenyl azo dyes.

The photostabilities of III, VIII, IX, X and XI were compared under mildly basic conditions (0.02 *M* NaOH in MeOH). The UV-visible absorption at λ_{max} was measured before irradiation and after 5 and 56 min of irradiation

TABLE 3

PERCENT OF INITIAL ABSORPTION REMAINING AFTER 5 AND 56 min IRRADIATION OF NaOH (0.02 *M*)/MeOH SOLUTION OF AZO DYES OF EQUAL INITIAL OPTICAL DENSITIES (100% AT $t = 0$)

	λ_{max} (nm)	%, t = 5 min	%, t = 56 min
III	520	79	78
VIII	530	100	99
IX	630	99	91
X	505	100	100
XI	505	100	100

TABLE 4

PERCENT OF INITIAL ABSORPTION REMAINING AFTER IRRADIATION OF NaOH (0.2 *M*)/MeOH SOLUTIONS OF VIII AND XI OF EQUAL INITIAL OPTICAL DENSITIES (100% AT $t = 0$)

	λ_{max} (nm)	%, t = 4 min	%, t = 11 min	%, t = 22 min	%, t = 56 min
VIII	530	100	100	96	89
XI	505	100	99	97	89

(Table 3). The highly hindered dye VIII was more stable photolytically than the 4-dimesitylborylphenyl-substituted dye III. In addition, VIII is nearly as stable as the two parent compounds X and XI. Compound VIII, when compared with the parent compound XI under strongly basic conditions (0.2 *M* NaOH in MeOH), showed the same dark stability and had identical photodecomposition rates (Table 4).

In earlier work the tetrahedral "ate" type structure was shown to undergo

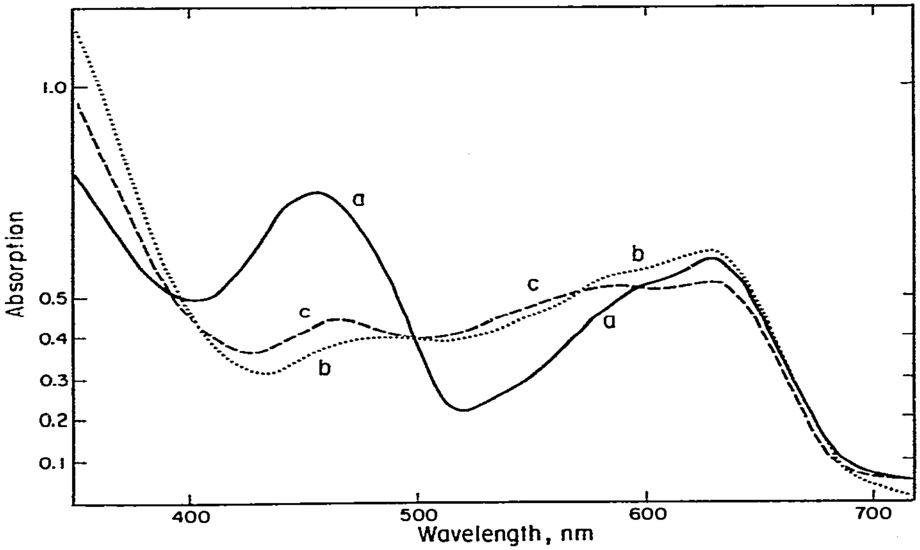
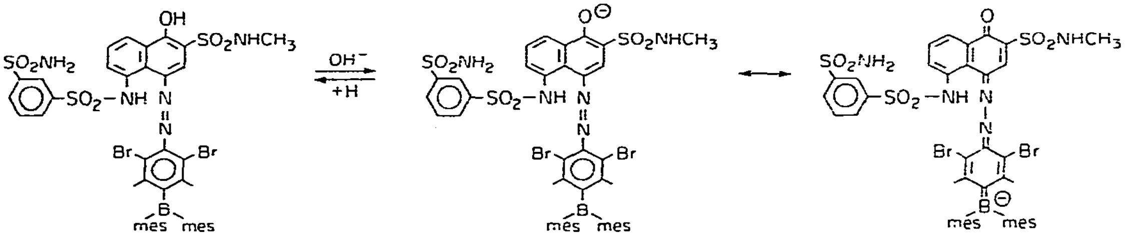


Fig. 1. Absorption spectra of IX at various pHs in 1/1 dioxane/H_2O. (a) pH 3.96, (b) pH 6.96; (c) pH 12.0.

facile photolytic rearrangement, whereas the trigonal boron structure was relatively inert to light [4,5]; thus the photolytic stability of compounds VII, VIIa, and VIII suggests that not only is the conjugation through the ring to boron inhibited by the steric crowding, but that these dyes remain trivalent even in basic, donor solvents.

