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FLUORESCENCE SPECTRA OF AMINOBORANES. THE NATURE OF EMISSION IN BORON—NITROGEN ANALOGS OF STILBENE AND STYRENE AND CHARACTERIZATION OF AMINOBORANE SINGLET EXCITED STATES

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Summary

Fluorescence spectra of ten aminoborane analogs of stilbenes and styrenes are generally structureless, even at 77 K; have modest (ca. 8 kcal/mol) Stokes shifts; are significantly red-shifted in polar solvents; and are in-plane polarized. The fluorescence spectra contrast with the more structured absorption spectra, which also show smaller solvent shifts. The data are interpreted in terms of π—π^* emission from a polar excited state to a less polar, more rigidly planar ground state. The possible involvement of σ—π^* transitions and the differences between these systems and the related, but sterically crowded, (anilino)dimesitylboranes are discussed.

Introduction

Aminoboranes have been shown recently to have exciting and diverse photochemical reactivity, comparable in some instances and contrasting in others to their carbon—carbon and carbon—oxygen analogs, the olefins and ketones. Boron—carbon cleavage [1-4], geometrical (*cis—trans*) isomerization [3,5], oxidative electrocyclization [6], and sigmatropic 1,3-shifts of boron [4,7] have been identified as primary photochemical processes. Additionally, boron—boron [8] and boron—nitrogen [3b,8b,9] cleavages have been reported in higher homologs of the aminoborane chromophore. As a first step towards elucidating the nature of the reactive excited states involved in these reactions and developing detailed reaction mechanisms, we have studied the emission spectroscopic properties of some aminoboranes analogous to the styrene and stilbene chromophores. Recent, similarly motivated reports of unusual luminescence behavior

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in phenyl- [10] and anilinodimesitylboranes [11] provided further impetus to establish emission norms for boron—nitrogen chromophores.

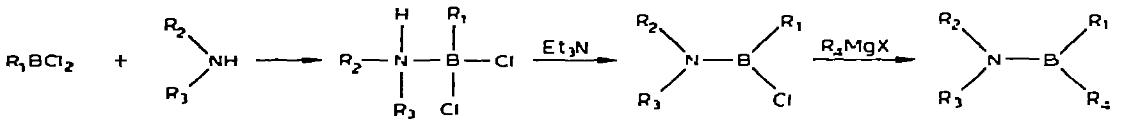
Ten aminoboranes were examined, namely:
(diethylamino)methylphenylborane (I),
(dimethylamino)phenyl-n-propylborane (II),
(dimethylamino)but-2-en-1-ylphenylborane (III),
(anilino)diethylborane (IV),
(*N*-methylanilino)diethylborane (V),
(*N*-methylanilino)ethylphenylborane (VI),
(*N*-methylanilino)isopropylphenylborane (VII),
(*N*-methylanilino)chlorophenylborane (VIII),
(*N*-methylanilino)cyclopropylphenylborane (IX), and
(*N*-methylanilino)allylphenylborane (X).

This group was intended to provide a limited, but representative probe of aminoborane emission spectra. Included were five B—N styrene analogs (I-V), three *B*-phenylated (I-III) and two *N*-phenylated (IV and V), and five B—N stilbene analogs (VI-X). The various boron- and nitrogen-substituents included groups chosen to reveal any effects of halogen (VIII), allylic homo-conjugation (III and X), and cyclopropyl pseudo-conjugation (IX).

Excepting IV and V, the aminoboranes I-X were synthesized according to modifications [3,4] of the synthetic route developed originally by Niedenzu and Dawson [12] (Scheme 1), which involves reaction of an organoboron dichloride with a secondary amine, dehydrohalogenation of the amine-borane with triethylamine, and Grignard coupling of the (amino)organochloroborane with an alkyl halide. For V, an analogous scheme was employed, starting with boron trichloride, reaction with *N*-methylaniline, dehydrohalogenation, and Grignard coupling with two equivalents of ethylmagnesium iodide. The anilinoborane IV was synthesized by transamination of (dimethylamino)diethylborane

SCHEME 1

SYNTHETIC SCHEME FOR AMINOBORANES



I: R_1 = Ph; R_2, R_3 = Et, Et; R_4 = Me
II: R_1 = Ph; R_2, R_3 = Me, Me; R_4 = n-Pr
III: R_1 = Ph; R_2, R_3 = Me, Me; R_4 = butenyl

VI: R_1 = Ph; R_2, R_3 = Me, Ph; R_4 = Et
VII: R_1 = Ph; R_2, R_3 = Me, Ph; R_4 = i-Pr
VIII: R_1 = Ph; R_2, R_3 = Me, Ph; R_4 = Cl [a]
IX: R_1 = Ph; R_2, R_3 = Me, Ph; R_4 = c-Pr
X: R_1 = Ph; R_2, R_3 = Me, Ph; R_4 = allyl

[a] Grignard coupling step omitted.

(XI) with aniline at 150° [4]; XI had been prepared from boron trichloride, dimethylamine, and two equivalents of ethyl iodide [4].

All of the aminoboranes were carefully purified by vacuum distillation shortly before use and were stored under argon. Solvents were also purified where necessary to eliminate solvent emission, and all transfers were carried out in a dry box under a nitrogen atmosphere. Details are discussed in the Experimental section.

Results

Fluorescence in hydrocarbon solvents. Absorption and fluorescence spectra for aminoboranes II, IV and VI are shown in Figs. 1-3 as representative of all the spectra. Salient features of the experimental absorption, activation, and fluorescence spectra in hydrocarbon solvents are summarized in Table 1, along with the Stokes Shifts calculated from the spectra

The reported spectra were recorded on degassed (three freeze-pump-thaw cycles) samples at ca. 10^{-4} *M* concentrations. However, except for reduced fluorescence intensity, non-degassed samples gave identical spectra. Reductions in concentration of the aminoboranes similarly led only to proportional reductions in fluorescence intensity with no alteration of other spectral features. Neither the fluorescence nor activation spectra were corrected for wavelength sensitivity of the photomultiplier/monochromator detection assembly since a test spectrum of purified aniline recorded under our experimental conditions closely matched the published corrected fluorescence spectrum [13].

