

BORON PHOTOCHEMISTRY

XI. A STUDY OF THE UNUSUAL LUMINESCENCE AND SPECTRAL PROPERTIES OF ANILINODIMESITYLBORANES

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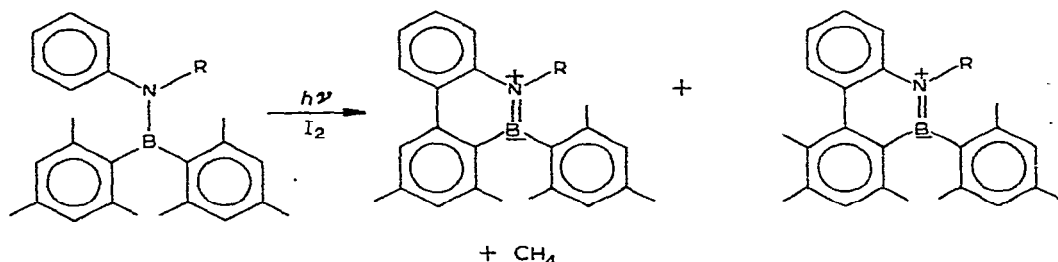
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Summary

Anilindimesitylboranes fluoresce showing the largest Stokes shifts yet reported, which correspond to energy losses of 35.3–61.8 kcal/mole. The dependence of wavelengths of fluorescence on the polarity of the solvent indicates that the first excited singlet state is highly dipolar in nature. A scheme involving an excited-state dipolar >B=N^+ species is used to explain the large loss of energy corresponding to the Stokes shifts for the anilindimesitylboranes. Delayed emission found at 77 K corresponding to fluorescence is attributed to electron ejection–recombination-type luminescence. No emission was found at longer wavelengths corresponding to triplet emission. It is proposed that the photochemical rearrangements of anilindimesitylboranes in the presence of iodine occur by interception of an excited singlet or excited charge-transfer state.

We reported that the photocyclization of anilindimesitylborane to borazarophenanthrenes in a cyclohexane solution in the presence of iodine is accompanied by either an unusual photoinitiated methyl-group migration or a methyl-group elimination [1].



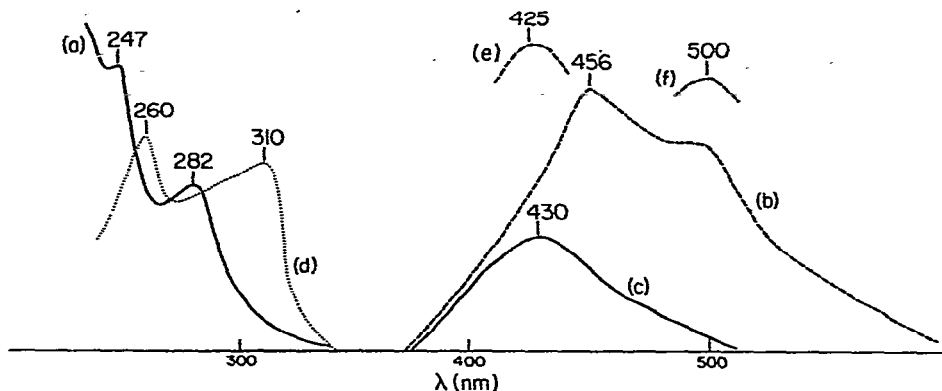
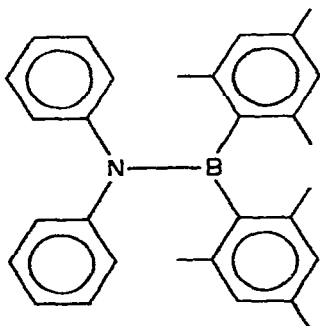


Fig. 1. Spectral characteristics of diphenylaminodimesitylborane: (a) absorption spectrum; (b) fluorescence spectrum in cyclohexane at room temperature; (c) delayed-fluorescence spectrum at 77 K; (d) activation spectrum; (e) fluorescence maximum at 77 K; (f) fluorescence maximum in acetonitrile at room temperature.

