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BORON PHOTOCHEMISTRY

IX. SYNTHESIS AND FLUORESCENT PROPERTIES OF DIMESITYLPHENYLBORANES

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SUMMARY

A series of *p*-substituted phenyldimesitylboranes has been synthesized by reaction of dimesitylboron fluoride with appropriately substituted phenyllithium derivatives. The quantum yields of fluorescence in cyclohexane vary with the nature of the *p*-substituent as follows: $Br \approx Cl < CN < CH_3 \approx H < N(CH_3)_2 < N(C_6H_5)_2$.

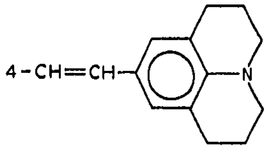
The wavelengths of fluorescent emission of a number of these compounds shift to longer wavelengths in polar solvents such as methanol. The sensitivity to solvent polarity is attributed to a change from a nonpolar ground state to a highly polar species in the excited state.

In previous studies we have examined the photochemistry of various boron-containing compounds. We have observed that photochemical reactions occur much more readily in those compounds involving tetrahedrally bonded boron than those containing trigonally bonded boron. For example, tetraphenylborate anion photolyses rapidly, but triphenylborane, on a similar time scale, is inert[1]. However, the addition of various donor solvents to solutions of triphenylborane facilitates the photodegradation, and typical borate-type photochemistry and products result. By contrast, trimesitylborane is photochemically inert in all solvents because of the severe steric hindrance of the six *o*-methyl groups, which prevent any donation to the empty *p*-orbital. Even four such *o*-methyl groups are sufficient to impart unusual stability to boranes and we have reported the isolation of an air-stable substituted phenyldimesitylborane[2]. Like trimesitylborane, phenyldimesitylborane is photochemically inert and the energy absorbed is released as fluorescence. The quantum yields of fluorescence of trimesitylborane, dimesitylphenylborane, and bis(2,6-dimethylphenyl)phenylborane are 0.11, 0.08, and 0.10, respectively, in cyclohexane solution. The finding that dimesitylphenylborane was stable led us to investigate the effect of substitution in the phenyl ring. To this end a series of *p*-substituted aryldimesitylboranes were prepared. They are shown in Table 1.

With the exception of the cyano-substituted compounds (IX) and (X), the boranes listed in Table 1 were prepared by the reaction between fluorodimesitylborane and the appropriate aryllithium in ether. The aryllithium compounds were

TABLE 1

PHYSICAL PROPERTIES AND YIELDS OF SUBSTITUTED ARYLDIMESITYLBORANES

Compound	*Substituent*	*M.p. (°C)*	*Yield (%)*	*Recryst. solvent*	*Formula*	*Found (calcd.) (%)*			
						C	*H*	*B*	*N(Br)*
(I)	4-$N(CH_3)_2$	159–161	58	CH_3CN	$C_{26}H_{32}BN$	84.7 (84.6)	8.8 (8.8)	3.0 (2.9)	4.2 (3.8)
(II)	2-CH_3-4-$N(CH_3)_2$	134–137	48	CH_3CN	$C_{27}H_{34}BN$	84.2 (84.6)	8.7 (8.9)	2.8 (2.8)	3.8 (3.7)
(III)	4-$N(C_6H_5)_2$	141–142	73	$CH_3CN/CHCl_3$	$C_{36}H_{36}BN$	87.3 (87.7)	7.6 (7.4)	2.2 (2.2)	3.0 (2.8)
(IV)	4-$N(CH_2)_5$	129–131	40	CH_3CN	$C_{29}H_{36}BN$	85.1 (85.1)	8.6 (8.9)	2.9 (2.6)	3.6 (3.4)
(V)	4-$N(CH_2CH_2)_2O$	178–180	70	CH_3CN	$C_{28}H_{34}BNO$	81.4 (81.8)	8.6 (8.3)	2.8 (2.6)	3.6 (3.4)
(VI)	$N(CH_3)_2$ attached to 1-naphthyl	159–161	64	CH_3COOH	$C_{30}H_{34}BN$	85.9 (86.0)	7.9 (8.2)	2.4 (2.6)	3.5 (3.3)
(VII)		180–182	64	Diglyme	$C_{38}H_{42}BN$	86.8 (87.2)	8.3 (8.1)	2.0 (2.1)	2.5 (2.7)
(VIII)	4-$(CH{=}CH)_2$-C_6H_4-4-$N(CH_3)_2$	158–159	(27)[a]	$C_2H_5OCH_2CH_2OH$	$C_{36}H_{40}BN$	87.3 (87.6)	7.7 (7.3)	1.8 (2.1)	2.9 (2.8)
(IX)	4-CN	164–166	(30)[b]	CH_3CN	$C_{25}H_{26}BN$	85.9 (85.5)	7.8 (7.5)	2.8 (3.1)	4.2 (4.0)
(X)	2,5-$(CH_3)_2$-4-CN	185–187	63	CH_3CN	$C_{27}H_{30}BN$	85.4 (85.5)	7.7 (8.0)	2.8 (2.9)	3.7 (3.7)
(XI)	4-Br	186–187	(52)[b]	$CH_3OCH_2CH_2OCH_3$	$C_{24}H_{26}BBr$	70.8 (71.1)	6.2 (6.5)	2.4 (2.7)	20.1(Br) (19.7(Br))
(XII)	2,5-$(CH_3)_2$-4-Br	202–204	90	$CH_3OCH_2CH_2OCH_3$	$C_{26}H_{30}BBr$	72.2 (72.1)	7.0 (7.0)	2.5 (2.5)	18.3(Br) (18.5(Br))

