The Si–B chromophore: A joint experimental and theoretical investigation

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ABSTRACT

Silylboranes with aromatic substituents linked to boron and silicon exhibit an unexpected absorption band in the UV–Vis spectral region. When polar groups were introduced, a marked solvatochromic effect was observed in their fluorescence emission spectra, revealing a strong excited state dipole moment. Semi-empirical MNDO/d and AM1 calculations showed that, upon UV excitation, the polarity of the Si–B bond increased and the aromatic π-electrons migrated toward the Si–B bond, consistent with experimental observations.

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1. Introduction

Although the first silylboranes containing trivalent boron and silicon atoms were reported some 40 years ago [1–3], this class of compounds had received little attention until the recent discovery of new chemical properties, coupled with improved synthetic methodologies. In this regard, they provide attractive intermediates for synthesis, *via* regio- and stereospecific addition reactions to various unsaturated substrates, in the presence of transition metal-based catalysts [4–6]. Indeed, they have long been accessible according to limited synthetic routes and a few reports on their physico-chemical properties can be found in the literature. Moreover, theoretical studies have scarcely been published, mainly on perhydrogeno derivatives and very small-sized molecules [7,8]. Because boron is electron-deficient and silicon is electropositive, it is expected that the Si–B bond stability depends mainly on the electronic properties of the substituent groups. Previously reported organosilylboranes were stabilized by electron-donating heteroatoms linked to boron or highly nucleophilic organosilyl groups [9–13]. As boron contains a vacant p orbital and silicon vacant d orbitals, (Pauling electronegativities: B ~ 2.04, Si ~ 1.90), one might consider that hyperconjugative effects involving the Si–B bond presumably occur in the case of electron-rich derivatives. We have previously described the synthesis of silylboranes bearing aromatic groups linked to boron and silicon, where bulky mesityl groups played a crucial role concerning their stabilization [14,15]. Despite their crowded structure, these compounds react smoothly with terminal acetylenic hydrocarbons in the presence

of a Pd₂(dba)₃etpo catalyst [17]. Interestingly, they exhibit an unexpected absorption band in the UV–Vis spectral region. In order to have a better knowledge of these new electronic properties, a study by UV–Vis absorption and fluorescence emission spectroscopy was carried out on organosilylboranes and compared with reference compounds. Herein, we report our results in this domain, as well as a theoretical approach using semi-empirical MNDO/d [17] and AM1 methods [18].

2. Results and discussion

2.1. Organosilylboranes

Organosilylboranes used in this study (Table 1, compounds **1–5**) are distinguishable from the previously published derivatives by the absence of nucleophilic heteroelement bound to the boron atom. Their structures display various aromatic and organic groups bound to silicon, including the strongly electron-withdrawing dimesitylboryl moiety [19,20]. In addition to its steric encumbrement, this group has been previously recognized to induce charge-transfer transitions in organoboranes [21]. Compounds **1–5** exhibited a deep yellow-green fluorescence when dissolved in organic solvents, as well as in the solid state. Most of them were stable for months at room temperature under inert atmosphere in the dark, but were very sensitive to visible light, rapidly decomposing into non-identified by-products, probably issued from the Si–B bond cleavage [22].
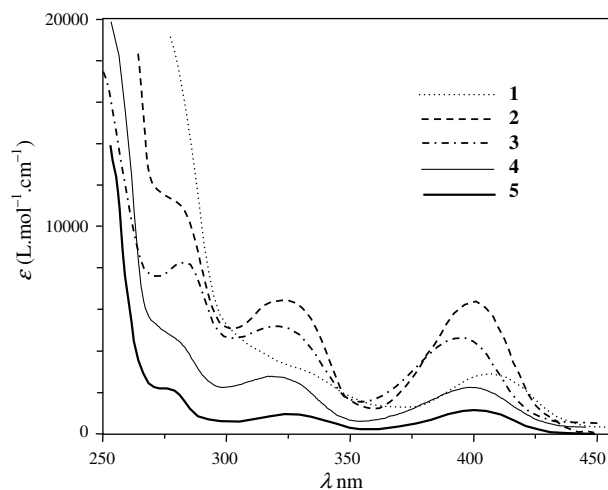
2.2. UV–Vis absorption spectra