Aminoboranes I-X all gave strong (Φ_f ca. 0.2), structureless fluorescence at 25° in isopentane. Determination of 0—0 band positions was impossible, so Table 1 records only emission maxima. Styrene analogs I-V had fluorescence

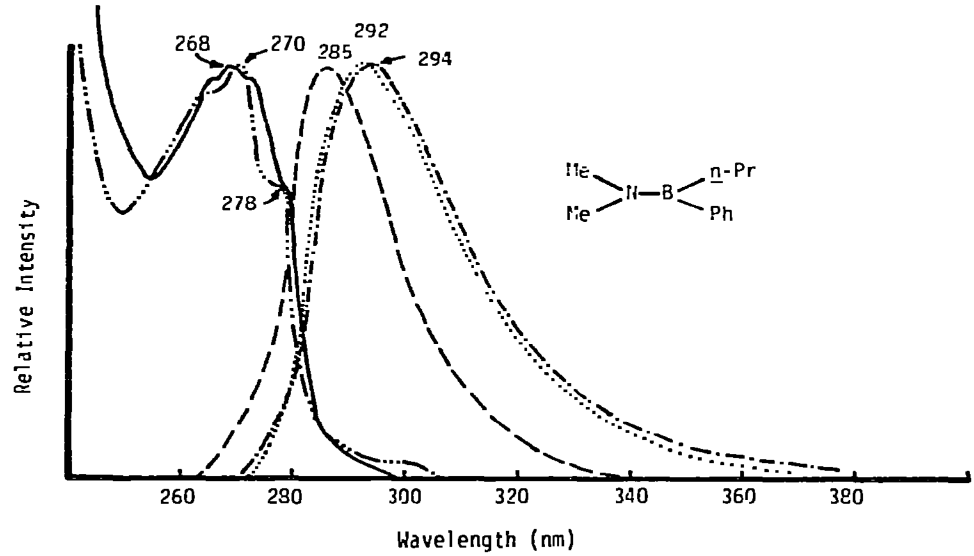


Fig. 1. Absorption and fluorescence spectra of (dimethylamino)phenyl-n-propylborane (II): (a) absorption in cyclohexane, 25° (—); (b) absorption in acetonitrile, 25° (—··—); (c) fluorescence in isopentane, 25° (·····); (d) fluorescence in acetonitrile, 25° (——); (e) fluorescence in isopentane, 77 K (- - -).

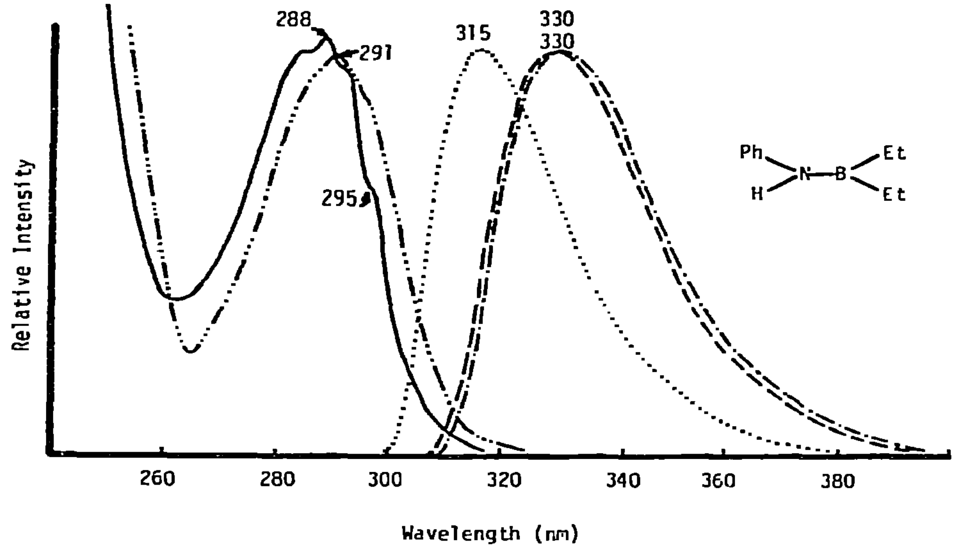


Fig. 2. Absorption and fluorescence spectra of (anilino)diethylborane (IV): (a) absorption in cyclohexane, 25° (—); (b) absorption in acetonitrile, 25° (—··—); (c) fluorescence in isopentane, 25° (·····); (d) fluorescence in acetonitrile, 25° (——); (e) fluorescence in isopentane, 77 K (- - -).

maxima in the range 287-323 nm, with the *B*-arylated aminoboranes (I-III) closely grouped at 287-293 nm, and the anilinoboranes (IV and V) at substantially longer wavelengths. The stilbene-like systems (VI, VII, IX and X) were also closely grouped at 324-327 nm; the only exception was the chlorinated system (VIII), with fluorescence λ_{max} blue-shifted to 293 nm.

Absorption spectra at 25° in isopentane and/or cyclohexane were more

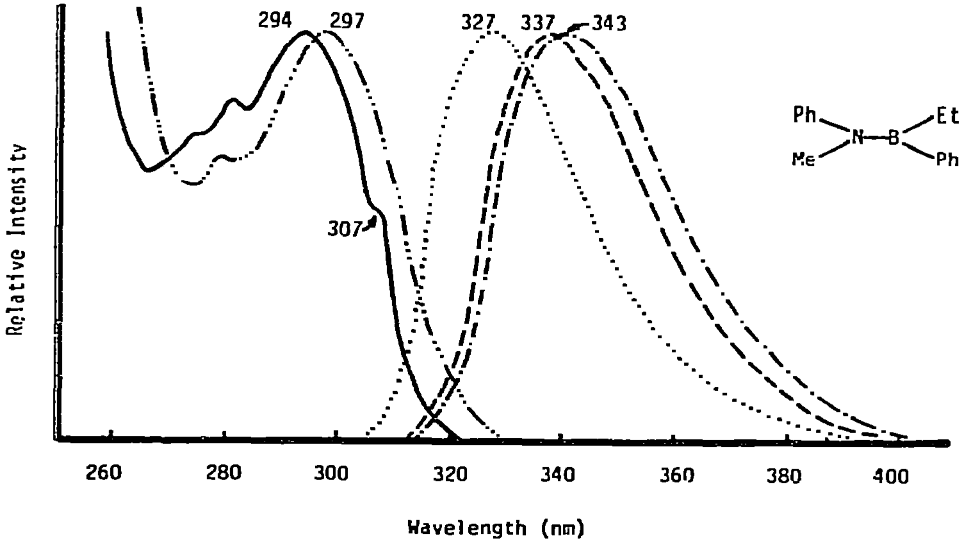


Fig. 3. Absorption and fluorescence spectra of (*N*-methylanilino)ethylphenylborane (VI): (a) absorption in cyclohexane, 25° (—); (b) absorption in acetonitrile, 25° (—··—); (c) fluorescence in isopentane, 25° (·····); (d) fluorescence in acetonitrile, 25° (——·). (e) fluorescence in isopentane, 77 K (- - -).