[a] Crude material obtained as a complex with unchanged bromo compound. See experimental section. [b] Crude yield, physical data reported for the product purified by preparative TLC from traces of unknown impurities.

TABLE 2

CORRECTED[a] QUANTUM YIELDS OF FLUORESCENCE FOR *p*-SUBSTITUTED PHENYLDIMESITYLBORANES

Compound	*Cyclohexane*	*Tetralin*	*Chloroform*	*Dichloromethane*	*Isopropanol*	*Methanol*
(I)	0.42	0.34	0.26	0.28	0.12	0.046
(II)	0.44	0.36	0.37	0.38	0.33	0.34
(III)	0.88	0.53	0.75	0.71	0.63	0.55
(IV)	0.43	0.35	0.29	0.27	0.23	0.043
(V)	0.43	0.36	0.31	0.29	0.25	0.062
(VI)	0.19	0.47	0.40	0.34	0.34	0.20
(VII)	0.70	0.28	0.37	0.39	0.36	0.45
(VIII)	0.65	0.31	0.64	0.69	0.70	0.91
(IX)	0.016	0.016	0.034	0.032	0.056	0.059
(X)	0.025	0.018	0.036	0.029	0.042	0.046

[a] Corrected for index of refraction.

derived from the corresponding bromo compounds by treatment with butyllithium. Sources, references to, or preparations of the bromo compounds are included in the experimental section. Physical data for the boranes (I)–(X) are listed in Table 1. Included are the data for (4-bromophenyl)dimesitylboranes (XI) and (4-bromo-2,5-dimethylphenyl)dimesitylboranes (XII), from which the cyano-substituted compounds (IX) and (X) were prepared using cuprous cyanide in dimethylformamide.

The quantum yields of fluorescence of the dimesitylphenylborane system are markedly increased by introduction of electron-donating groups into the *p*-position of the phenyl group. The quantum yields of fluorescence (Φ_f) of compounds (I)–(X) were determined in a series of solvents of different polarities. The corrected quantum-yield data summarized in Table 2 include a correction for refractive index as suggested by Dawson and Windsor[3]. In general, the electron-donating amino group causes marked increases in the quantum yield and the electron-withdrawing cyano group causes a decrease. Compounds (I), (II), (IV) and (V), which are fairly similar alkylamino structures, exhibit Φ_f between 0.42 and 0.44. The *p*-diphenylamino derivative (III) has the highest Φ_f (0.88) of the present series; the values for the two unsaturated alkylamino compounds (VII) and (VIII) are somewhat lower (0.70 and 0.65). On the other hand, halogen and cyanide substituents, (IX)–(XII), lead to values of Φ_f in the range of 0.01–0.07.