UV–Vis absorption spectra of organosilylboranes **1–5** recorded in non-polar *n*-hexane are shown in Fig. 1, and the absorption

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Table 1
Organosilylboranes (**1**–**5**) and reference compounds (**6**,**7**)

Formula	R groups	Compound number
Ph\Ph—Si—B/Mes, R^1 /\ Mes	R^1 = Me	1
	R^1 = Ph	2
	R^1 = Mes	3
	R^1 = p-Me$_2$NC$_6$H$_4$	4
	R^1 = tert-Bu	5
Ph$_3$SiMe		6
PhBMes$_2$		7

Mes, mesityl.

Fig. 1. UV–Vis absorption spectra of organosilylboranes **1**–**5** (solvent: n-hexane).

Fig. 2. UV–Vis absorption spectra of reference compounds **6** and **7** and of their equimolar mixture (solvent: n-hexane).

Table 3
Absorption maxima (λ_{max}) of organosilylboranes **1**–**5** in solvents of different polarities ($C = 5.0 \times 10^{-5}$ M)

Solvent	Dielectric constant (ε_r)	λ_{max} (nm)				
		1	2	3	4	5
Cyclohexane	2.023	401	405	397	409	401
Benzene	2.284	402	405	397	411	402
Chloroform	4.335	401	405	397	409	402
Diethyl ether	4.806	401	404	397	410	–
Acetonitrile	37.50	401	403	396	409	402

2.3. Fluorescence emission spectra

The fluorescence emission spectra of silylboranes were recorded at room temperature (excitation at 400 nm) using degassed solutions maintained in the dark before measurements, because of their high photosensitivity (a partial degradation of the compounds was observed upon light exposure, ca. 10 min, at the 400 nm excitation wavelength of the spectrometer). The fluorescence emission maxima for **1**–**5** are listed in Table 4. The fluorescence spectra displayed a weak, non-structured band (quantum yields Φ_F (±15%) **1**: 3×10^{-3}, **2**: 8×10^{-3}, **4**: 2×10^{-3}, **5**: 6×10^{-3}) with a maximum dependent on the compound and the solvent. As an illustration, the spectra of **1** and **2** are shown in Fig. 3. The excitation spectra monitored at different emission wavelengths were similar and matched the absorption spectra, proving that the organosilylborane structure was at the origin of the fluorescence. With respect to the absorption spectra (Table 2), the maxima of the long-wavelength emission shifted by values ranging from 2959 cm^{-1} for **5** to

bands maxima and molar extinction coefficients are listed in Table 2. The spectra of the reference compounds Ph$_3$SiMe (**6**) and PhBMes$_2$ (**7**), recorded under the same experimental conditions, are given in Fig. 2. Compared with the reference compounds **6** and **7**, the spectra of the silylboranes display an additional absorption band maximum around 400–410 nm. As the spectrum of an equimolecular mixture of **6** and **7** corresponds closely to the sum of the individual spectra, it appears that the extra absorption band for compounds **1**–**5** is specific to the organosilylboranes and is due to the presence of the Si–B bond. The electronic absorption spectra, especially the band localized at 400–410 nm were not sensitive to the polarity of the solvent, even for compound **4** bearing a strong electron-donating p-dimethylaminophenyl substituent on the silicon atom (Table 3). This shows that the dipole moment of organosilylboranes in the ground state is rather weak and may be neglected for the estimation of the dipole moment in the excited state (vide infra) in the presence of solvent.

Table 2
Absorption maxima (λ_{max}) and molar extinction coefficients (ε) of organosilylboranes (**1**–**5**) and reference compounds (**6**,**7**), (solvent: n-hexane)

Compound number	λ_{max} (nm)	ε (L Mol^{-1} cm^{-1})
1	401	1510
2	405	4530
3	397	3770
4	409	3730
5	401	1460
6	270	–
7	325	–

Table 4
Fluorescence emission maxima (λ_{max}^{fluo}) of compounds **1**, **2**, **4** and **5** (excitation wavelength λ_{exc} = 400 nm) in solvents of increasing polarity