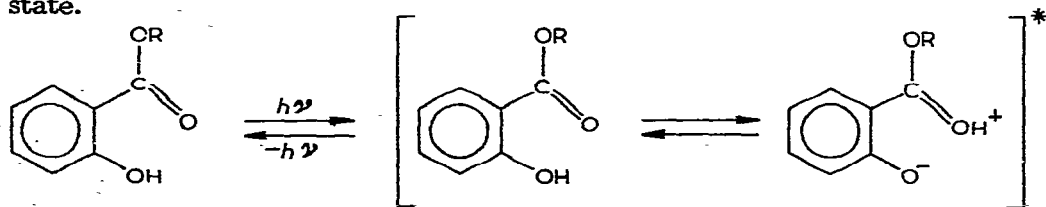
As a first step towards understanding the mechanisms involving photocyclization, alkyl-group migration, and elimination, we decided to investigate the nature of the states that might be involved in the absence and presence of iodine. We therefore report herein the first phase: the absorption and emission characteristics of anilindimesitylboranes.

Figure 1 shows corrected absorption, emission, and activation spectra for diphenylaminodimesitylborane (Id), which exhibit several unusual features. At

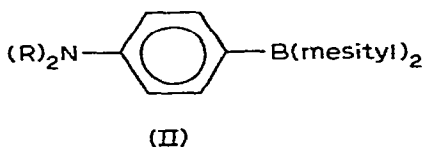


(Id)

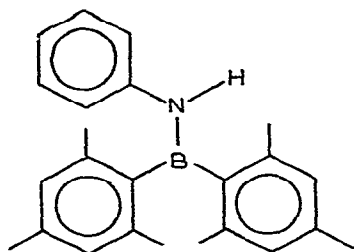
room temperature Id in cyclohexane solution shows an energy gap (Stokes loss) between the absorption and fluorescence maxima (curves a and b) of 39.1 kcal/mole corresponding to a Stokes shift of 174 nm. Weller [2] accounted for the large Stokes shift corresponding to 13.5 kcal/mole in the cases of salicylic acid and its methyl ester in terms of an intramolecular proton transfer in the excited state.



Phenanthrene in cyclohexane solution shows a Stokes shift typical of aromatic hydrocarbons corresponding to 10.3 kcal/mole [3]. The threefold size of the energy gap we observe for diphenylaminodimesitylborane (Id) appeared extraordinary in view of these previous studies. It was especially so when compared with our results using a series of *p*-substituted phenyldimesitylboranes (II) [4], for which Stokes losses as high as 23.5 kcal/mole were found. The ener-



gy loss for (II) was accounted for by formation of a dipolar species in the excited state. Additional unusual spectral features of (Id) are: the fluorescent emission spectra and Stokes shift like those of (II) are highly dependent on the polarity of the solvent, (Fig. 1, curves b and f); the fluorescence activation spectrum (Fig. 1, curve d) for (Id) does not resemble the absorption spectrum (Fig. 1, curve a) since a longer-wavelength band (λ_{max} , 310 nm) attributable to a charge-transfer transition (CT) is predominant in the activation spectrum but is barely detectable in the absorption spectrum; and a delayed emission occurs at low temperatures (77 K) at wavelengths corresponding to fluorescence.



We have also studied in detail anilindimesitylborane (Ia), which exhibits essentially the same spectroscopic features as does (Id), except that the long-wavelength or CT band in the activation spectrum is less pronounced and the yield of delayed emission is reduced. The energy gap between absorption and fluorescence for (Ia) was found to be larger than that of (Id) and amounted to 49.0 kcal/mole. A Lippert plot [5] of Δf (a polarity factor) vs. the Stokes shift was made for (Ia) where

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

D = dielectric constant of the solvent, and n_D = refractive index (Fig. 2). Lippert plotted Δf vs. the Stokes shift for 4-nitro-4-(dimethylamino)stilbene and obtained a slope of 11.0. He estimated that this represented a contribution of approximately 50% of the dipolar form of 4-nitro-4-(dimethylamino)stilbene to