During the fluorescence studies of these *p*-substituted phenyldimesitylboranes, it was noted that the fluorescent emission maximum of dimesityl[*p*-(dimethylamino)-phenyl]borane in methanol solution is located at 512 nm compared to 386 nm in cyclohexane solution. This was surprising since the absorption maximum in methanol is shifted bathochromically only 5 nm from that in cyclohexane. In comparison, trimesitylborane shows only a 5-nm bathochromic shift in fluorescent emission maximum between methanol and cyclohexane solutions. Similar solvent shifts of fluorescence emission maxima were found for the other *p*-substituted phenyldimesitylboranes, (I)–(X), as summarized in Table 3. The values in wave numbers, ($\nu_a - \nu_f$) of the Stokes shifts of solutions of (I)–(X) in methanol and in cyclohexane are tabulated in Table 4. Lippert[4] described a relationship between the Stokes shift in different

TABLE 3

ABSORPTION AND FLUORESCENCE MAXIMA OF TRIARYLBORANES IN DIFFERENT SOLVENTS

Compound	*Cyclohexane*	*Tetralin*	*Chloroform*	*Dichloromethane*	*Isopropanol*	*Methanol*
Absorption (λ_{max} *in nm*)						
(I)	353	360	359	359	356	358
(II)	361	368	366	366	363	364
(III)	377	381	380	379	377	376
(IV)	354	361	360	361	357	359
(V)	345	351	348	349	347	348
(VI)	372	377	374	375	371	370
(VII)	416	435	420	432	420	422
(VIII)	411	428	417	431	412	411
(IX)	328	332	330	326	327	325
(X)	322	324	323	323	323	324
Fluorescence (λ_{max} *in nm*)						
(I)	386	427	465	491	489	512
(II)	418	458	478	495	500	520
(III)	412	438	455	469	456	474
(IV)	392	428	477	497	490	520
(V)	383	414	453	472	478	502
(VI)	432	458	487	507	502	530
(VII)	472	527	558	585	575	604
(VIII)	468	537	570	594	589	621
(IX)	394	415	428	444	439	461
(X)	389	412	421	432	429	444

TABLE 4

STOKES SHIFTS OF ARYLBORANES IN METHANOL AND CYCLOHEXANE

Compound	*Methanol* (cm^{-1})	*Cyclohexane* (cm^{-1})	*Diff. in Stokes shifts*	
			(cm^{-1})	(*kcal/mole*)
(I)	6747	2636	4111	11.75
(II)	7595	3546	4049	11.58
(III)	5345	2402	2943	8.42
(IV)	8052	2674	5378	15.38
(V)	7450	3079	4371	12.50
(VI)	7264	2799	4465	12.77
(VII)	6746	2488	4258	12.18
(VIII)	7205	2754	4451	12.73
(IX)	8267	4820	3447	9.86
(X)	8277	5062	3215	9.19
Trimesitylborane	3441	2981	460	1.32
Dimesitylphenylborane	6932	3951	2981	8.52

solvents and a constant (Δf) based on the dielectric constants and indices of refraction of the respective solvents. The relationship is described by the following equation:

$$\Delta f = \frac{D-1}{2D+1} - \frac{N_D^2-1}{2N_D^2+1}$$

A large shift in fluorescent emission maxima was attributed to a stabilization, by polar solvents, of a large dipole moment species in the excited state of the solute molecules.

By use of the data in Table 3 the Stokes shifts for (I)–(X) were calculated for each solvent and plotted against Δf according to Lippert's method. The greater the slope of the plot the greater is the contribution of the dipolar form in the excited state. The slopes and correlation coefficients for (I)–(X) are shown in Table 5. Fig. 1 is a typical plot of the data obtained. It appears that in the excited state a large contribution is made by a dipolar form for (I)–(X). The three dialkylamino-substituted boranes (I), (IV) and (V) are the most polar whereas the diphenylamino- and cyano- substituted

TABLE 5

SLOPE OF THE LINE OBTAINED FROM "LEAST-SQUARES" CALCULATED PLOT OF $\nu_a - \nu_f$ (1000 cm^{-1}) *versus* Δf

Compound	*Slope*	*Correlation coefficient*
(I)	18.5	0.984
(II)	13.5	0.990
(III)	9.18	0.944
(IV)	18.3	0.981
(V)	18.7	0.993
(VI)	13.5	0.984
(VII)	13.2	0.989
(VIII)	15.5	0.986
(IX)	11.6	0.973
(X)	8.36	0.959

