Journal of Organometallic Chemistry, 216 (1981) 1—8
Elsevier Sequoia S.A., Lausanne — Printed in The Netherlands

BORON PHOTOCHEMISTRY

XIV *. THE DIMESITYLBORYL GROUP AS AN AUXOCHROME IN DYES: THE SYNTHESIS OF *para*-SUBSTITUTED DIMESITYLBORYLPHENYLAZONAPHTHOL DYES

M.E. GLOGOWSKI and J.L.R. WILLIAMS

Research Laboratories, Eastman Kodak Company, Rochester, New York 14650 (U.S.A.)

(Received January 23rd, 1981)

Summary

The dimesitylboryl group is a new auxochrome. This group was evaluated by comparison of 4-[*p*-dimesitylborylphenylazo]-1-naphthol (III) with 4-[*p*-nitrophenylazo]-1-naphthol (IV) and of the substituted *N*-[5-hydroxy-8-(4-dimesitylborylphenylazo)naphthyl]-1,3-benzenedisulfonamide (VIIIa) with *N*-[5-hydroxy-8-(4-nitrophenylazo)naphthyl]-1,3-benzenedisulfonamide (VIIIb). The syntheses of 5-hydroxy-8-(4-dimesitylborylphenylazo)-1-naphthyl amine (IX) and α-[3-(4-dimesitylborylphenylazo)-4-hydroxynaphthoxy]propionic acid (X) are reported. The visible spectra of the dimesitylboryl-containing dyes and those of the nitro analogs were similar in shape. The spectral shifts of the dimesitylboryl compounds are as great as those of the corresponding nitro analogs. However, the boryl-substituted dyes required a nondonor medium for alkalinity-induced spectral shifts. As an auxochrome the dimesitylboryl group is roughly equivalent to a nitro group.

Introduction

In our work on photochemically stable, substituted dimesitylphenylboranes, we found that such highly hindered boranes are also stable to air oxidation [1] and that the dimesitylboryl group ($[Mes]_2B$-) is extremely electron withdrawing. Thus we reasoned that dimesitylboryl groups could be used as *meta*-directing or electron-withdrawing groups to replace nitro groups across the board in organic and organometallic chemistry. This concept is based on three factors:

---

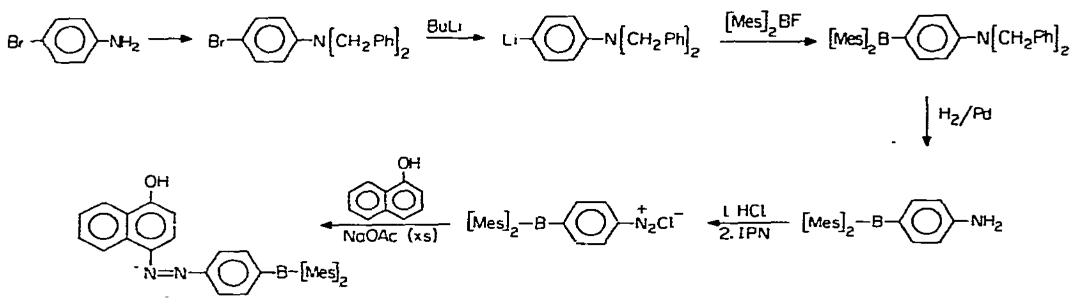
[*] For part XIII see ref. 3.

(1) the highly shielded boron atom cannot react with oxygen; (2) the boron atom is extremely high in electron-attracting power; (3) photoreduction, a problem with nitro groups, does not occur in the dimesitylboryl-substituted compounds.