structured, with four or five vibrational bands generally discernible within the long-wavelength absorption envelope. The *B*-phenylated styrene analogs (I-III) were quite similar to one another, with λ_{max} and 0—0 band ranges of 268-273 and 276-280 nm. The *N*-phenylated aminoboranes (IV and V) had absorption red shifts of ca. 17 and 25 nm, respectively. Excepting VIII, which showed a 24 nm blue shift relative to the other stilbene-like aminoboranes, the diarylated aminoboranes (VI-X) were closely similar with λ_{max} and 0—0 band ranges of 294-295 and 307-308 nm. Molar extinction coefficients (cf. Table 1) averaged ca. 400-500 (log ϵ 2.6) at the λ_{max} for the *B*-phenylated boranes (I-III), and ca. 2000 for the *N*-phenylated systems (IV-X) (log ϵ 3.4).

Activation (excitation) spectra (Table 1) were shifted towards longer wavelengths from the absorption spectra recorded at ca. 10^{-4} *M* aminoborane concentrations. The size of the shift at the λ_{max} was ca. +7 nm for I-III, +13 nm for IV and V, and +17 nm for VI, VII, IX, X. However, at high aminoborane concentrations, part of a structureless, low-intensity band was generally discernible on the long-wavelength end of the strong absorption band found in the 270-295 nm region. The weak band is nearly totally submerged in the stilbene-type aminoboranes (VI-X), and is most pronounced where the intense band is blue-shifted, as in the case of the *B*-arylboranes (I-III) (cf. Fig. 1). The effect of the low-intensity transition is clearly more pronounced in the activation spectrum than in the absorption spectrum. Fluorescence spectra were recorded with excitation as close as possible to the activation λ_{max}, consistent with reasonable separation from Rayleigh and Raman light-scattering peaks.

Stokes shifts were calculated as the energetic difference between the absorption and fluorescence maxima [11]. The Stokes losses averaged about 8 kcal/mol for the ten aminoboranes, slightly lower for the *B*-arylated styrene-like systems (I-III), slightly higher for the *N*-arylated aminoboranes (IV-X).

Solvent effects. All the aminoboranes studied displayed bathochromic shifts when the solvent was changed from isopentane to acetonitrile; no differences outside of experimental error were noted between spectra recorded in isopentane, cyclohexane and methylcyclohexane. The bathochromic polar solvent shifts (cf. Table 2, also Figs. 1-3) were smallest for the *B*-arylated aminoboranes (I-III) analogous to styrene (+1 to +7 nm), larger for the *N*-arylated styrene (IV, V) and stilbene (VI, VII, X) analogs (+13 to +17 nm), and most dramatic (+47 nm) for the chlorinated aminoborane (VIII).

For (*N*-methylanilino)ethylphenylborane (VI), taken as typical of the set of aminoboranes studied, a more detailed analysis of the fluorescence solvent dependence was made (Table 3). Lippert [14] defined the solvent polarity factor Δf (eqn. 1) as

$$\Delta f = \frac{D-1}{2D+1} - \frac{n_D^2-1}{2n_D^2+1} \qquad (1)$$

where D and n_D are the solvent dielectric constant and refractive index, respectively. Correlations between the solvent polarity factor and the magnitude of the Stokes shifts in various solvents were used by Lippert [14] to estimate the polarity of fluorescent excited states. A Lippert plot of $(\nu_A - \nu_F)$ vs. Δf for aminoborane VI (Fig. 4) was linear with a slope of +10.4 kcal/mol.

(continued on p. 30)

TABLE 1

ABSORPTION, ACTIVATION, AND FLUORESCENCE SPECTRA OF AMINOBORANES IN HYDROCARBON SOLVENTS, TOGETHER WITH CALCULATED STOKES SHIFTS

Compound	UV absorption spectrum [a]			Activation [f] λ_{max} (nm)	Fluorescence spectrum [f]		Stokes shift (kcal/mol) [g]
	0–0 (nm) [b]	λ_{max} (nm) [c]	(log ε)		Excitation λ (nm)	Emission max. (nm)	
I	280 [e]	273 [e]	(2.0)	280	275	293	7.2
II	278 [e]	268 [e]	(2.7)	278	276	292	8.8
III	276 [i]	269 [i]	(2.6)	273	270	287	6.7
IV	295 [e]	288 [e]	(3.3)	301	302	315	8.5
V	305 [e]	294 [e]	(3.6)	309	300	323	8.4
VI	307 [d,e]	294 [d,e]	(3.3)	310	310	327	9.8
VII	307 [e]	206 [e]	(3.2)	310	310	324	8.7
VIII	281 [e]	273 [e]	(h)	280	270	293	7.2
IX	307 [e]	295 [e]	(3.4)	312 [e]	310 [e]	325 [e]	8.9
X	308 [e]	295 [e]	(3.4)	315	310	327	9.5

[a] Recorded on Cary 14 and 15 spectrometers in spectroquality isopentane or cyclohexane or both. [b] Estimated, ± 2 nm. [c] Estimated, ± 1 nm. [d] In isopentane. [e] In cyclohexane. [f] Recorded on a Hitachi–Perkin–Elmer MPF-2A spectrometer in isopentane at 25°, uncorrected. [g] Calculated from absorption and fluorescence λ_{max}. [h] Not recorded. [i] Data taken from ref. 4b.