The UV-visible spectra of IX measured in dioxane/water (1/1) at pH 3.96, 6.96, and 12.0 are shown in Fig. 1. The absorption at 460 nm, ϵ 9,800, in pH 3.96 solutions initially decreased in intensity as the pH was increased. This short-wavelength peak is attributed to the protonated hydroxy form of the dye IXa. A maximum wavelength of absorption was observed at 628 nm at all pHs with ϵ 8,830, 11,000, and 12,400, respectively. At low pH the intensity of the 628 nm peak decreased slowly with time as the peak at 460 nm increased, indicative of a slow acid-base equilibrium reaction. The similarity in the spectra of IX to the spectra of III, IV, and V in basic solution is attributed to the mesomeric character of the bromine groups. The spectra observed for basic solutions of VII, VIIa, and VIII indicate that the extended conjugated structure, analogous to IXb, is not obtainable in these dyes. For this reason IX was chosen for further stability studies.



IX a

IX b

A 10/1/0.1 acetone/water/sodium hydroxide solution of IX stored in the dark showed no change in the 628 nm absorption. In the same solvent III shows >50% loss at λ_{max} after 20 min. When acetone/sodium hydrixode solutions of IX were acidified, a maximum was observed at 530 nm. The 628 nm peak could be regenerated with excess sodium hydroxide with no loss in the extinction coefficient. When IX was irradiated in methanol containing 0.02 *M* NaOH, it also was more stable photolytically than III (Table 3). The slightly increased rate of photodecomposition of IX over VIII may be the result of any one of a number of decomposition mechanisms enhanced by the proximity of the bromine groups *ortho* to the azo group.

In 0.5 *M* methanolic sodium hydroxide, an absorption at λ_{max} 545 nm was measured for V versus 625 nm for IX. Exposure to visible light caused a decrease of 20% in the 545 nm peak of V within 6 min and a corresponding 3.2% decrease in the 625 nm peak of IX. These results show OR^- attack on V and reflect the base stability of IX.

Since the ^{11}B NMR spectra show solvent-dependent and hybridization-dependent linewidth behavior [6,7], we exploited the phenomenon to study the solution structure of these dyes. Relatively narrow linewidths are a strong indication of a ^{11}B nucleus in a tetrahedrally coordinated sp^3-hybridized boron complex, whereas wide linewidths show sp^2-hybridized boron. The interconversion of sp^2 and sp^3 hybridized boron is common during adduct formation. Simply requiring the boron nucleus to be sp^3 hybridized even though the ensuing molecule has C_{3v} symmetry relaxes the requirement for T_d symmetry necessary for obtaining sharp lines in the ^{11}B NMR spectra. A case in point would be boron trifluoride etherate $F_3B \cdot O(C_2H_5)_2$, which is commonly used as a reference in ^{11}B NMR spectroscopy.

A saturated solution of III in methanol-d_4 was first examined by ^{11}B NMR. A linewidth of ~25 Hz was observed. When the solution was made alkaline by the addition of NaOD, the signal collapsed to a sharp line ~4 Hz wide. The behavior of the more sterically hindered compound VII under analogous conditions was completely different; it gave a broad spectrum in MeOD with an estimated linewidth of 1,600 Hz. To elucidate the source of the lineshape differences between the two compounds, we recorded their spectra in a non-donor solvent, namely toluene-d_8. Both compounds displayed very broad lines (>1,600 Hz) in this solvent. The addition of increasing quantities of MeOD to a toluene solution of III gave rise to a sharp line superimposed on the broad background. The proportion of the sharp component increased roughly in proportion to the amount of MeOD added. Compound VII again differed in its properties in that no line sharpening was observed at any MeOD level.