Results and discussion

To show that the dimesitylboryl group would produce the same spectral shifts in dyes as those substituted with a single, similarly positioned nitro group, 4-[*p*-dimesitylborylphenylazo]-1-naphthol (III) was synthesized via Scheme 1. Each step of the Babb synthesis [2] of dimesityl-*p*-aminophenylborane (I) occurs in yields greater than 90%. Tetrahydrofuran (THF) was used as the solvent for the diazotization because of the insolubility of I in water. Isopentyl nitrite (IPN) was added after the THF solution of I had been saturated with gaseous HCl. The coupling step of II with 1-naphthol required the presence of aqueous sodium acetate (water was added to facilitate dissolution) and was relatively slow. The effects of acid and base on the visible absorption spectrum of III are shown in Fig. 1. The spectrum of III in neutral media has an

SCHEME 1



III II I

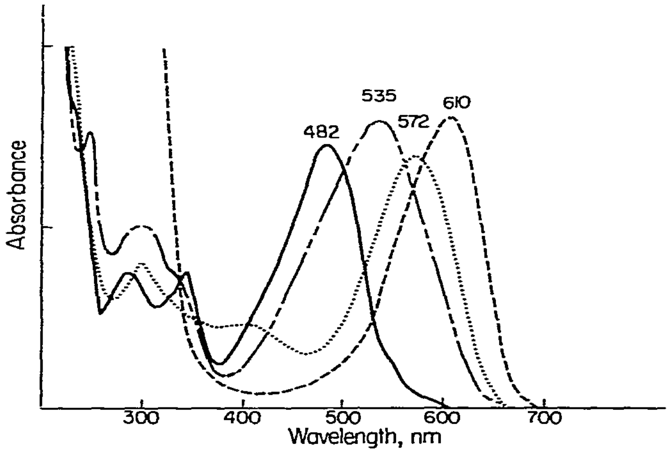


Fig. 1. Absorption spectra of 4-[*p*-dimesitylborylphenylazo]-1-naphthol; (———) methanol, ϵ 29 000; (— • • —) methanol/NaOH, ϵ 31 400; (· · · · · ·) methanol/HCl, ϵ 28 000; (- - - - - -) acetone/NaOH, ϵ 32 000.

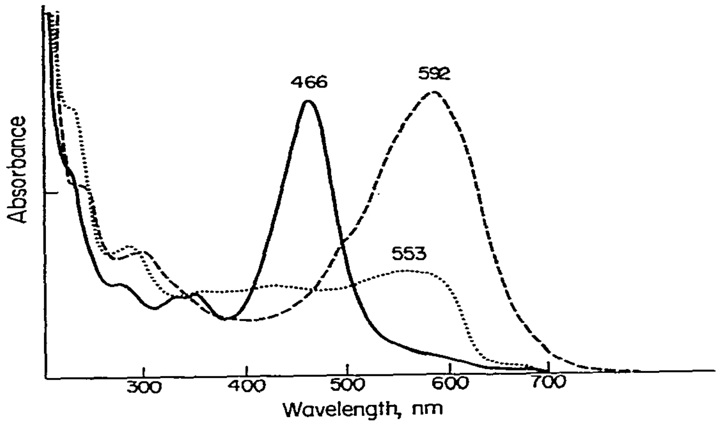
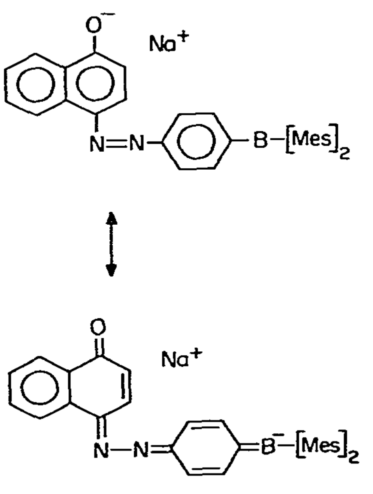


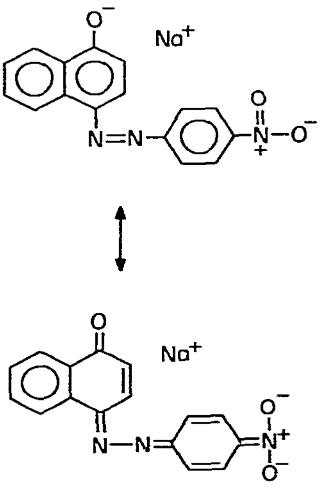
Fig. 2. Absorption spectra of 4-[*p*-nitrophenylazo]-1-naphthol; (———) methanol, ϵ 29 400; (- - - - -) methanol/NaOH, ϵ 30 600; (· · · · · ·) methanol/HCl, ϵ 11 200.

absorption band with λ_{max} 482 nm and, except for minor wavelength shifts, is nearly identical with that of the nitro-substituted analog 4-[*p*-nitrophenylazo]-1-naphthol (IV) (Fig. 2). When acid was added to solutions of the dye pair, the λ_{max} of III shifted to 572 nm and that of IV to 553 nm, a shift of about 90 nm in each case. The chemical difference between the nitro and the dimesitylboryl groups is shown in these spectra by the subdued absorption at λ_{max} of the nitro compound. The relatively small spectral shift produced by the addition of sodium hydroxide to methanolic solutions of III demonstrates the increased base sensitivity of III.