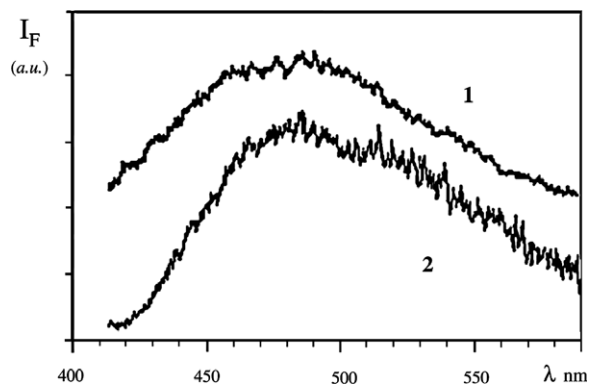| Solvent	ε_r (20 °C)	Δf	λ_{max}^{fluo} (nm)			
			1	2	4	5
Cyclohexane	2.023	0.098	486	480	480	455
Benzene	2.284	0.109	487	480	525	456
Di ethyl ether	4.335	0.251	491	492	560	–
Chloroform	4.806	0.252	492	495	580	–
Tetrahydrofuran	7.500	0.309	–	–	–	457
Dichloromethane	9.080	0.319	–	–	–	457
Acetonitrile	37.50	0.393	495	515	620	457

Fig. 3. Corrected fluorescence spectra of compounds **1** and **2** in degassed cyclohexane at room temperature (λ_{exc}: 400 nm, $C = 1.0 \times 10^{-5}$ M).

Fig. 5. Normalised fluorescence emission spectra of **4** in solvents of different polarity (λ_{exc} = 400 nm), $C \approx 1.0 \times 10^{-5}$ M in each solvent.

4360 cm^{-1} for **1** in cyclohexane, the Stokes shift increasing with the solvent polarity (vide infra). The fluorescence emission spectra of the reference compounds (λ_{exc}: 300 nm in cyclohexane) showed a non-structured band peaking at 320 nm for **6** and 370 nm for **7**, respectively (Fig. 4). Besides, the spectrum of an equimolecular mixture of compounds **6** and **7** correspond closely to the envelope of the sum of the individual spectra of the two components. Unlike silylboranes, no band peaking at longer wavelength (above 400 nm) could be detected, corroborating the intramolecular origin of the spectroscopic properties of compounds **1**–**5** and ruling out any intermolecular process. The emission maxima wavelengths of silylboranes **1**, **2**, **4** and **5**, as well as the dielectric constant ε_r, the optical refractive index n of the solvent and the polarity factor Δf [23,24] of the solvents are listed in Table 4. Unlike the absorption spectra, the fluorescence spectra were found to be very sensitive to the polarity of the solvent and the nature of the substituents. Thus, a significant red shift was found for compounds **1** and **2**, which contained aromatic groups, while a weaker effect was observed for **5** that incorporated a bulky *tert*-butyl group, which probably perturbed the global electronic effect on the silicon atom. Interestingly, a very large solvatochromism was revealed for compound **4** that differed from the other derivatives by the presence of the strong electron-donating *p*-dimethylaminophenyl group. The emission band was shifted by 4700 cm^{-1} (λ shift $\approx$140 nm) from cyclohexane to acetonitrile (Fig. 5) and the Stokes shift reached 8320 cm^{-1} in acetonitrile (λ shift $\approx$210 nm). These results clearly underline the charge transfer nature of the long-wavelength emission. The excited state's dipole moment μ_{ct} could be evaluated by the following equation that was derived from the Lippert–Mataga relationship [25]:
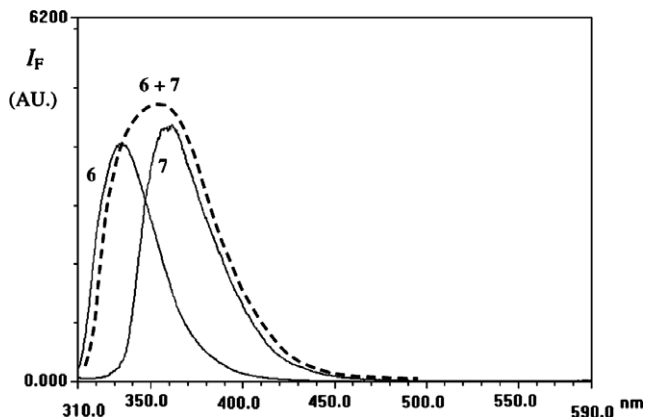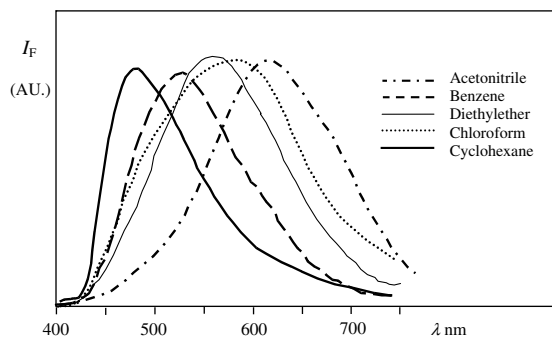
$$\tilde{v}_{ct} = \tilde{v}_{ct}(0) - \frac{2\mu_{ct}^2}{hca^3}\Delta f + \text{constant}$$