The intensities of the broad and narrow components in the spectra are directly proportional to the concentration of the sp^2 and sp^3 hybridized boron species, respectively. The intensity ratio allows a qualitative estimate of the concentration of each species present. Thus, in donor solvents, compound III readily forms a donor-acceptor complex, producing an "ate" structure. The "ate" complex is dominant; however, it is not formed quantitatively. In the presence of hydroxide ion the production of the "ate" species is probably quantitative. The sterically hindered dye VII did not appear to form an "ate" structure either in methanol or with hydroxide ions.

When the ^{11}B NMR spectrum of the substituted derivative V was measured in MeOD, the signal was quite broad. The addition of NaOD produced a small sharp peak superimposed on a broad line. In contrast to the other compounds, however, over 48 h the sharp peak intensified. The fact that V does not exhibit "ate" character in methanol and only a small amount at high pH is quite surprising. It is possible that this compound either adopts a conformation that sterically hinders access of nucleophiles to boron or undergoes aggregation which prevents complexation with donor solvents. The latter was supported by UV-visible measurements which showed a λ_{max} 522 nm, ϵ 20,700, at 5×10^{-4} *M* with a 0.1 cm cell and λ 548, ϵ 30,600, at 5×10^{-6} *M* with a 10 cm cell, suggesting an "H type" aggregate.

Compound VIII, as expected, exhibited a single broad resonance which was insensitive to the addition of donor solvent and base.

To further confirm the effect of the *ortho* methyl groups on the solvent complex with boron, the parent compounds dimesitylphenylborane (XII) and trimesitylborane (XIII) were studied. These compounds have adequate solubility only in less polar solvents and were examined solely in toluene-d_8 solution. They gave spectra identical to those of the corresponding dyes III and VII. Upon addition of methanol, XII gave a two-component signal with sharp line superimposed on a very broad background. On the other hand, XIII showed a single broad resonance regardless of the amount of methanol added.

To determine if five *ortho* methyl groups about boron were enough to prevent donor attack on boron, we examined dimesityl-2-methylphenylborane (XIV) in toluene in the presence of various amounts of MeOD and NaOD. No evidence for complex formation was obtained.

Conclusions

We have shown that *p*-dimesitylborylphenyl-containing azo dyes, when placed in a basic medium, suffer base attack upon boron to produce the photosensitive "ate" structure. Dyes containing six methyl groups *ortho* to boron are insensitive to the presence of base. In these highly hindered dyes the boron remains trivalent. As a result they are photolytically more stable. The shorter than expected λ_{max} observed for compounds VII, VIIa, and VIII raises the question of whether the boron nucleus remains trivalent when these compounds are in a basic medium. Using ^{11}B NMR we have demonstrated that complexation to boron in these hindered compounds does not occur even though complexation of donor solvent and base does occur in the less sterically hindered dimesitylborylphenyl system of III, IV, and V. A plausible explanation of the hypsochromic shift in the UV-visible spectra of VII, VIIa, and VIII is that the steric requirements of the two *ortho* methyl groups cause the boron group to twist so that resonance through the phenyl ring to boron is prevented. By using ^{11}B NMR to study the coordination chemistry of boron dyes, we established correlations between the solution chemistry of boron dyes and their photochemical stability.

Experimental

The ^{11}B NMR spectra were obtained at 28.88 MHz on a Bruker HX-90 nuclear magnetic resonance spectrometer modified for multinuclear experimentation. Because of the fast spin-lattice relaxation time of the boron nucleus, no delay was used between acquisitions. Typically 10^3 free induction decays were coherently averaged to obtain spectra with adequate signal/noise. The samples were run in deuterated solvents in 10 mm NMR tubes and were kept in the dark when not in use.

UV-visible spectra were obtained on a Cary 15 spectrophotometer. Chromatographic separations were made with Quantum Industries silica gel, 75—250 μm, Cat. No. 4962-250. Solution light stabilities were obtained by measuring the decrease at λ_{max} upon exposure to a photoflood lamp at a distance of 8 in. No attempt was made to control temperature during the exposures.