The sodium salts of III and IV were prepared (V and VI, respectively). When these were dissolved in acetone, similarities were seen in the visible absorption spectral shifts of the long-wavelength absorption bands caused by forming the sodium salts. The long-wavelength absorption shift is attributed to increased conjugation in the sodium salts.



V, λ_{max} 610nm

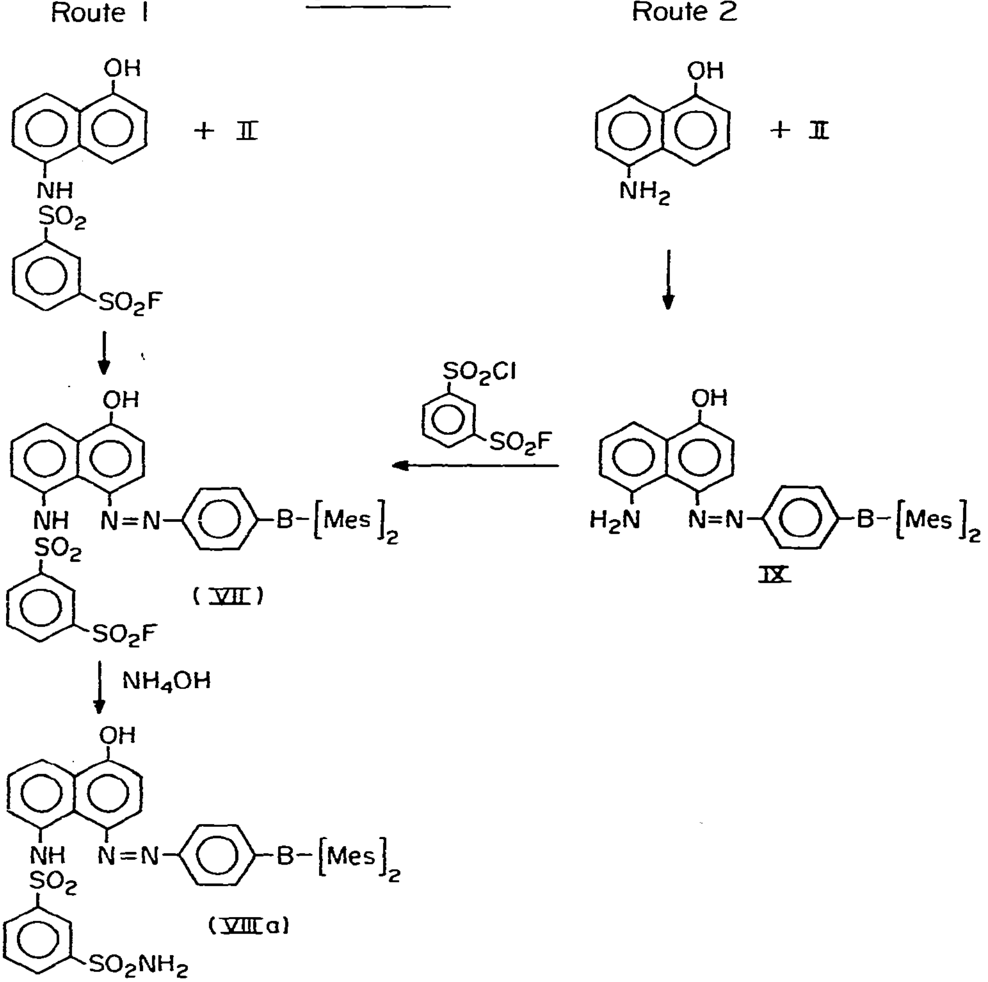


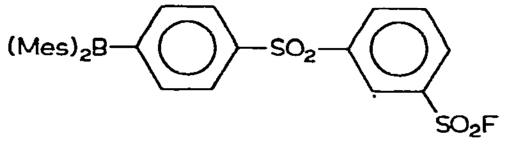
VI, λ_{max} 592nm

The synthesis of *N*-[5-hydroxy-8-(4-dimesitylborylphenylazo)naphthyl]-3-fluorosulfonylbenzenesulfonamide (VII), *N*-[5-hydroxy-8-(4-dimesitylborylphenylazo)naphthyl]-1,3-benzenedisulfonamide (VIIIa), *N*-[5-hydroxy-8-(4-dimesitylborylphenylazo)naphthyl] amine (IX), and α-[3-(4-dimesitylborylphenylazo)-4-hydroxynaphthoxy]propionic acid (X) show the general applicability of the use of the diazonium salt II for the formation of substituted azonaphthol dyes.

The substituted azonaphthol dye VIIIa was synthesized via two routes which illustrate the chemical stability of the dimesitylboryl group (Scheme 2). Both routes gave low yields of VII and VIII. Route 1 was plagued by the formation of non-dye side products as well as isomeric derivatives of VII. The major side products were *p*-chlorophenyldimesitylborane (XI), phenyldimesitylborane (XII), and dimesityl-4-(3-fluorosulfonylphenylsulfonyl)phenylborane (XIII). The formation of XI and XII occurs directly from the decomposition of II. At high temperatures, II decomposed to a 60/40 mixture of XI/XII.