TABLE 2

SOLVENT EFFECTS ON ACTIVATION AND FLUORESCENCE SPECTRA OF AMINOBORANES AND CALCULATED SOLVENT SHIFTS

Compound	Cyclohexane spectra		Acetonitrile spectra		Solvent shift (nm) ^{d}
	Act. λ_{max} (nm) ^{a}	Fl. λ_{max} ^{b} (excit. λ) ^{c}	Act. λ_{max} (nm) ^{a}	Fl. λ_{max} ^{b} (excit. λ) ^{c}	
I	280	293 (280)	281	294 (275)	+ 1
II	276	292 (276)	280	294 (276)	+ 2
III	^{e}	^{e}	280	294 (270)	+ 7
IV	302	317 (302)	312	330 (304)	+13
V	313	325 (270)	325	342 (325)	+17
VI	310	326 (310)	324	343 (310)	+17
VII	307	323 (307)	314	340 (307)	+17
VIII	^{e}	293 (270)	302	340 (270)	+47
IX	312	325 (310)	^{e}	^{e}	
X	311	326 (311)	326	342 (310)	+16

[a] Maximum intensity of uncorrected activation spectrum (± 1 nm) recorded on a Hitachi—Perkin—Elmer MPF-2A spectrometer. [b] Maximum intensity of uncorrected fluorescence spectrum (± 2 nm) recorded on H—P—E MPF-2A spectrometer. [c] Excitation wavelength (nm) for fluorescence spectrum. [d] Calculated from fluorescence maxima in acetonitrile (Table 2) minus those in isopentane (Table 1). [e] Not recorded.

TABLE 3

LIPPERT ANALYSIS OF THE SOLVENT EFFECT ON THE STOKES SHIFT OF (N-METHYLANILINO)ETHYLPHENYLBORANE

Molecular parameter	Solvent			
	cyclohexane	isopentane	dichloromethane	acetonitrile
Absorption λ_{max} of VI (nm) ^{a}	294	294	297	297
Absorption λ_{max} of VI (kcal/mol) ^{b}	97.3	97.3	96.3	96.3
Fluorescence λ_{max} of VI (nm) ^{c}	326	327	339	343
Fluorescence λ_{max} of VI (kcal/mol) ^{b}	87.7	87.5	84.4	83.4
Stokes shift (kcal/mol) of VI ^{d}	9.55	9.82	11.93	12.91
Solvent's dielectric constant ^{e}, D	2.023 ^{e}	1.843 ^{e}	9.08 ^{e}	37.45 ^{f}
Solvent's refractive index ^{e}, n_D	1.4266	1.3537	1.4242	1.342
Lippert's Solvent polarity constant ^{g}, Δf	−0.00143	−0.00145	+0.2180	+0.3060

[a] Recorded on a Cary Model 14 spectrometer. [b] Calculated. [c] Recorded on a Hitachi—Perkin—Elmer MPF-2A spectrometer. [d] Calculated, $(\nu_A - \nu_F)$ in kcal/mol. [e] From ref. 35; values at 20° [f] From ref. 36; value at 20°. [g] Calculated from $(D-1)/(2D+1) - (n_D^2-1)/(2n_D^2+1)$ according to Lippert [14].

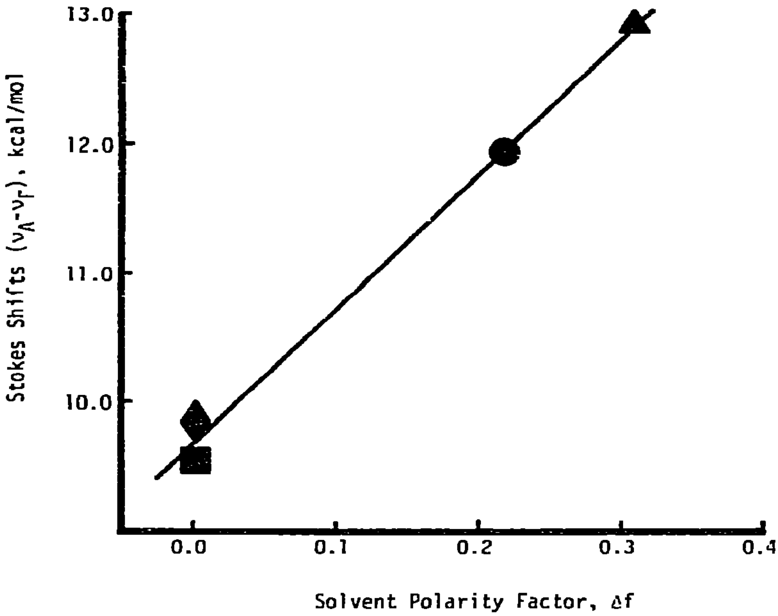


Fig. 4. Lippert plot of the fluorescence Stokes shift as a function of the solvent polarity factor Δf (ref. 14) for cyclohexane (■), isopentane (♦), dichloromethane (●), and acetonitrile (▲).

Emission at 77 K. Fluorescence spectra recorded at 77 K (Table 4) in isopentane glass showed little increased resolution of vibrational fine structure relative to spectra recorded in isopentane solution at 25°. However, shifts of the λ_{max} were noted. Relative to the ambient temperature spectra (Table 1), the *B*-arylated styrene analogs (I-III) showed blue shifts of 1-8 nm at 77 K, whereas the *N*-arylated systems (IV-X) (including both styrene and stilbene analogs) showed red shifts of 5-15 nm at 77 K. The 298-77 K temperature change produced a blue shift (3-30 nm) in the activation spectra of all the aminoboranes.

Neither phosphorescence nor delayed fluorescence were detected for any

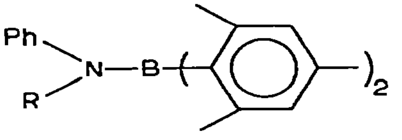
TABLE 4

FLUORESCENCE SPECTRA OF AMINOBORANES [a] AT 77 K IN ISOPENTANE

Compound	Activation max (nm)	Excitation λ (nm)	Fluorescence max (nm)	Polarization (%)
I	267	255	285	13.6
II	267	262	285	15.6
III	264	264	286	13.8
IV	274	300	330	14.3
V	306	250	338	15.2
VI	288	300	337	17.9
VII	280	310	335	15.8
VIII	250	270	298	23.6
X	290	300	334	22.7

[a] Recorded on a Hitachi—Perkin—Elmer MPF-2A fluorescence spectrophotometer for degassed samples.

of the ten aminboranes, despite the report [11], that delayed fluorescence has been observed for the somewhat similar anilinodimesitylboranes (XIIa-c).