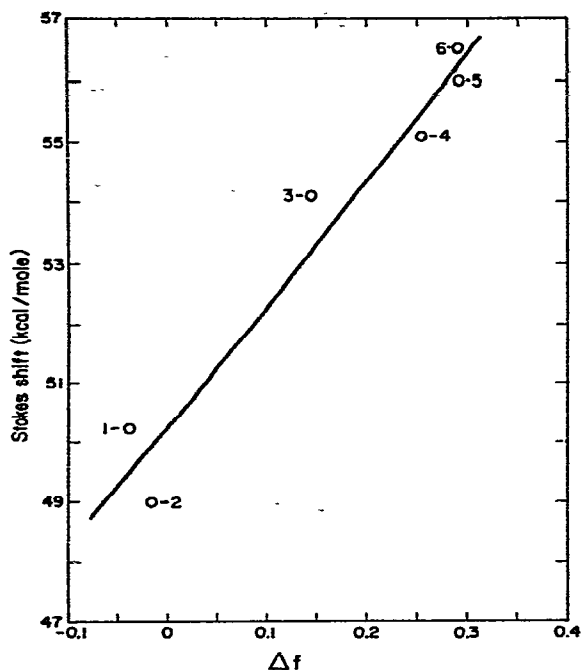


Fig. 2. Lippert plot of Δf vs. Stokes shift for anilindimesitylborane.

the overall structure of the first excited state. In Fig. 2 a slope of 22.4 was obtained, which indicates that the first excited state of (Ia) is even more dipolar than that of 4-nitro-4-(dimethylamino)stilbene or *p*-dimethylaminophenyldimesitylborane (slope of 18.5) [4].

The observation that these two molecules exhibited extraordinarily large energy gaps or Stokes shifts led us to investigate the scope of this phenomenon by studying the related compounds: 2,6-dimethylanilindimesitylborane (Ib), *N*-methylanilindimesitylborane (Ic), 1-naphthylaminodimesitylborane (Ie), and *N*-methyl-1-naphthylaminodimesitylborane (If). The spectroscopic data for (Ia)–(If) are summarized in Table 1. All of the boranes exhibit large Stokes shifts both in cyclohexane or acetonitrile solution and in glasses at 77 K. The largest Stokes shift at room temperature was found for *N*-methylanilindimesitylborane (Ic) and amounted to 61.8 kcal/mole. This amount of energy is 5–6 times the magnitude heretofore found for organic molecules and almost three times that reported by us for the *p*-substituted phenyldimesitylboranes [1].

In the absence of iodine no photochemical reaction occurred and the materials were recovered unchanged after irradiation. This eliminated the possibility of emission from a photochemical product. It is not possible to account for the large energy loss in terms of excited-state tautomerism such as was suggested for salicylic acid by Weller [2]. We therefore considered that changes of polarity or formation of a dipolar species in the excited state together with steric effects were the cause of the energy losses. The slope of 22.4 for the Lippert plot proved that (Ia) was a highly dipolar species in the first excited singlet state. Comparison of the structures of the *p*-aminophenyldimesitylboranes studied

TABLE 1

SPECTROSCOPIC DATA FOR THE SUBSTITUTED AMINODIMESITYLBORANES:

(Ia) anilindimesitylborane; (Ib) 2,6-dimethylanilinodimesitylborane; (Ic) *N*-methylanilinodimesitylborane; (Id) diphenylaminodimesitylborane; (Ie) 1-naphthylaminodimesitylborane; (If) *N*-methyl-1-naphthylaminodimesitylborane.