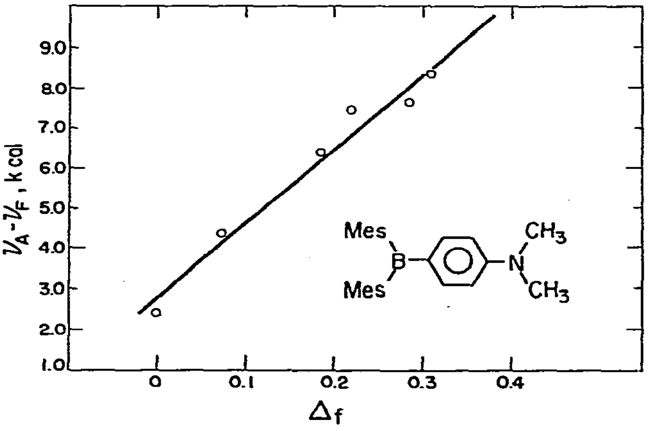


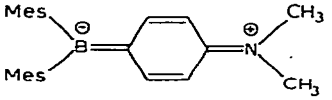
Fig. 1.

derivatives (III), (IX) and (X) are the least. It is interesting that in (II) and (X) the presence of a hindering methyl group *ortho* to boron decreases the dipolar contribution in the excited state.

A dipolar or internal charge transfer, first excited-singlet state has been proposed by Ramsey[5] for triphenylborane. The presence of a large Stokes shift in the case of amino-substituted boranes would indicate electron donation from nitrogen to the phenyl ring. This would facilitate the $\pi^* \leftarrow p$ transition proposed by Ramsey. It is, however, difficult to rationalize the similar behavior of the cyano-substituted derivatives on an electron-withdrawing basis unless one assumes that any perturbation of the phenyl π-system facilitates the existence of the dipolar form in the excited state.

The fact that the absorption spectra of compounds (I)–(X) are not changed significantly by solvent indicates that the ground-state molecules have small dipole moments. Thus, upon excitation of the molecules to the first excited-singlet state, a large increase in dipole moment must occur with formation of a dipolar species. The dipolar species can be best stabilized by polar solvents, which lower the energy of the first excited state, as evidenced by a red shift in the fluorescent emission spectrum.

Lippert[4] estimated from the slope (11.0) of the plot of $(\nu_a - \nu_f)$ versus Δf that 4-nitro-4'-(dimethylamino)stilbene was approximately 50% in the dipolar form in the first excited state. The slope of the plot for (I) is 18.5, indicating that the (aminophenyl)borane is in a highly dipolar form in the first excited state. The dipolar form of (I) would be as follows:



Such a dipole can only be formed if the boron atom is capable of strong resonance interaction via a phenyl group. In order to form this dipole a high degree of planarity must exist between the boron and the *p*-substituent. Of the compounds reported, (III) and (X) have the greatest steric hindrance to planarity and thus their experimental values deviate from the calculated line more than those of the other compounds, in which this steric interference is less.

EXPERIMENTAL

Measurements

The various solutions were adjusted to 5×10^{-5} *M* for measurement of fluorescent emission and absorption spectra. The methanol, isopropanol, chloroform, and dichloromethane used were all Eastman spectro grade and were used without further purification. Cyclohexane (Eastman spectro grade) and tetralin (Eastman) were purified by passing them through a 3-ft.-long column of activated alumina. The absorption spectra were measured with a Cary model 15 spectrophotometer.

The spectrofluorimeter was assembled from the following components. A Hanovia 1000-W xenon arc lamp was focused on the entrance slit of a Bausch and Lomb grating monochromator and the monochromatic light focused upon the face of a quartz cell. The emission was measured at 45° from the face of the cell and focused upon the entrance slit of a second Bausch and Lomb 500-nm grating monochromator. An EMI 9558A photomultiplier tube was attached at the exit of the second monochromator. The output signal was amplified with a Keithley model 149 micromillivoltmeter and then recorded simultaneously using a Hewlett–Packard digital voltmeter, paper-tape punch combination and the y axis of a Hewlett–Packard x–y recorder. The signal from the wavelength drive of the second monochromator was used to drive the x axis of the recorder and an encoder on the wavelength drive mechanism signaled the digital recorder to record at specific wavelength intervals.

The spectral sensitivity of the emission measuring equipment was calibrated by measuring the output of a quartz-iodide lamp of known color temperature.

An IBM 1130 computer program was written to read the paper tape, convert the spectra from wavelengths to wave numbers, compute the correction factor to correct the measured output of the lamp to that calculated, and then use these correction factors to correct subsequent spectra. The corrected spectra were then plotted by the IBM 360/65 computer-controlled plotter.