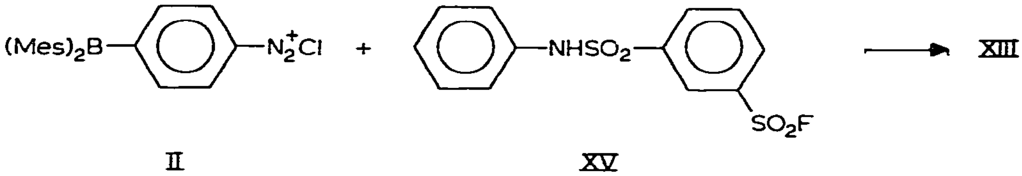
Scheme 2





XIII

Compound XIII was synthesized by the reaction of II with 3-fluorosulfonylbenzenesulfonyl chloride (XIV) in water/methanol. Infrared, NMR, and mass spectra agree with the given structure. The possibility that XIV was an impurity in the coupler used to form VII that reacted with the boryl-substituted azo dye was ruled out when it was shown that XIV did not react with the naphthoazo dye III. The diazonium salt II did react with XV to yield XIII. It was concluded that XIII arises from a side reaction of II with the coupler and not from decomposition of the boryl-substituted azo dye.



In Route 2 of Scheme 2, the purification of IX, the major product, was complicated by the presence of a large amount of the five other isomeric derivatives formed during the coupling step. The spectrum of VIIIa (Fig. 3) is similar to that of the corresponding nitro-substituted compound, VIIIb (Fig. 4). The nitro compound has λ_{max} 638 nm in acetone solutions treated with a drop of 5% aqueous sodium hydroxide, compared to only 595 nm for acetone solutions of VIIIa similarly treated; this reflects the difference in acidity and the reluc-

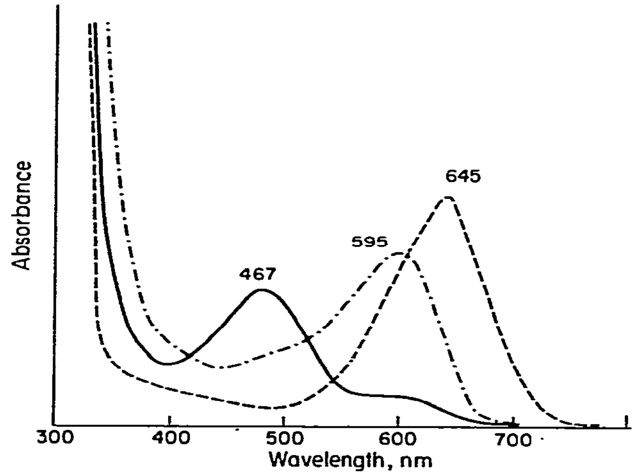


Fig. 3. Absorption spectra of *N*-[5-hydroxy-8-(4-dimesitylborylphenylazo)naphthyl]-1,3-benzenedisulfonamide; (————) acetone/HCl, ϵ 4000; (— · — · —) acetone/NaOH, ϵ 5000; (- - - - -) sodium salt, ϵ 9600.