Compound	(Ia)	(Ib)	(Ic)	(Id)	(Ie)	(If)
<i>Cyclohexane solution</i>						
Absorption, λ_{\max} (nm)	265	254	255	282	304	294
Absorption (kcal/mole)	108.0	113.5	113.3	102.0	94.6	97.2
Emission, λ_{\max} (nm)	485	523	500	456	512	550
Emission (kcal/mole)	59.0	54.8	57.6	62.9	56.4	52.4
Stokes shift (kcal/mole)	49.0	58.7	55.7	39.1	38.2	45.4
<i>Acetonitrile solution^a</i>						
Absorption, λ_{\max} (nm)	264	250	255	282	302	292
Absorption (kcal/mole)	108.0	114.5	113.3	102.0	95.5	98.4
Emission, λ_{\max} (nm)	550	—	563	500	528	570
Emission (kcal/mole)	52.0	—	51.2	57.5	54.5	49.4
Stokes shift (kcal/mole)	56.0	—	61.8	44.5	41.0	49.0
<i>77 K Matrix</i>						
Emission, λ_{\max} (nm)	480 ^a	460	465	428	470	475
Emission (kcal/mole)	59.5 ^a	62.3	64.2	66.7	60.8	60.2
Stokes shift (kcal/mole)	48.5 ^a	51.2	49.1	35.3	33.8	37.7

^aSee experimental part.

earlier [1] with (Ia) and (Id) reveals that any dipolar form would involve a greater boron–nitrogen interaction than in the earlier case, where a benzene ring separated the boron and nitrogen atoms. The fact that the absorption spectra of the anilindimesitylboranes are not modified by the polarity of the solvent does not negate the possibility of their having some dipolar character in the ground state, since the steric effects of the four *ortho* methyl groups of the two mesityl residues could make the B–N pair inaccessible to solvent interactions. However, the strength of the solvent interaction in the excited state indicates that either the ground state exists as a nonpolar species or an unusually large excited-state deformation occurs. The steric interference around the B–N system in going from the ground state to the excited state was, therefore, of primary interest.

The use of tetramesitylethylene as a model permitted separation of the steric effects from the polarity changes involved in the boron–nitrogen bond system. The spectra of tetramesitylethylene (Fig. 3) relate to each other in the normal manner with the long-lived, low-temperature triplet emission at 570 nm (curve c) and the room-temperature fluorescence (curve b) occurring at 425 nm. The Stokes shift, which is equivalent to 24.4 kcal/mole, is, however, the largest yet reported for a hydrocarbon. The absorption, activation, and emission spectra showed no solvent effects, indicating that tetramesitylethylene, as expected, is nonpolar in both the ground and excited states. The fluorescent maxima of tetramesitylethylene, (Id) and (Ia) all undergo a hypsochromic shift when the temperature is lowered from room temperature to 77 K. The energies involved are 3.3, 4.5, and 1.2 kcal/mole, respectively, and are attributed to loss of mobility upon cooling. This effect is expected since the spectra reported for stilbene

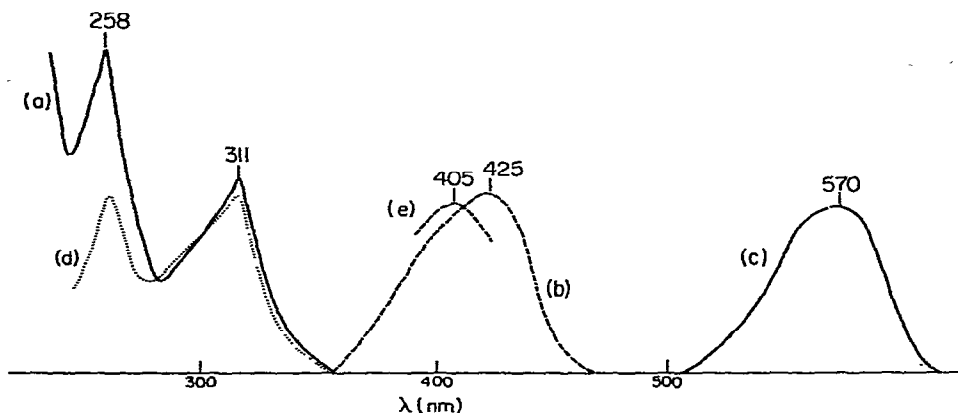


Fig. 3. Spectral characteristics of tetramesitylethylene: (a) absorption spectrum; (b) fluorescence spectrum at room temperature; (c) phosphorescence spectrum at 77 K; (d) activation spectrum; (e) fluorescence maximum at 77 K.

by Malkin and Fischer [6] show a similar shift from which we estimate an energy difference of approximately 2.5 kcal/mole. The exceedingly large Stokes shifts and energy gaps found for the anilindimesitylboranes, (Ia)–(If), therefore, can result from a steric contribution of 20–25 kcal/mole together with an additional loss of 20–40 kcal/mole by formation of a dipolar species in the excited state.