Trimesitylborane (XIII) was synthesized by the procedure of Brown and Dodson [8]. Dimesitylphenylborane (XII) and dimesityl-2-methylphenylborane (XIV) were synthesized by the general procedure described by Babb and Grisdale [9].

The syntheses of 4-(4-dimesitylborylphenylazo)-1-naphthol (III), *N*-[5-hydroxy-8-(4-dimesitylborylphenylazo)naphthyl]-1,3-benzenedisulfonamide (IV), α-[3-(4-dimesitylborylphenylazo)-4-hydroxynaphthoxy]propionic acid (VI), and 4-(4-nitrophenylazo)-1-naphthol (II) were reported earlier [2,3].

4-Dimesitylborylbenzenediazonium chloride (XV)

The synthesis of XV was described earlier [3]. Because of the low yields of dye obtained, 50/50 water/methanol was used. A heterogeneous system resulted, with the white, solid 4-aminophenyldimesitylborane hydrochloride reacting with isopentyl nitrite at 0°C within 30 min to yield the yellow solid diazonium chloride. Better yields of dye were obtained by using XV prepared by this method. The diazonium salt was not isolated.

N-[5-Hydroxy-6-methylsulfamyl-8-(4-dimesitylborylphenylazo)naphthyl]-1,3-benzenedisulfonamide (V)

A solution containing 1 g of *p*-aminophenyldimesitylborane which had been diazotized as described above was added to a solution containing 1.04 g of *N*-(5-hydroxy-6-methylsulfamylnaphthyl)-1,3-benzenedisulfonamide (XVI) in 20 ml of THF/MeOH (1/1). A deep-red color formed immediately. After 16 h the solids were separated by filtration, and the filtrate was diluted with 6 parts of water. The precipitate which formed was separated and added to the first crop. The solids were then leached with toluene, leaving 1.2 g of solid; λ_{max} (acetone) 575 nm, ϵ 30,400. The sample decomposed rapidly in the presence of NaOH; m.p. 194°C with decomposition.

4-Bromo-3,5-dimethylaniline

A chloroform solution of 100 g of 3,5-dimethylaniline was treated with 200 g of solid pyridinium bromide perbromide. Reaction began instantly, and additional chloroform was required as solids formed. The solids were collected by filtration, placed in toluene, and extracted with 10% aqueous NaOH. The toluene was evaporated, and the solids were dissolved in chloroform; yield 56 g of desired compound; m.p. 75—76°C; *m/e* 199. NMR: 2.1 ppm (6H, singlet), 3.3 ppm (2H broad singlet), 6.2 ppm (2H, singlet). The chloroform filtrate was evaporated to dryness, and the solids were dissolved in toluene. Treatment with HCl gas produced a solid which proved to be the hydrochloride of the *ortho* bromo isomer; *m/e* 199. NMR 2.1 ppm (3H, singlet), 2.8 ppm (3H, singlet), 3.3 ppm (2H, broad singlet), 6.2 ppm (1H, singlet), 6.25 ppm (1H, singlet). The toluene-soluble material was mostly starting amine.

N,N-Dibenzyl-4-bromo-3,5-dimethylaniline

4-Bromo-3,5-dimethylaniline (18.6 g, 0.093 mol) was treated with 16 g of sodium bicarbonate and 25 g of α-chlorotoluene in 100 ml of toluene for 16 h on a steam bath. The mixture was extracted with water, and the toluene solution was dried with magnesium sulfate, concentrated, and passed through a large column of silica gel to remove unreacted starting materials. The solvent containing the desired compound was evaporated, and the solids were recrystallized in methanol/ethanol/toluene/acetone (300/35/25/25); yield 22 g; m.p. 123—123.5°C resolidified 145—150°C; *m/e* 304. NMR: 7.0 ppm (10H, singlet), 6.2 ppm (2H, singlet), 4.4 ppm (4H, singlet), 2.2 ppm (6H, singlet).