where $\tilde{v}_{ct}$ is the wavenumber of the maximum of the lowest energy fluorescence in a given solvent; $\tilde{v}_{ct}(0)$ is the wavenumber of the maximum in vacuum; h, the Planck's constant; c, the light velocity; a, the Onsager radius of the cavity in which the fluorophore resides and Δf, the solvent polarity parameter, derived from its dielectric constant ε_r and its optical refractive index n, according to: $\Delta f = \frac{\varepsilon_r - 1}{2\varepsilon_r + 1} - \frac{n^2 - 1}{4n^2 + 2}$.

Thus, the variation of the dipole moment values (in Debye) between the excited state and the ground state $\Delta\mu = \mu_{ct} - \mu_0$ (which can be assimilated to μ_{ct}, if we assume that the dipole moments of all the molecules in the ground state μ_0 are negligible, vide supra) were estimated from the slopes of the straight lines drawn after plotting the emission maxima wavenumbers $\tilde{v}_{ct}^{max}$ against Δf (Fig. 6). Taking the Onsager cavity radius a equal to 6.62 Å for the fluorophore [15], the dipole moment enhancement $\Delta\mu$ varied from 3.1 D for compound **5** to 19.6 D for compound **4** (Table 5). These values are consistent with the behaviour of the electron-donating groups attached to Si and B atoms, leading us to infer that a significant charge redistribution occurred upon UV excitation [25], which could in turn explain the weakening of the Si–B linkage in the presence of visible light.

2.4. Theoretical study

The rare theoretical studies on silylboranes consist mainly in ab initio and DFT methods devoted to the simplest hydrogenosilylboranes, with the objective of determining the geometries, energetics and spectroscopic characteristics [7,8]. For our part, we have reported recently on a detailed experimental and theoretical IR study concerning various series of organosilylboranes [26]. Due to the
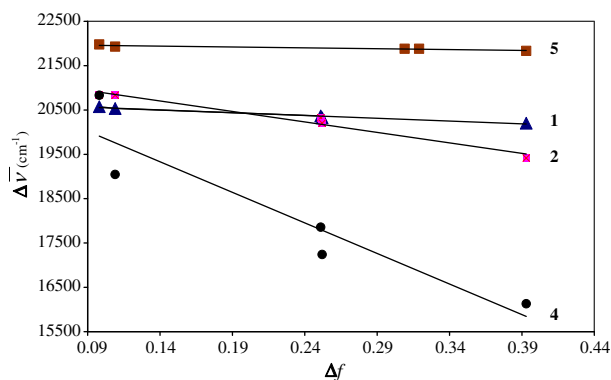

Fig. 4. Fluorescence emission spectra of reference compounds **6** and **7** (λ_{exc} = 300 nm, solvent: cyclohexane).

Fig. 6. Plots of the emission maxima wavenumbers of compounds **1**, **2**, **4** and **5** vs. the polarity factor of solvents Δf (room temperature).