The delayed emission (Fig. 1, curve c) for the cyclohexane solutions of (Id) is visible for longer than 30 sec after irradiation. The possibility of emission from the triplet state is eliminated by the location of the delayed emission, as well as the fact that it is not quenched by oxygen. These delayed emissions, therefore, are attributed by us to electron ejection–recombination-type fluorescence, since the intensity of emission is linearly dependent on the intensity of the exciting light [7]. Laser flash photolysis study of (Id) in cyclohexane solution at 77 K revealed that the delayed emission had a nonlinear, nonexponential decay rate typical of electron recombination luminescence.

The refractive index is a measure of a solvent's ability to compensate instantaneously for a separation of charge upon absorption of light by a solute. Therefore, we studied the effect of refractive index of the solvent upon the wavelength of maximum activation of (Id). The nonlinear dependence upon the refractive index and a lack of any correlation with the polarity factor (Fig. 4) indicate that the 310 nm peak in the activation spectrum is probably due to charge separation upon absorption of light. The fluorescence spectrum showed no direct dependence upon the refractive index though it did show a dependency on the polarity factor Δf .

Figure 5 illustrates our idea of the relationship by which the various states interact. The nonpolar nature of the S_0 state suggests that the nitrogen atom of the B–N system is sp^3 hybridized, whereas the polar characteristics of the S'_1 and S'_0 states suggest that the nitrogen is sp^2 hybridized. This hybridization is also consistent with the fact that the fluorescent spectra ($S'_1 \rightarrow S'_0$) show more detail than the absorption spectra. This would be expected owing to the more rigid structure of the proposed excited state, S'_1 .

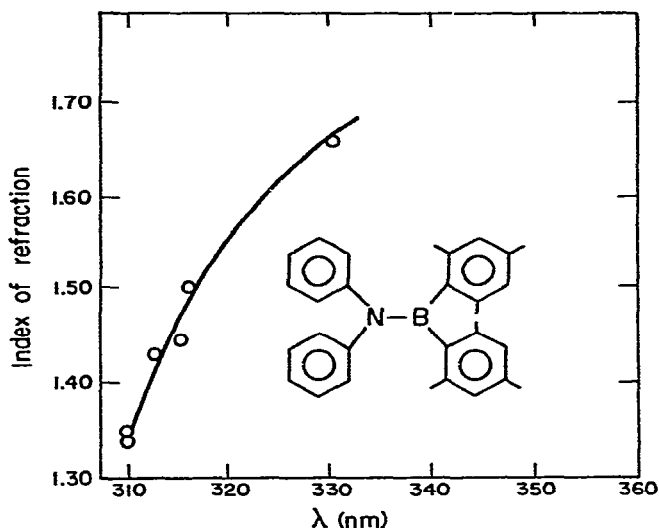


Fig. 4. Maximum wavelength of activation of diphenylaminodimesitylborane vs. index of refraction of the solvent.

The pathway for energy dissipation to account for the Stokes shifts of (Ia)–(If) would be as follows: Excitation of the ground state, S_0 , would occur to S_1 or CT, which undergoes radiationless transition to the dipolar species S'_1 , from which emission will occur with energy loss to S'_0 , which decays without radiation to S_0 . The configuration of states S_0 , CT, and S_1 would be similar, in accord with the Franck-Condon principle, since the time for the transitions $S_0 \rightarrow S_1$ or $S_0 \rightarrow CT$ is of the order of 10^{-13} sec. A configurational change occurs in going from S_1 or CT to the polar S'_1 state. States S'_1 and S'_0 are both similar polar configurations since the time for the fluorescent transition $S'_1 \rightarrow S'_0$ is of the order of 10^{-9} sec. S'_0 then undergoes radiationless transition with change to