4-(4-Dimesitylboryl-3,5-dimethylphenylazo)-1-naphthol (VII)

A solution of 0.05 g of 4-amino-2,6-dimethylphenyldimesitylborane and 6 drops of concentrated hydrochloric acid in 20 ml of ethanol was treated with

0.4 g of isopentyl nitrite at 0°C. To this was added 0.05 g of 1-naphthol in ethanol. Upon addition of sodium acetate, a red color appeared. The mixture was extracted with toluene/water and chromatographed to yield two colored zones. The slower-moving zone (VII) was collected (~0.06 g), λ_{max} (acetone/NaOH) 578 nm. NMR: 6.8—8.6 ppm (12H, multiplet), 2.2 ppm (18H, singlet), 2.28 ppm (6H, singlet). The material from the faster-moving zone (VIIa, 0.02 g) gave λ_{max} (acetone/NaOH) 553 nm.

N-[5-Hydroxy-6-methylsulfamyl-8-(4-dimesitylboryl-3,5-dimethylphenylazo)-naphthyl]-1,3-benzenedisulfonamide (VIII)

4-Amino-2,6-dimethylphenyldimesitylborane (0.18 g) in 25 ml of ethanol was treated with 17 drops of concentrated hydrochloric acid, cooled to 0°C, and allowed to react for 30 min with 0.08 g of isopentyl nitrite. To this was added 0.23 g of *N*-(5-hydroxy-6-methylsulfamylnaphthyl)-1,3-benzenedisulfonamide (XVI) and excess sodium acetate. A red color formed immediately. The solution was extracted with toluene and water, and the toluene solution was dried with magnesium sulfate and evaporated. The solids were dissolved in acetone, placed on a silica gel column, and eluted first with toluene and then with 50/50 toluene/ethanol; yield 0.3 g; λ_{max} (acetone/NaOH) 555 nm; m.p. 200—201°C (softens), 225°C (decomposes). Analysis: Found: C, 60.9; H, 5.4; N, 8.0. Calcd. for $C_{43}H_{46}B_1H_5S_3O_7$: C, 60.6; H, 5.4; N, 8.2%. NMR: 6.7 ppm (4H, singlet), 6.9—8.2 ppm (10H, multiplets and broad absorption), 5.8 (1H, broad), 2.0—2.3 ppm (31H, several singlets).

4-(N,N-Dibenzylamino)-2,6-dimethylphenyldimesitylborane

4-Bromo-3,5-dimethyl-*N*,*N*-dibenzylaniline (7.6 g, 0.02 mol) in 100 ml of anhydrous ether was treated with 9 ml of 2.6 *M* n-butyllithium in hexane. The mixture was heated to reflux under N_2, and 100 ml of anhydrous tetrahydrofuran was added. After 15 min, the reaction mixture was cooled, and 5.36 g (0.02 mol) of dimesitylboron fluoride was added. The mixture was heated to just below reflux for 16 h. The mixture was extracted with toluene and water, and the toluene solution was dried with magnesium sulfate and evaporated. The residue was dissolved in hexane and eluted through a silica gel column. The large fluorescent zone was collected, and the solvent was evaporated to yield 4.2 g of desired compound: m.p. 176—176.5°C; *m/e* 549.

4-Amino-2,6-dimethylphenyldimesitylborane

4-(*N*,*N*-Dibenzylamino)-2,6-dimethylphenyldimesitylborane (3.5 g) was placed in 250 ml of ethanol. To this was added 0.5 g of palladium on carbon and 0.5 g of *p*-toluenesulfonic acid, and the mixture was hydrogenated at 40 lbs of hydrogen pressure for 16 h. The solution was filtered on Celite, and the solids were washed with toluene and then with acetone. The solutions were evaporated, and the residue was dissolved in a small amount of acetone and placed on a column and eluted. The center portion of the desired zone was collected and rechromatographed. The center portion was again collected, the solvents were evaporated, and the residue was recrystallized from 2-ethoxyethanol to yield 0.41 g; m.p. 225—226°C; *m/e* 369.