Table 5
Augmentation of dipole moments ($\Delta\mu$) of organosilylboranes in the excited state

Compound	1	2	4	5
Slope (cm^{-1})	−1251	−4726	−13785	−388
$\Delta\mu$ (D)	5.8	11.5	19.6	3.1

Table 6
Comparison between theoretical and experimental results concerning some spectroscopic properties of silylboranes 1–5

Compounds studied	Exp. λ (nm)[a]	MNDO/d, λ (nm)	Oscillator strength	MNDO/d, μ_0 (D)[b]	MNDO/d, μ^* (D)
1	401	384	0.10	0.53	0.21
2	405	382	0.10	0.51	0.41
3	397	381	0.09	0.37	0.64
4	409	389	0.23	1.95	3.48
5	401	387	0.08	0.45	0.25

[a] Solvent: cyclohexane.
[b] The quantities μ_0 and μ^* are, respectively, the calculated dipole moments in the singlet electronic ground state and in the singlet electronic excited state associated with the allowed vertical transition characterized mainly by an HOMO → LUMO transition ("vertical" means: no geometrical optimization in this state).

large number of atoms in the compounds of interest, semi-empirical approaches were employed [27]. In particular, the MNDO/d approach was considered most appropriate because silicon contains d orbitals. Indeed, MNDO/d could be successfully used to describe geometrical and electronic structures, IR vibrational frequencies of these derivatives, including the Si–B stretching vibration band in molecules containing a large number of atoms as previously shown [15,26]. Calculations were also performed using another semi-empirical method: AM1 [18]. This method does not consider d orbitals, but is well known to be a reliable approach to describe interatomic interactions between non-linked atoms. We obtained similar qualitative results from both methods, showing that d orbitals do not play a major role in this case and more importantly lends weight to our conclusions concerning electronic changes under irradiation. The optimization of the molecular geometries was performed by using simulated annealing in a first step [28], and the Newton–Raphson method to refine the results in a second one. The corresponding energy values were calculated at the lowest Hartree–Fock MNDO/d (and AM1) fundamental singlet state. Equilibrium geometries have been obtained at the Hartree–Fock MNDO/d (and AM1) levels [17,18]. In order to keep the ground state energetically unchanged (according to the Brillouin theorem), we performed suitable configuration interaction (CI) calculations based on monoexcitations only, using the set of orbitals including the 20 highest occupied MO and the 20 lowest virtual MO. This CI calculations show the occurrence of an allowed electronic transition in the 400 nm range, in accordance with the experimental spectra (Table 6) within a systematic difference of roughly 20 nm with MNDO/d results. A thorough analysis of the corresponding wavefunctions leads to the conclusion that this transition should be mainly assigned to an Si–B HOMO–LUMO excitation. It is interesting to note that the HOMO–LUMO energy difference $\varepsilon_{LUMO} - \varepsilon_{HOMO}$ varies in the same order as the transition energies across this series of five compounds. As expected, the smallest $\varepsilon_{LUMO} - \varepsilon_{HOMO}$ difference (0.252 + 8.246 = 8.498 eV) corresponds to compound 4 which exhibits the largest absorption wavelength. It is clear that this spectroscopic behaviour is chiefly governed by the frontier orbitals.