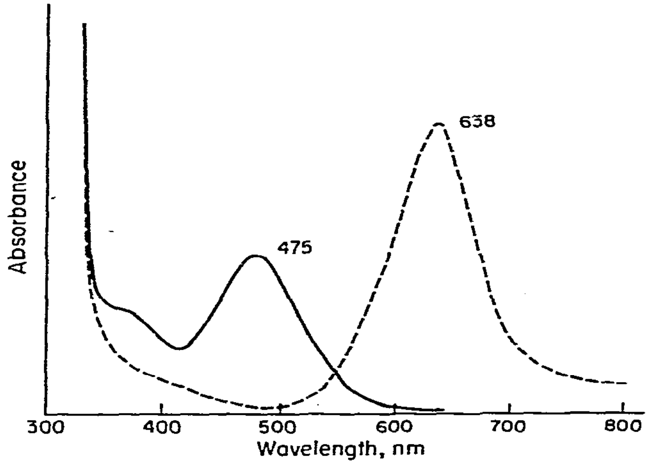


Fig. 4. Absorption spectra of N-[5-hydroxy-8-(4-nitrophenylazo)naphthyl]-1,3-benzenedisulfonamide; (———) acetone/HCl, ε 11 000; (- - - - -) acetone/NaOH, ε 23 000.

tance of VIIIa to form the sodium salt. When VIIIa is isolated as the sodium salt and dissolved in acetone, or when acetone solutions of VIIIa are treated with excess solid sodium hydroxide, the λ_{max} shifts to 645 nm.

Conclusions

The foregoing data show that the dimesitylboryl group is approximately equal to a nitro group as an auxochrome in naphthol dyes.

The premise that the dimesitylboryl group is sufficiently sterically shielded against oxygen attack has proven to be correct. Furthermore, the series of syntheses show that the dimesitylboryl group is stable and can be carried through a number of synthetic steps.

The differences in the spectral shifts of the dimesitylboryl- and nitro-substituted analogous dyes are attributed to differences in the respective electronic interactions within the two dye groups. The inductive and mesomeric effects of the dimesitylboryl group will be discussed in a subsequent paper pertaining to the determination of the Hammet σ value of the *p*-dimesitylboryl group.

Experimental

The *p*-nitrophenylazonaphthols were synthesized by diazotizing a small quantity (0.05 g) of *p*-nitroaniline in THF at 0°C and treating this diazonium salt solution with the appropriate coupler. The UV-visible spectra were measured on a Cary 14 spectrometer.

p-(Dimesitylboryl)benzenediazonium chloride (II)

A solution of 1 g of *p*-aminophenyldimesitylborane in 10 ml of THF was treated with gaseous HCl and cooled to 0°C. To this was added 0.36 g of isopentyl nitrite, and the reaction was allowed to proceed for 10 min. The diazonium salt solution was used without further purification.

4-[p-Dimesitylborylphenylazo]-1-naphthol (III)

A solution containing 1 g of *p*-aminophenyldimesitylborane converted to the diazonium salt was slowly added to a chilled THF/H_2O solution of 0.5 g of 1-naphthol and excess sodium acetate. Reaction was allowed to proceed for 2 h at 0° C, during which time a deep-red compound (0.6 g, 40%) formed. λ_{max} (MeOH, HCl): 572 nm, ext 28 000; λ_{max} (acetone, NaOH): 608 nm, ext 32 000.

N-[5-Hydroxy-8-(4-dimesitylborylphenylazo)naphthyl]-3-fluorosulfonylbenzenesulfonamide (VII)

p-Aminophenyldimesitylborane (3.41 g) was diazotized in H_2O/MeOH as described above. This was slowly added to a chilled THF/H_2O solution containing 2.81 g of 3-fluorosulfonyl-*N*-(5-hydroxynaphthyl)benzenesulfonamide and excess sodium acetate. The solids were filtered and leached with high-boiling ligroin. The remaining solids gave a spectrum with λ_{max} 605 nm, ext 10 400.