Tribromo-3,5-xylidene

A solution of 100 g of 3,5-xylidene in 150 ml of high-boiling ligroin was treated with 179 g of chlorotrimethylsilane and 174 g of sodium carbonate. A large amount of fluffy solids formed. After 16 h, 30 ml of bromine was added slowly, and more solid formed. The reaction mixture was treated with excess hydrochloric acid to decompose the remaining sodium carbonate and bicarbonate. The solution was neutralized with sodium hydroxide and extracted with toluene. Evaporation of the toluene and addition of HCl yielded a solid. The desired compound was isolated by filtration and a second treatment with base: m.p. 195—195.5°C; *m/e* 355.

4-Dimesitylboryl-2,6-dibromo-3,5-dimethylaniline

Tribromo-3,5-xylidene (17 g) in 100 ml of anhydrous ethyl ether was treated with 0.05 mol of chlorotrimethylsilane. The reaction mixture was then treated with 0.05 mol of n-butyllithium. The procedure was repeated to yield the xylyldi(trimethylsilyl)amine. A third portion of 0.05 mol of n-butyllithium was added. To this was added 100 ml of THF, and the mixture was refluxed for 16 h. The ether was slowly evaporated during this time. The mixture was then extracted with toluene and water. The toluene layer was evaporated, and the residue was placed on a column of silica gel and eluted with increasing amounts of acetone in high-boiling ligroin. After repeated chromatographs the compound was obtained pure. Mass spectral analysis gave a parent at 584 mass units. (Isomer peaks were observed at 586, 585, 583, 582, and 581 mass units.)

N-[5-Hydroxy-6-methylsulfamyl-8-(4-dimesitylboryl-2,6-dibromo-3,5-dimethylphenylazo)naphthyl]-1,3-benzenedisulfonamide (IX)

4-Dimesitylboryl-2,6-dibromo-3,5-dimethylaniline (0.3 g) was treated with 0.1 g of isopentyl nitrite at 0°C for 2 h in water/methanol. To this was added 18 drops of hydrochloric acid and 0.1 g more of isopentyl nitrite. This was allowed to react for 1 h at 0°C, and then 0.26 g of coupler XVI was added. The solution turned red, but clumps of white material remained unreacted and were filtered off. The methanol was removed under vacuum, and the solution was acidified with hydrochloric acid. The solids were filtered off, dissolved in methanol, and placed on a silica gel column. By use of increasing amounts of isopropyl alcohol in toluene, a blue and a yellow compound were obtained. The blue zone was rechromatographed until no contaminants could be seen; yield 0.075 g of solid; λ_{max} (acetone) 628 nm; m.p. >305°C. Mass spectral analysis was not possible.

N-(5-Hydroxy-6-methylsulfamyl-8-phenylazonaphthyl)-1,3-benzenedisulfonamide (X)

A THF/H_2O (1/1) solution of 1 g of aniline acidified with HCl was diazotized at 0°C with isopentyl nitrite. This was added to a THF solution of 0.3 g of XIV and excess sodium acetate. The resulting mixture was extracted with toluene and chromatographed on silica gel. The predominant colored zone was collected; λ_{max} (acetone/NaOH) 533 nm, λ_{max} (MeOH/NaOH) 505 nm; m.p. 206°C. Anal. Found: C, 47.9; H, 3.7; N, 11.8. Calcd. for $C_{23}H_{21}N_5S_3O_7$: C, 48.0; H, 3.66; N, 12.17%.

N-[5-Hydroxy-6-methylsulfamyl-8-(3,5-dimethylphenylazo)-naphthyl]-1,3-benzenedisulfonamide (XI)

A solution of 0.12 g of 3,5 dimethylaniline in ethanol, acidified with HCl and cooled to 0°C, was diazotized with isopentyl nitrite. After 15 min an alcohol solution of XIV was added, followed by excess sodium acetate. The resulting red mixture was extracted with toluene and water. The toluene solution was passed through a silica gel column eluted with 10/1 toluene/acetone. The major colored product gave: λ_{max} (acetone/NaOH) 523 nm, λ_{max} (MeOH/NaOH) 505 nm; m.p. 222—223°C. Anal. Found: C, 49.8; H, 4.2; N, 11.4. Calcd. for $C_{25}H_{25}N_5S_3O_7$: C, 49.8; H, 4.1; N, 11.6; S, 18.6%.

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