(XII)

a, R = H;
b, R = Me;
c, R = Ph

Polarization of the fluorescence at 77 K was measured by the photoselection method [15], with two polarizers separating the sample from the excitation and emission monochromators. By this method, the corrected value of the polarization, $P_{\text{corr.}}$, is given (eqn. 2) as

$$P_{\text{corr.}} = \frac{V_V - L_V(V_H/L_H)}{V_V + L_V(V_H/L_H)}\,, \tag{2}$$

in which V and L are the vertical and horizontal components of the fluorescence, and subscripts H and V are the directions of polarization of the light incident to the sample.

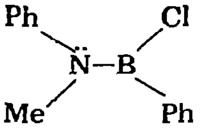
The experimental polarizations (Table 4) ranged from 13.6% for I to 23.6% for VIII, with a typical value of ca. 16%. As a calibration point, the polarization of the ^1L_a transition of phenanthrene was determined. With excitation at 294 nm, the 346 nm emission band at 77 K in isopentane gave −20.0% polarization, compared with a previously reported value of −19.5% [16]. At 330 nm, the measured polarization was +15%, compared with a reported value of +10% [16]. Thus, the aminoboranes all display substantial positive (in-plane) polarization of their fluorescence. However, while the polarization was always positive in all cases, the degree of polarization did vary within the structureless emission band (strongest on the high-energy end) and varied also with the excitation wavelength.

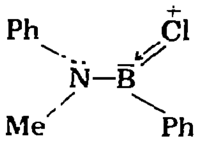
Discussion

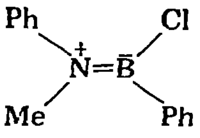
Absorption spectra. General similarity of the electronic absorption spectra of aminoboranes and their olefinic counterparts, a reasonable expectation for the isoelectronic and nearly isosteric [17] (but not isomorphous [18]) chromophores, was experimentally verified in 1961 by Coates and Livingstone [19] for (diphenylamino)diphenylborane (λ_{max} 282 nm, log ϵ 4.3) and tetraphenylethylene (λ_{max} 312 nm, log ϵ 4.1). A superficial similarity is also noticeable in the ultraviolet absorption spectra of (diphenylamino)dimesitylborane (XIIc) and tetramesitylethylene [11]. As the data in Table 1 indicate, the general similarity extends to the absorption spectra of the (phenylamino)phenylboranes (VI-X) and their stilbene analogs. Thus, VI-X have absorption maxima at 294-295 nm (log ϵ 3.2-3.4), which compare closely with the spectrum of *trans*-stilbene (*K*-band, λ_{max} 295 nm [log ϵ 4.4]). Similarity is also seen in the spectra of styrene (maxima at 244 [log ϵ 4.1] and 282 nm [log ϵ 2.7]) and the *B*-aryl aminoboranes (I-III) (maxima at ca. 225 [log ϵ 4.0] and 270 nm [log ϵ 2.6]). However, anilinoborane (IV) (λ_{max} 234 [log ϵ 4.0] and 288 nm [3.3]) and *N*-methylanilinoborane (V) (λ_{max} 243 [log ϵ 4.4] and 295 nm [3.6]) more closely resemble aniline (λ_{max} 230 [log ϵ 3.9] and 280 nm [3.2]) and dimethylaniline (λ_{max} 251 [log ϵ 4.2] and 298 nm [3.4]) than styrene. Becker and Baechle have noted this effect of *N*-phenyl conjugation earlier [20].

Ramsey [21] has assigned the intense, long-wavelength bands (260-280 nm [log ϵ ca. 3]) observed in a series of phenylboranes $\mathrm{Ph_{3-n}BY_n}$ (Y = X, $\mathrm{NR_2}$, OR [22]) to the perturbed ^1L_b benzenoid transition, and the next intense bands (210-250 nm [log ϵ ca. 4]) to a red-shifted ^1L_a transition; rather than to a charge-transfer transition analogous to that seen in triarylboranes [23]. These assignments are in substantial agreement with semi-empirical SCF calculations carried out by Armstrong and Perkins [24], and are directly comparable to the band assignments for the isoelectronic styrene system. The same assignments fit the observed spectra of aminoboranes I-X. However, both ab initio [25] and iterative semi-empirical computations [26,27] suggest the lowest excited state in simple aminoboranes may be σ—π^*. The weak bands which appear in vinylborane absorption spectra at lower energies than the charge-transfer π—π^* transitions [28] have also been explained theoretically as σ_{BC}—π^* [29]. It thus seems reasonable to speculate that the weak, partially-to-completely submerged band on the long-wavelength end of the aminoborane ^1L_b band be assigned to the σ_{BC}—π^* transition. Although an apparently analogous long-wavelength band in the absorption spectrum of (diphenylamino)dimesitylborane (XIIc) was attributed instead to a charge-transfer transition [14], such an assignment seems less suitable for I-X where steric distortions play at most a minor role in the electronic spectra. Unlike XIIc, aminoboranes I-X are probably approximately planar in the ground state (vide infra), a geometry for which the σ—π^* state is predicted to lie lowest at least in the case of the parent molecule, $\mathrm{H_2NBH_2}$ [25-27].

The significant absorption blue shift in (amino)chloroborane (VIII) relative to the other stilbene-like systems is probably a reflection of cross-conjugation involving the halogen substituent; i.e., to the extent that canonical structure VIIIa is important in the ground state of VIII, conjugation through the $\mathrm{N{\rightarrow}B}$ bond (VIIIb) may be reduced. No significant substituent effects were noted for the cyclopropyl, allyl, and but-2-en-1-yl groups in the appropriate aminoboranes.


