

# First evidence of visible-range absorbing Si–B chromophores

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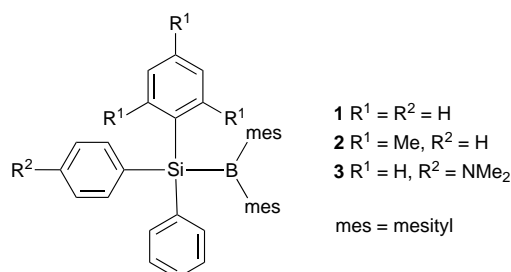
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Novel aromatic silylboranes involving trigonally bonded boron display absorption and fluorescence emission in the visible range due to the Si–B bond; these results are supported by MNDO calculations.

We have recently described the synthesis and characterisation of novel organosilylboranes (compounds **1–3**) possessing a dimesitylboryl moiety linked to a triarylsilyl group.<sup>1</sup>



Surprisingly, these reasonably stable silylboranes strongly absorb in the visible region as evidenced by their yellow or yellow–green colour. Meanwhile, it has been pointed out by others<sup>2</sup> that a toluene solution of a bis(amino)silylene–tris(pentafluorophenyl)borane adduct exhibits a deep yellow colour. This Lewis adduct slowly isomerizes into a new silylborane possessing a trigonally bonded boron, but no information was given concerning the origin of the coloration of this compound. Here we report our preliminary results demonstrating the close connection between the electronic absorption and fluorescence emission properties of silylboranes and the presence of the Si–B bond.

The UV spectra of organosilylboranes **1–3** and two reference compounds, Ph<sub>3</sub>SiMe **4** and (mes)<sub>2</sub>BPh **5** in a non-polar solvent, are shown in Fig. 1. Compounds **1–3** display a broad absorption band around 400 nm which is independent of the concentration. This band does not appear in phenylsilanes and phenylboranes which usually present λ<sub>max</sub> at appreciably shorter wavelengths.<sup>3,4</sup> Thus, the UV spectra of both reference compounds **4** and **5** in *n*-hexane (insert of Fig. 1) only exhibit absorption bands around 270 and 320 nm, respectively, and the spectrum of an equimolar mixture of these two compounds roughly corresponds to the sum of the spectra of each component. Therefore, the new band peaking in the visible range for derivatives **1–3** is due to the presence of the Si–B bond.

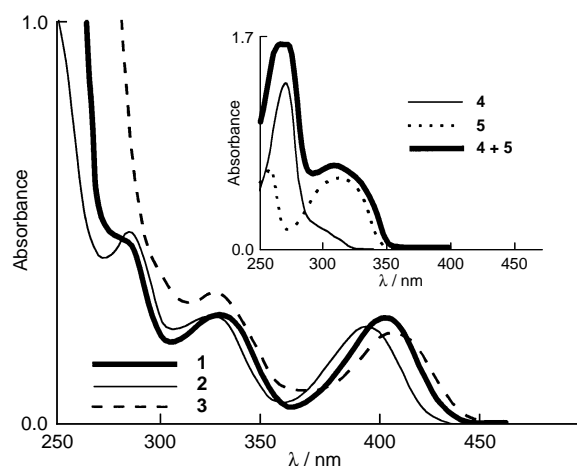
Interestingly, this long-wavelength absorption shifts from 397 nm for **2** to 405 nm for **1**. This bathochromic effect might be connected to a stronger interaction between boron and silicon in **1**. For **3**, a marked bathochromic effect is revealed (λ<sub>max</sub> = 409 nm), anticipating a much larger interaction between Si and B: the presence of the dimethylamino group probably augments the electron-donating ability of the silyl group to boron. This is consistent with the strong electron-acceptor ability of the

dimesitylboryl group which was reported to behave in an analogous manner to a nitrile one.<sup>5</sup> Likely, these electronic factors might contribute to increase the electron density on the Si–B link and therefore the strength of this bond. The UV absorption spectra of compounds **1–3** are weakly sensitive to the polarity of the solvent, suggesting that their ground state does not exhibit a significant charge-transfer character.

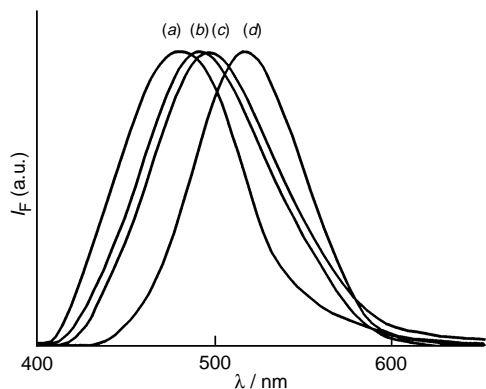
The fluorescence emission of compounds **1–3** is characterised with a low fluorescence quantum yield (Φ<sub>f</sub> ca. 5 × 10<sup>−3</sup> for **1**) indicating efficient non-radiative deactivation pathways for the singlet excited state. Upon excitation at 300 nm, **1–3** display two fluorescence emission bands (λ<sub>max</sub> ca. 340 and 480 nm) and only one (ca. 480 nm) upon excitation at 400 nm. On the other hand, the two reference compounds **4** and **5** present an emission band at 320 and 370 nm respectively, when excited at 300 nm. Addition of their spectra results in a broad band around 350 nm, which roughly matches the position of the high energy band observed for organosilylboranes **1–3** when excited at the same wavelength. Therefore, the second emission band at 480 nm can be attributed to the Si–B chromophore. Moreover, excitation spectra recorded in the 480 nm region indicate that an efficient intramolecular energy transfer occurs from aromatics to the Si–B bond.