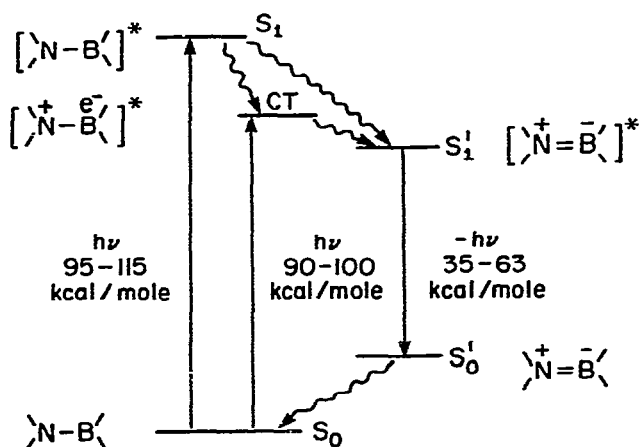


Fig. 5. Scheme illustrating the relationship between the various states of anilindimesitylboranes.

the nonpolar state S_0 . Iodine at a concentration of 10^{-3} mole quenches both the prompt and the delayed fluorescence, most probably at S'_0 and CT.

We therefore conclude that the photochemical reactions of the anilinodimesitylboranes take place with interception of singlet excited (S' or CT) anilinodimesitylboranes by iodine. The triplet state is not involved. The exact interaction with iodine is not known but is under study at present. The data presented above also lead us to conclude that the features leading to large Stokes shifts for anilinodimesitylboranes are the presence of sterically interfering groups in conjunction with formation of a dipolar species in the excited state.

Experimental

Preparation of samples

The synthesis of the anilinodimesitylboranes is described in the previous paper [1]. Tetramesitylethylene was prepared according to the method of Zimmerman and Paskovich [8]. All solvents were Eastman spectrograde and were used as received except cyclohexane, which was distilled from sodium hydride to remove traces of moisture. Solutions for measurements were prepared containing 5×10^{-3} mole of the compounds under study. The luminescence measurements were made at atmospheric pressure. Special precautions such as degassing were found unnecessary since six repeated freeze-thaw degassing cycles under high-vacuum conditions had shown no increase in delayed emission above that found in nondegassed samples. Degassing produced no effect on the spectral features. There was no change observed in quantum yield or spectral features when the concentration of solute was reduced from 5×10^{-3} mole to 5×10^{-6} mole.

Spectroscopic determinations

Absorption spectra were determined using a Cary model 14 instrument. The spectrofluorimetric measurements were carried out using the apparatus described by Costa et al. [9] or where indicated by footnote *a* in Table 1, the apparatus described by Doty et al. [4]. The spectral data, corrected for lamp output and photomultiplier spectral sensitivity, are shown in Table 1.

The data relating Stokes shift in terms of energy to the polarity factor Δf of solvents are summarized in Table 2. Table 3 contains the data relating refractive index of the solvent to the λ_{\max} of activation or excitation.

TABLE 2

STOKES SHIFT DATA FOR ANILINODIMESITYLBORANE (Ia) VERSUS SOLVENT POLARITY FACTOR Δf (Fig. 2)

Fig. 2 point no.	Solvent	Δf of solvent	λ_{\max} (nm)		Stokes shift (kcal/mole)
			Abs.	Fluor.	
1	Cyclohexane	-0.050	265	495	50.1
2	Benzene	0.016	265	485	49.0
3	Chloroform	0.145	265	530	54.1
4	Isopropanol	0.255	265	540	55.1
5	Methanol	0.292	265	555	56.5
6	Acetonitrile	0.293	265	550	56.0

TABLE 3
DEPENDENCE OF λ_{\max} OF ACTIVATION ON SOLVENT REFRACTIVE INDEX (Fig. 4)

Solvent	<i>RI</i>	Activation λ_{\max} (nm)
Methanol	1.33	310
Acetonitrile	1.346	310
Cyclohexane	1.436	312
Chloroform	1.446	315
Benzene	1.50	315
1,1,2,2-Tetrabromoethane	1.638	330

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