(VIII)


(VIIIa)


(VIIIb)

Fluorescence spectra. The salient features of the fluorescence spectra of the aminoboranes I-X were that all systems gave structureless emission, with moderate Stokes losses (ca. 8 kcal/mol), red shifts in polar solvents, and posi-

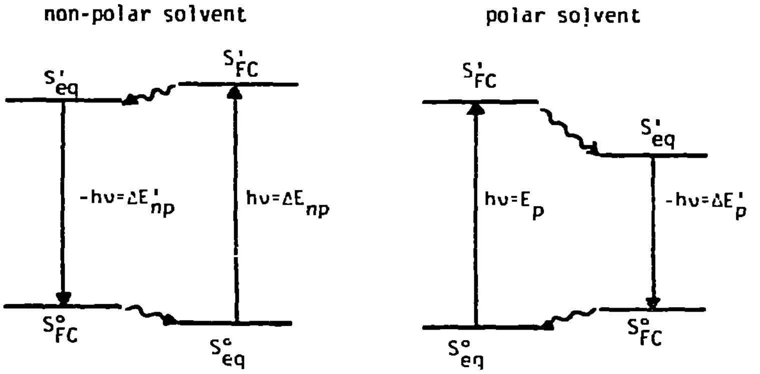
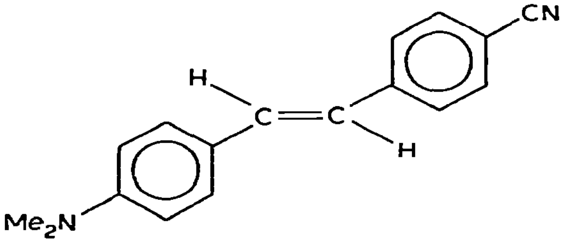


Fig. 5. Schematic energy-level diagram illustrating solvent effects on absorption and fluorescence spectra of aminoboranes. Subscripts p and np refer to polar and non-polar solvents; ΔE refers to absorption transition energy, $\Delta E'$ refers to emission transition energy; S^0 and S^1 refer to ground and lowest excited singlet states; subscripts eq and FC denote equilibrium and Franck—Condon states, respectively.

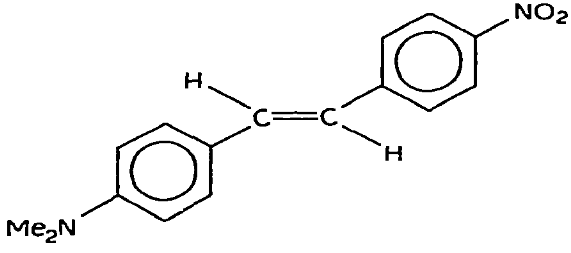
tive, in-plane polarization. The onsets of absorption and emission were approximately coincident, although no mirror-image relationship was noted between the shapes of the absorption and emission spectra. The lack of vibrational structure in the fluorescence and the substantial polar solvent red shifts contrast with the structured absorption, which showed only a minimal shift to lower energy in polar solvents. Taken together, these spectral features of the aminoboranes suggest a picture in which the ground state is approximately planar and relatively non-polar and in which the excited state is much more polar and possibly less rigid.

The solvent effect in such a system is illustrated schematically in Fig. 5. The small absorption red shift ($\Delta E_{np} > \Delta E_p$) in a polar solvent (cf. Table 3: +3 nm for VI) is compatible with increased solute polarity in the excited state, as are the larger emission red shift ($\Delta E'_{np} > \Delta E'_p$) and the increase in Stokes loss ($[\Delta E_p - \Delta E'_p] > [\Delta E_{np} - \Delta E'_{np}]$) with increased solvent polarity. All result from greater stabilization of the more polar solute excited state, in both Franck—Condon and equilibrium solution environments, in the polar solvent.

The aminoboranes' Stokes shifts of 6.7 to 9.8 kcal/mol (Table 1) are comparable in magnitude to the Stokes losses in the styrene and stilbene hydrocarbon analogs [13], which are also thought to have greater polarization in the singlet excited state than in the ground state. The aminoboranes' Stokes shifts are also roughly comparable to those observed in borazaro analogs of aromatic hydrocarbons [30]. The quantitative dependence of the Stokes shift on solvent polarity was analyzed by Lippert's method (cf. Table 3 and Fig. 4). In the case of VI, for example, the Stokes shift ranged from 9.5 kcal/mol in non-polar solvents (e.g., cyclohexane) to 12.9 kcal/mol in a very polar medium (e.g., acetonitrile). The slope (least-squares analysis) of 3.6×10^3 cm^{-1} (10.4 kcal/mol) compares with slopes of 10.5 and 11.0×10^3 cm^{-1} for 4-dimethylamino-4'-cyanostilbene (XIII) and 4-dimethylamino-4'-nitrostilbene (XIV), respectively [14], and with a slope of 22.4 kcal/mol (7.8×10^3 cm^{-1}) for (anilino)dimesitylborane (XIIa) [11]. Similar analysis of IV gave a Lippert plot slope of 8.2 kcal/mol (2.9×10^3 cm^{-1}); however, the *B*-aryl systems (I-III) showed minimal solvent polarity dependence of the size of the Stokes shift.

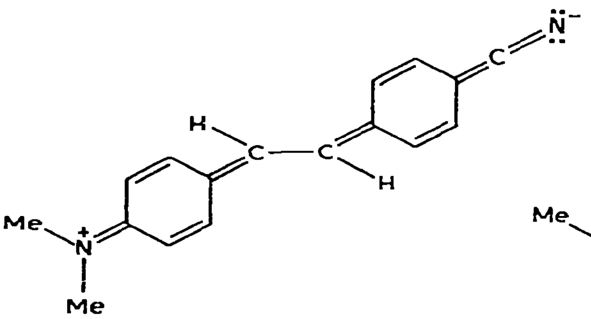


(XIII)

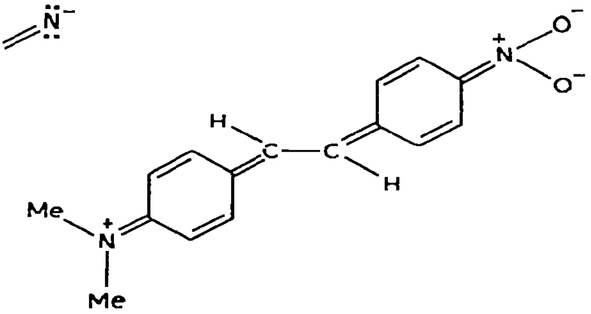


(XIV)

Electronic configuration of the fluorescent singlet. From the known ground-state dipole moments of XIII and XIV (6.1, 7.6 D) and their molecular dimensions, Lippert calculated excited-state moments of 29 and 32 D, respectively. The magnitude of the change in moment between ground and excited states was estimated by Lippert to correspond to ca. a 50% contribution by dipolar forms such as XIIIa and XIVa to the excited state structure [14].