Materials

All melting points are corrected. All operations involving Grignard reagents or lithium reagents were conducted under a nitrogen atmosphere. Fluorodimesitylborane and trimesitylborane were prepared by the methods of Brown and Dodson[6]. The sources of the aryl bromides used in the preparation of the aryldimesitylboranes (I)–(XII) are listed below. 1,4-Dibromobenzene, 1,4-dibromo-2,5-dimethylbenzene, and 4-bromo-*N*,*N*-dimethylaniline were Eastman reagent grade chemicals. *N*-(4-Bromophenyl)piperidine[7], (4-bromophenyl)diphenylamine[8], 4-bromo-*N*,*N*-dimethyl-1-naphthylamine[9], and 4-bromo-3-methyl-*N*,*N*-dimethylaniline[10] were prepared by published procedures. *N*-(4-Bromophenyl)morpholine was prepared by bromination of *N*-phenylmorpholine in chloroform at 0°. The crude product had m.p. 110° (lit.[11] 115°) and was used without further treatment.

Diethyl (4-bromobenzyl)phosphonate. This intermediate, used in the synthesis of the boranes (VII) and (VIII), was prepared in 81% yield by the general method[12]. It had b.p. 183°/0.6 mm. (Found: C, 42.7; H, 5.2; Br, 25.6; P, 9.7. $C_{11}H_{16}BrPO_3$ calcd.: C, 43.1; H, 5.3; Br, 26.0; P, 10.0%.)

The following unsaturated derivatives were prepared from the diethyl (4-bromobenzyl)phosphonate and the appropriate aldehyde using the modified Wittig olefin synthesis[13].

9-(*4-Bromostyryl*)-1,2,3,4,5,6-*hexahydro-7H-benzo*[*i,j*]*quinolizine*. Yield 74%, yellow prisms from acetonitrile; m.p. 110–113°. (Found: C, 67.6; H, 6.0; Br, 22.7; N, 3.7. $C_{20}H_{20}BrN$ calcd.: C, 67.8; H, 4.7; Br, 22.6; N, 4.0%.)

1-(*4-Bromophenyl*)-4-[*4-*(*dimethylamino*)*phenyl*]-1,3-*butadiene*. Yield, 74%, orange prisms from diglyme, m.p. 163–165°. (Found: C, 65.5; H, 5.4; Br, 24.0; N, 4.2. $C_{18}H_{18}BrN$ calcd.: C, 65.9; H, 5.5; Br, 24.4; N, 4.3%.)

Preparation of the substituted aryldimesitylboranes (I)–(VIII), (XI), and (XII)

A solution of the aryl bromide (0.1 mole) in dry ether (250 ml) was stirred and treated with one equivalent of n-butyllithium solution (Alfa Inorganics). Stirring was continued for 5 min and a solution of fluorodimesitylborane (0.1 mole) in dry ether (250 ml) was added slowly. The mixture was heated under reflux for 30 min and poured into water. The ether layer was separated, washed with lithium sulfate solution, and dried over magnesium sulfate. The solvent was evaporated to yield the crude borane. Physical data, yields, and recrystallizing solvents are listed in Table 1. Compound (VIII) was the exception to the general work-up. Analytical data of samples of m.p. 235–237° prepared by crystallization of the crude material from a variety of solvents indicated that the material was a 1/1 complex of the desired borane and the corresponding bromo compound. When this crude material was crystallized from benzene, the bromo compound crystallized as yellow plates which after some time started to turn orange. At this stage the bromo compound was removed by filtration and the mother liquors were evaporated to dryness. The orange-red residue was crystallized from 2-ethoxyethanol to yield the desired borane.

Dimesityl(4-cyanophenyl)borane (IX). A mixture of dimesityl(4-bromophenyl)-borane (15 g, 0.04 mole) and cuprous cyanide (4 g, 0.045 mole) was heated under reflux in dimethylformamide (50 ml) for 4 h. The hot solution was poured into a solution of ethylenediamine (50 ml) in water (150 ml). The mixture was filtered, cooled, and the brown solid recrystallized from acetonitrile to give the borane as white needles, m.p. 162–165°, yield 30%. A sample purified by thin-layer chromatography (15% acetone in cyclohexane on 2-mm silica gel plates) had m.p. 164–166°. The recovery was 80%. Analyses are listed in Table 1.

Dimesityl(4-cyano-2,5-dimethylphenyl)borane (X). This compound was prepared from the corresponding bromo compound (XIII) as above. It crystallized from acetonitrile as white needles, m.p. 185–187°, 63%. Analyses are listed in Table 1.

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