Analysis of the electronic distributions of the HOMO and the LUMO shows that, for all the compounds, except molecule 4 which contains an amino-phenyl substituent, the HOMO electronic density is mainly localized on the Si–B bond and on the mesityl groups linked to the boron atom (Fig. 7). The LUMO electronic density is mainly located on the phenyl groups linked to the silicon atom
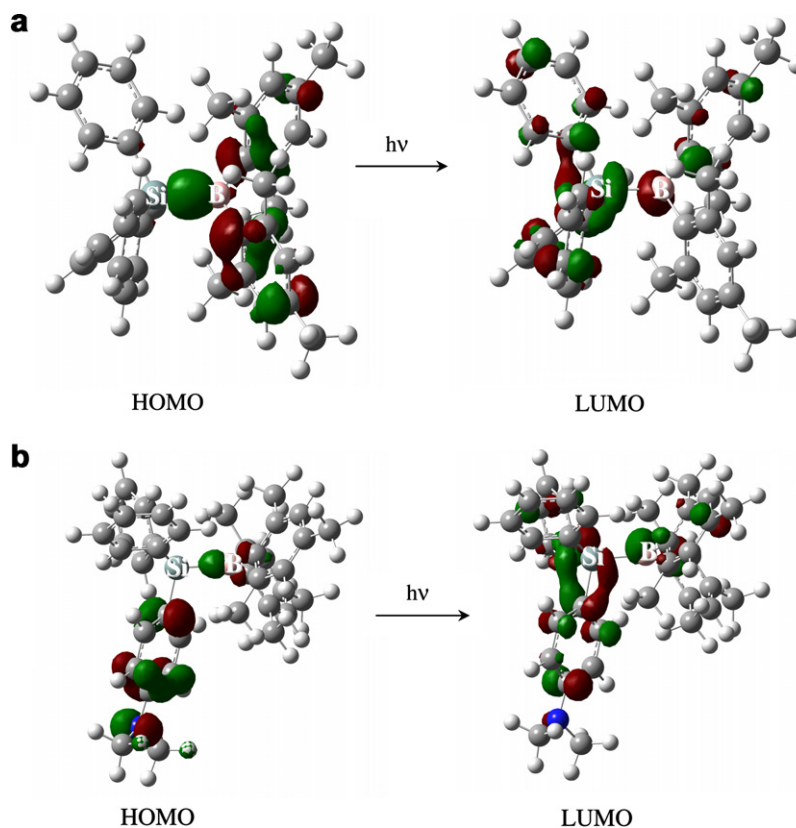
Fig. 7. Calculated distribution of charge densities in the ground and excited states: (a) compound 2, (b) compound 4.

and the antibonding character of the Si–B bond is apparent. Fig. 7a illustrates this behaviour in the case of compound **2**. In the case of compound **4**, while the bonding character of the Si–B part of the HOMO still exists, the electronic density is also located on the amino phenyl group rather than on the mesityl groups (Fig. 7b). In the LUMO, an electronic transfer towards the silicon atom is observed and again the antibonding character of the Si–B orbital part is apparent. This behaviour leads to the fact that the optical Si–B HOMO–LUMO transition probably accounts for the poor stability of the molecule upon visible light irradiation.

This HOMO/LUMO analysis, coupled with the calculation of the electric dipole moments of compounds **1–5** in the ground state and in the relevant excited state (Table 6), shows clearly the specific behaviour of compound **4** for which the nature of the transition is somewhat different from the other molecules and explains its peculiar solvatochromism. Although the calculated dipole moments correspond to molecules in a vacuum, it is clear that the largest electronic change upon irradiation is due to the aminophenyl group of compound **4**. One might expect that similar calculations in the presence of a very polar solvent like acetonitrile would lead to a much larger value of this dipole moment in the singlet excited state, as the application of the Lippert–Mataga relationship showed.

3. Conclusion

Organosilylboranes containing aromatic groups linked to silicon and boron exhibited absorption bands with maxima around 400 nm. The maxima of fluorescence emission were substantially shifted, showing an important Stokes effect. Unlike their absorption spectra, the marked solvatochromic effect observed in the fluorescence emission spectra, which is dependent on the presence of polar groups, led to the conclusion that a strong charge transfer occurred in the excited state. Additionally, this study allowed the excited state dipole moment to be estimated for each compound. Semi-empirical calculations were in good agreement with experimental results. This study has shown that the spectroscopic properties and photo-stability of these organosilylboranes are to a large extent due to the Si–B chromophore, specifically a HOMO–LUMO transition, which in turn weakens the Si–B bond during the excited state lifetime.

4. Experimental

4.1. Samples and solvents

The synthesis of organosilylboranes and reference compounds has been reported elsewhere [14,16]. All the samples were prepared and kept under argon in the dark. Spectroscopy grade solvents were used for the UV–Vis and fluorescence studies.

4.2. Spectral measurements

The UV–Vis absorption spectra were recorded on a HITACHI U-3300 spectrometer (samples concentrations C ranged from $C = 1.0 \times 10^{-5}$ to 8.4×10^{-5} M). The emission spectra were recorded on a HITACHI F-4500 spectrofluorimeter ($C = 1.0 \times 10^{-5}$ M).

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