(XIIIa)



(XIVa)

Using the equation developed by Lippert (eqn. 3), dipole moments for the fluorescent excited states of aminoboranes can be similarly calculated from the molecular dimensions and dipole moment of the ground state, and the variation of the Stokes shift with solvent polarity. In this relationship, μ_e and μ_g represent the excited-state and ground-state dipole moments, h is Planck's con-

$$\mu_e - \mu_g = \pm \sqrt{\frac{hcma^3}{2}} \approx \pm\, 0.10\sqrt{ma^3} \tag{3}$$

stant, c is the velocity of light, a is the molecular radius in Å, and m is the slope of the Lippert plot in cm^{-1}.

Dipole moments in aminoboranes are typically small [19,31], reflecting opposing polarizations of the σ (towards N) and π electrons (towards B). Excluding aryl substituent effects, known values range from 1.4 D towards N (dimethylaminodimethylborane [31]) to 1.6 D towards B (dimethylaminodiphenylborane [19]), with nitrogen the negative end of the dipole in the isolated aminoborane chromophore [25,26], where σ-polarization dominates π electron charge-transfer. The dipole moment of VI was estimated from earlier determinations [19,31] and group moments as 1.2 D towards nitrogen*. Dipole moments

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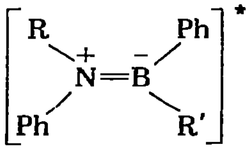
* Dipole moments for VI, VII, IX and X should be quite similar, as their similar Stokes shift solvent dependency indicates.

of the (anilino)dialkylboranes (IV and V) should be larger; those of the (dialkylamino)arylboranes (I-III) would be small and probably towards boron [19]. Using the 1.2 D (towards N) ground-state moment for VI in the Lippert analysis (eqn. 3) leads to a calculated excited-state dipole moment of 5.5 D towards boron[*]. The (anilino)dialkylboranes (IV and V) are also strongly polarized in the excited state. This dramatic shift of polarity in the singlet excited state seems most compatible with the charge-transfer, π—π^* excited state; i.e., substantial contribution to the excited state by a dipolar canonical structure which can be abbreviated as XV. Goodman et al. [32] have also shown that π—π^* excited state moments μ_e are greater than ground-state moments μ_g, and related the moments to the fluorescence and absorption frequency shifts between polar and non-polar solvents by the equation $\mu_e/\mu_g = \Delta\nu_f/\Delta\nu_a$. This analysis leads to the same conclusion: i.e., for IV-X, $\mu_e \gg \mu_g$, implying a π—π^* transition. However, the absence of a Stokes shift solvent effect in the *B*-aryl aminoboranes (I-III) suggests that for these systems, $\mu_e \approx \mu_g$.



(XV)

Even more compelling evidence that the fluorescence involves the π—π^* transition is found in the low-temperature spectra (Table 4). Within the singlet manifold, π—π^* transitions are in-plane polarized, whereas σ—π^*, like n—π^*, transitions are polarized out-of-plane. The strong, positive in-plane polarization of all the aminoborane emission spectra at 77 K requires a dominant π—π^* (charge-transfer) component in the transition and characterizes the emitting singlet state as π—π^*. The lack of fluorescence vibrational band structure, even at 77 K suggests, however, that the π—π^* aminoborane excited singlet may not be rigidly planar.

There is admitted uncertainty in the conclusion that the aminoborane fluorescence in "borazarostyrenes" and "borazarostilbenes" is from a π—π^* state. The red shift of the activation spectra relative to the absorption spectra (ca. 10-20 nm) was suggested to result from a strong σ—π^* excitation component. Molecular orbital calculations on H_2NBNH_2 [25,26] and related (un-arylated) systems [26,27] predicted the lowest excited singlet to be a twisted σ—π^* state, which would be compatible with the lack of vibronic structure to the aminoborane fluorescence spectra. In a twisted conformation, even a small π—π^* component to a state largely σ—π^* in nature could give rise to net in-plane polarization because of the far greater oscillator strength for the former transition. This mixing could acount for the observed variations in the degree of fluorescence polarization.

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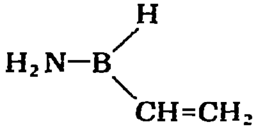
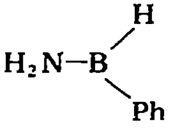
[*] The alternative mathematical solution of eqn. 3, a 7.9 D moment towards nitrogen, does not appear compatible with the charge distribution in either a σ—π^* or π—π^* excited state, since either transition populates an orbital which significantly increases the electron density at boron [25-27]. In either case, however, the excited-state moment greatly exceeds the ground-state moment.

However, CNDO calculations [33] on (amino)phenylborane [4], carried out to probe further theoretically the effect of conjugating substituents on aminoborane energy-level ordering, clearly support the suggestion made earlier [7,27] that conjugation may significantly alter the energies of the σ—π^* and π—π^* transitions. In both (amino)vinylborane (XVI) [27] and (amino)phenylborane (XVII) [4], the σ—π^* state has been raised relative to the parent compound, H_2NBH_2, and the π—π^* state lowered, so that the two are nearly degenerate. In (anilino)phenylboranes, where delocalization is more extensive, the π—π^* state quite possibly lies lower, as also suggested by the apparent burial of the σ—π^* absorption transition under the ^1L_b band. Thus, both theoretical and experimental results suggest the fluorescent state of I-X is best characterized as largely π—π^* (intramolecular charge-transfer), at least for IV-X. For I-III the evidence again favors a π—π^* state, but with less charge-transfer to boron.