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

p-Aminophenyldimesitylborane (3.41 g) was diazotized in THF as described above. This was slowly added to a chilled THF/H_2O solution containing 2.81 g of 3-fluorosulfonyl-*N*-(5-hydroxynaphthyl)benzenesulfonamide and excess sodium acetate. The reaction mixture was treated with ammonium hydroxide and extracted with ethyl ether and water. Upon evaporation of the organic layer, a dark-red compound (0.4 g, 30%) was obtained. λ_{max} (acetone, NaOH): 595 nm, ext 7000.

N-[5-Hydroxy-8-(4-dimesitylborylphenylazo)-1-naphthyl] amine (IX)

A THF solution of 2 g of *p*-aminophenyldimesitylborane converted to the diazonium salt was slowly added to a solution of 0.93 g of 5-amino-1-naphthol in 30 ml of THF. A deep-blue color developed immediately. TLC showed 18 components, but only 1 major and 2 semi-major components (all colored). Three other colored minor zones were seen. The reaction mixture was column chromatographed, and the colored zones were collected, combined, and evaporated to dryness. The mixture was dissolved in MeOH and passed through an activated-carbon column, eluting with several volumes of MeOH. When no more components came off the column, the column was eluted with pyridine. A purple material was collected and evaporated to dryness. This was placed on a second column of silica gel and eluted with hexane/dichloromethane to yield 0.89 g (31%) of a deep-purple material, which TLC showed to have only one component. The mass spectrum shows the parent at 511 mass units.

α-[3-(4-Dimesitylborylphenylazo)-4-hydroxynaphthoxy]propionic acid (X)

A solution of 1 g of *p*-aminophenyldimesitylborane hydrochloride was diazotized in water/methanol as described above. This was added to a solution of 0.6 g of 4-hydroxynaphthoxypropionic acid in 20 ml of methanol at 0° C. After 30 min the reaction mixture was dark colored. The solids were filtered, dissolved in 1/1 acetone/ligroin, filtered, and evaporated; yield 1.02 g. The crude compound decomposed during further purification attempts. The crude mixture in acetone gave a spectrum with λ_{max} 635 nm. In the presence of sodium hydroxide, the mixture rapidly decomposed, giving a spectrum with λ_{max} 540 nm.

Dimesityl-4-(3-fluorosulfonylphenylsulfonyl)phenyl borane (XIII)

A solution of 0.3 g of *p*-aminophenyldimesitylborane hydrochloride diazotized in methanol/water at 0° C with 0.28 g of isoamyl nitrite was added to 0.4 g of 3-fluorosulfonylbenzenesulfonyl chloride (XIV) in 10 ml of methanol. The reaction mixture was allowed to warm to room temperature, and the solids were filtered and washed with water. Chromatography on silica gel gave a fast-moving yellow zone, m.p. 243—245° C, *m/e* 548. When 0.2 g of *p*-aminophenyldimesitylborane hydrochloride was diazotized as described and added to 0.2 g of 3-[*N*-phenylsulfamido]benzenesulfonyl fluoride (XV), only a slight change in color occurred. The reaction mixture was extracted with toluene and water. The toluene solution was dried with magnesium sulfate and evaporated to yield 0.38 g of crude material. This was eluted through a silica gel column to yield 0.13 g of material from the first set of zones, which was estimated by TLC to contain 10% XIII. A second zone gave 0.08 g of *p*-aminophenyldimesitylborane, and a third zone gave 0.05 g of tris(dimesitylborylphenyl)amine. Both of the latter compounds were major impurities in the isolated sample of XIII.

References

1 M.E. Glogowski and J.L.R. Williams, J. Organometal. Chem., 195 (1980) 123 and references therein.
2 B. Babb and P.J. Grisdale, Canadian Patent 912 019, October 10, 1972.
3 M.E. Glogowski and J.L.R. Williams, Proceedings of the First China, Japan, U.S. Symposium on Organometallic Chemistry, June 9, 1980, in press.