The fluorescence emission spectra of **1** in solvents of increasing polarity are shown in Fig. 2.

In contrast to the UV absorption, the fluorescence emission of compounds **1–3** is very sensitive to the polarity of the solvent (Table 1). Thus, a marked solvatochromic effect is found for compound **1**, even stronger for **3**, as the values of λ<sub>max</sub> shift from



**Fig. 1** Electronic absorption spectra of organosilylboranes **1–3** in *n*-hexane, room temp., conc. 5.8 × 10<sup>−5</sup> (**1**), 6.4 × 10<sup>−5</sup> (**2**) and 8.4 × 10<sup>−5</sup> M (**3**). Insert: spectra of the reference compounds in *n*-hexane, room temp., conc. 7.7 × 10<sup>−5</sup> (**4**), 8.4 × 10<sup>−5</sup> (**5**) and 4.1 × 10<sup>−5</sup> M for each component of the mixture **4 + 5**.



**Fig. 2** Emission fluorescence spectra of **1** in various solvent ( $\lambda_{\text{exc}} = 400$  nm): *n*-hexane (a); diethyl ether (b); chloroform (c); acetonitrile (d)

480 nm in *n*-hexane to 640 nm in acetonitrile. From the relationship<sup>6</sup> between the variation of  $\nu_{\text{max}}$ , the polarity factor  $\Delta f$ , and the radius of the solvent cavity  $\rho$  (estimated from space-filling molecular models), it is possible to estimate the dipole moment  $\Delta\mu$  in the excited state (on the assumption that  $\mu \approx 0$  in the ground state).<sup>7-9</sup> The calculated values are relatively high as they range from 11.3 D (**1**) to 19.5 D (**3**), pointing out the large charge-transfer character of the fluorescent excited singlet state.

To rationalise the photoelectronic properties of silyboranes **1-3**, MNDO/CI (single excitations and single and double excitations CI) calculations<sup>10</sup> based on 10 occupied and 10 unoccupied MOs around the Fermi level have been performed on **1**, **4** and **5**, using the AMPAC program.<sup>11</sup> In reference compounds **4** and **5**, theoretical singlet absorption wavelengths  $\lambda$  and relative oscillator strengths  $f$  (**4**:  $\lambda = 225$  nm,  $f$  ca. 1.5; **5**:  $\lambda = 260$  nm,  $f$  ca. 0.25;  $\lambda = 230$  nm,  $f$  ca. 0.5) appear to be in good semi-quantitative agreement with the experimental spectra shown in the insert of Fig.1, although the theoretical wavelengths are systematically blue-shifted by ca. 50 nm with respect to the experimental ones. Similar determinations performed on **1** reveal three singlet absorptions: 357 (0.08), 296 (0.08) and 233 nm (1.03) which are in good agreement with the

**Table 1** Maxima of the fluorescence emission bands of compounds **1** and **3** vs. polarity of the solvent ( $\lambda_{\text{exc}} = 400$  nm, room temp.)

Solvent	$\Delta f^a$	$\lambda/\text{nm}$	
		<b>1</b>	<b>3</b>
Cyclohexane	0.09	480	480
Benzene	0.10	480	525
Diethyl ether	0.25	492	560
Chloroform	0.25	495	580
Acetonitrile	0.39	515	640

<sup>a</sup>  $\Delta f = f - \frac{1}{2}f'$ ;  $f = (\epsilon - 1)/(2\epsilon + 1)$ ;  $f' = (n^2 - 1)/(2n^2 + 1)$ .

experimental spectrum (Fig. 1) within the 50 nm blue-shift range. Analysis of the relevant wavefunctions shows that (i) in **4**, the 225 nm transition corresponds to a  $\pi-\pi^*$  excitation involving the aromatic rings, the positively charged silicon atom being unchanged by this transition; (ii) in compound **5**, the 260 and 230 nm transitions are associated with a significant electronic transfer from the phenyl and mesityl groups to the boron atom (slightly positively charged in the ground singlet state); and (iii) in **1**, the first band (357 nm) corresponds to a noticeable charge transfer from silicon to boron atom, the second one (296 nm) to a transfer from mesityl groups to boron atom and the third one (233 nm) to a  $\pi-\pi^*$  excitation in the aromatic rings with a slight electronic depletion on silicon atom. Analogous studies using the MNDO/d method,<sup>12</sup> which take into account Si d atomic orbitals, do not qualitatively change these results.

To examine the role of the solvent polarity on the emission spectrum of **1**, calculations have also been performed on UV absorption and emission transitions with a continuum solvation model, the COSMO approach,<sup>13</sup> coupled to the MNDO/CI method. It turns out that the theoretical absorption spectrum of **1** is unaltered by the presence of a polar solvent, even a very high polar one like acetonitrile. Conversely, calculation indicates a bathochromic shift on the emission spectrum. This result is in excellent accord with the experimental findings.

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## Footnote and References

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