(XVI)



(XVII)

From the foregoing, a state diagram can be drawn for the B—N analogs of styrenes and stilbenes (Fig. 6). Two Franck—Condon singlet excited states, S^1_{FC} and S^2_{FC}, are believed to lie close together. The π—π^* singlet, arising from the ^1L_b transition, falls in about 11 kcal/mol range from 93 (stilbene analogs) to 104 (*B*-aryl styrene analogs); it has substantial N-to-B charge-transfer character. The σ—π^* singlet presumably lies at around 95 kcal/mol above S^0. Thus, which singlet actually lies lower probably depends on the identity of an individual molecule. The lowest equilibrium excited state, S^1_{eq}, reached by radiationless internal conversion with accompanying geometric reorganization from S^1_{FC} and S^2_{FC}, lies 83-100 kcal/mol above the Franck—Condon ground state, S^0_{FC}. This fluorescent state is apparently largely π—π^*, with a large intramolecular charge-transfer component; it is probably less rigidly planar than the ground state. The σ—π^* equilibrium excited state, not shown in Fig. 6, presumably lies

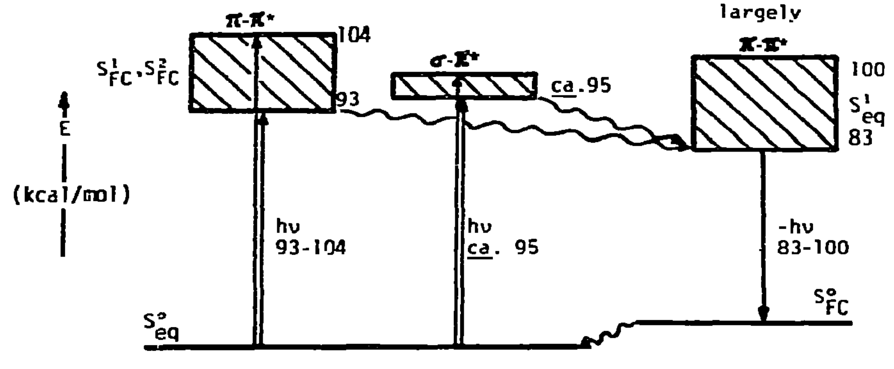


Fig. 6. Schematic state diagram for the lower singlet states of aminoboranes. Subscripts eq and FC refer to equilibrium and Franck—Condon states; superscripts 0, 1, and 2 refer to ground, first (σ—π^*) and second (π—π^*) excited singlet states, respectively.

very close in energy to the π—π^* state; the possibility that S^1_{eq} is even largely σ—π^* cannot be excluded.

The state diagram given in Fig. 6 differs from the one conceived for the (anilino)dimesitylboranes by Glogowski, Grisdale, Williams and Costa [11] in two important respects. The sterically hindered (anilino)dimesitylboranes are believed [11] to be forced into an sp^3 rather than sp^2 hybridization at N in the ground-state and Franck—Condon excited states, causing huge Stokes shifts to accompany reorganization to a planar, charge-transfer, fluorescent equilibrium singlet excited state analogous to the one we propose. A larger geometric change, therefore, must also follow emission as the Franck—Condon ground state of the (anilino)dimesitylborane equilibrates with the environment. The second difference is that the significant absorption transitions are also apparently altered in the (anilino)dimesitylboranes [11]. This change, too, is probably the result of the steric crowding in the (anilino)dimesitylboranes. Thus, our results provide a gauge of what could be called "normal" behavior in phenylated aminoboranes, such as I-X. Against this standard, the Stokes losses in the (anilino)-dimesitylboranes [11] are indeed abnormally enormous. The delayed fluorescence of the (anilino)dimesitylboranes may also be unique; we observed no such emission for I-X.

In conclusion we would note the recent reassignment to a σ—π^* transition of the long-wavelength, low-intensity absorption band in acylsilanes [37]; it would appear that σ—π^* transitions may have more importance in organometallic chemistry than previously supposed.

Experimental

Materials. Cyclohexane (Mallinckrodt spectrograde) was further purified by vacuum distillation over lithium aluminum hydride. Isopentane (Matheson, Coleman and Bell research grade) was washed with concentrated sulfuric acid, then with water, dried over anhydrous sodium sulfate, and refluxed and distilled over sodium. Dichloromethane (Mallinckrodt spectrograde) and acetonitrile (Matheson, Coleman and Bell spectrograde) were used without further purification. Blank tests were run on all solvents before use to ensure no interfering absorption and emission.

The syntheses of the aminoboranes have been described in detail previously [3b,4b]. All were purified by vacuum distillation (immediately before use where necessary), checked for purity by elemental analysis, and stored under argon in sealed ampoules. Periodic checking by NMR of samples so prepared and stored revealed no decomposition or reactions of aminoboranes with solvents. Transfers of materials were carried out in the dry box, with all possible precautions taken to avoid any air contact.

Apparatus and procedures. Absorption spectra were obtained with a Cary model 14 automatic recording spectrophotometer. Fluorescence measurements were made with a Hitachi—Perkin—Elmer MPF-2A fluorescence spectrophotometer which consisted of an Osram 150W high pressure Xenon Lamp, two grating monochromators, and a type R106 photomultiplier tube. Wavelength was calibrated with the 467.1 nm band of the xenon emission. Fluorescence excitation and emission spectra were not specifically corrected for wavelength sensitivity of the photomultiplier tube and the wavelength efficiency of the monochromators, since in a test of instrument response, the recorded MPR-2A emission spectrum of purified aniline (which is similar in wavelength and shape to those of the aminoboranes) compared quite closely with the published corrected spectrum [13]. Excitation wavelengths used were chosen to give the maximum possible emission intensity consistent with reasonable separation of the emission and excitation, and with non-interference by the Rayleigh and Raman light-scattering peaks. The strong emission required very low gain settings on the instrument. Typical concentrations of aminoboranes used were 10^{-4} *M*. Decreasing the concentration of the aminoboranes led to a decrease in the intensity of fluorescence which suggests that, at the concentrations of aminoboranes used, internal filter effects were not important. All measurements at room temperature were made in a 1 cm stoppered quartz cell. Spectra were taken immediately after preparation and outgassing (three freeze-pump-thaw cycles) of the solutions. All spectra were normalized and plotted as relative intensity vs. wavelength. The sample cell for low-temperature fluorescence consisted of a 2 mm ID quartz tube, kept at 77 K by insertion into a quartz Dewar of liquid nitrogen.

Fluorescence polarization for a particular excitation and emission wavelength (usually the maximum wavelength) was determined by the photoselection method [34]. The intensity of emission was recorded with the excitation beam polarizer in a vertical position (0°) and the emission beam polarizer first in a vertical (0°) and then in a horizontal (90°) position. The procedure was repeated with the excitation beam polarizer in the horizontal (90°) position. No correction was applied for depolarization caused by the monochromators and the quartz cell used; nevertheless, the polarization was checked with phenanthrene which showed the right direction and very nearly the same magnitude as in the literature [16].

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