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SHORT COMMUNICATION

TWISTED INTERNAL CHARGE TRANSFER EMISSION IN B,B-BIS(MESITYL)PYRROLOBORANES

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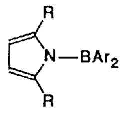
ABSTRACT

Spectral characteristics of several simple substituted B,B-bis(mesityl)pyrroloboranes are reported which support a theoretical treatment by Bonacic-Koutecky and Michl (*J. Am. Chem. Soc.* **107**, 1765 (1985)) describing the excited states of simple aminoboranes as an example of twisted internal charge transfer. In the aminoboranes the pyrrolo moiety functions as the electron donor group and the empty *p*-orbital of the boron atom as the acceptor.

The phenomenon of dual emission,[1] once thought to be anomalous, is in fact ubiquitous.[2] Organic donor–acceptor systems, D–A, often exhibit such behavior. Franck–Condon excitation of these systems gives an excited state (D–A)$_1^*$ which is highly polar but whose geometry is near that of the ground state. For appropriate D–A materials, a second state (D–A)$_2^*$ can be attained by geometry change, for example a rotation or pyramidalization process. The second state is best described as a fully charge separated ionic state $(D^+–A^-)^*$. A prototype of this phenomenon is *p*-dimethylaminobenzonitrile (D = Me_2N; A = PhCN). More subtle examples range from the exceedingly simple case of twisted C—C double bonds (sudden polarization[3]) to the highly organized systems represented by photosystem II in green plants and by the isomerization of the pigment of the visual process[4].

A computation by Michl and Bonacic-Koutecky[5] has addressed the case of twisting in the excited states of aminoborane, an isoelectronic counterpart of the sudden polarization phenomenon in olefins. We report the observation of spectral characteristics of several simple substituted B,B-bis(mesityl)pyrroloboranes, **1**, which support the theoretical picture. In the aminoboranes **1**, the pyrrolo moiety functions as the electron donor group and the empty *p*-orbital of the boron atom as the acceptor.



1 a, R = H
b, R = Me

Ar = Mesityl

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Pyrroloboranes **1** were synthesized by stoichiometric reaction of potassio pyrrole derivatives with fluoro-B,B-bis(mesityl)borane. Compounds were purified by repeated crystallization. The compounds are air stable. The ground state of colorless **1a** is probably planar with a small degree of N->B double bond character: $\nu_{B—N} = 1313\,cm^{-1}$; $\delta(^{11}B) = 53{\cdot}9\,ppm$; $\delta(^{14}N) = 181\,ppm$; $\delta(^{13}C) = 136{\cdot}4\,ppm$ (for the carbon bonded to boron); uv in hexane (λ, ε) 271, 15,200), in ethanol 272 (13,200). Pale yellow compound **1b** may be slightly skewed from planarity in the ground state: $\nu_{B—N} = 1294\,cm^{-1}$; $\delta(^{11}B) = 56{\cdot}4\,ppm$; $\delta(^{14}N) = 177\,ppm$; $\delta(^{13}C) = 139{\cdot}3\,ppm$ (carbon bonded to B); uv in hexane (λ, ε) 290 (17,300), 350 (730, sh) and in ethanol 290 (16,700), 350 (710, sh). The appearance of the new absorption near 350 nm in **1b** can be interpreted in terms of Michl's treatment to directly support the idea of significant ground state twisting in this molecule.[5]

Fluorescence spectra of **1a** and **1b** in a nonpolar (*n*-hexane) and a polar (acetonitrile) solvent are shown in Figure 1. Spectral maxima in these and other solvents are listed in Table 1. In all solvents, absorption and emission bands are observed at short wavelength (absorption near 280 nm and emission near 325 nm) independent of solvent polarity. At longer wavelengths, a

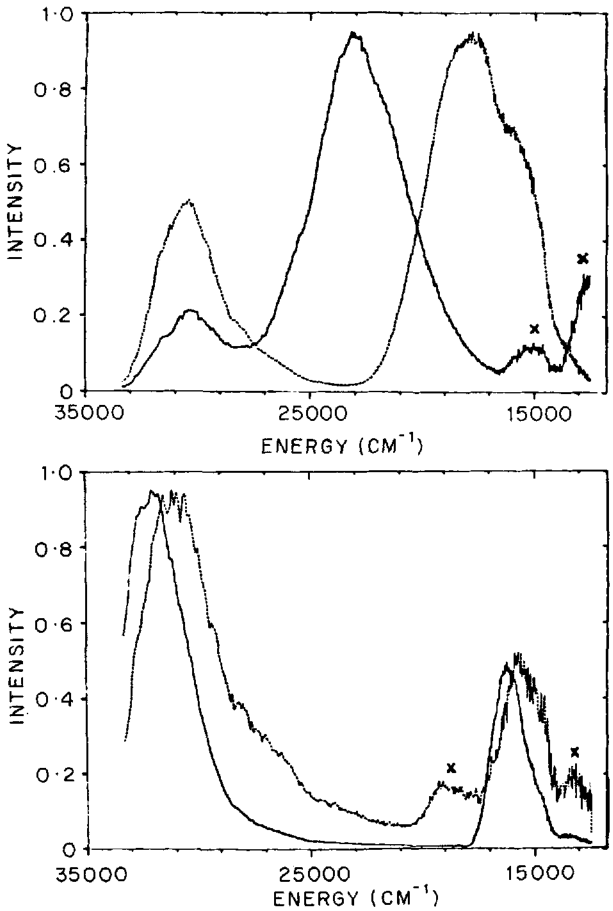

Figure 1. Fluorescence spectra (excitation 270 nm) of **1a** (——) and **1b** (– – –) in *n*-hexane (top spectra) and acetonitrile (bottom spectra) solvent. The features marked × are second order peaks. Intensities are relative only

Table 1. Absorption and emission data for pyrroloboranes **1a** and **1b**

Compound	Solvent	Absorption		Emission	
		λ_{max} (nm)	ε(l/m · cm)	Band 1	Band 2
1a	*n*-hexane	276	1·71 × 10^4	326	429 (0·39)[a]
		212	4·1 × 10^4		
	dioxane	276	6·18 × 10^4	316	478 (0·13)
		240	7·08 × 10^4	326	
	CH_2Cl_2	276	3·86 × 10^4	326	483 (0·25)
		232	3·90 × 10^4		
	CH_3CN	274	1·02 × 10^4	312	623 (8)
		206	4·84 × 10^4		
1b	*n*-hexane	292	1·42 × 10^4	326	536 (1·5)
		212	4·00 × 10^4		
	dioxane	294	1·52 × 10^4	327	~580 (5)
		240	8·1 × 10^3		
	CH_2Cl_2	294	2·00 × 10^4	318	635 (9)
		232	2·31 × 10^4		
	CH_3CN	286	4·66 × 10^4	316	662 (8)
		206	4·96 × 10^4		

[a] The number in parenthesis is the approximate ratio of the area of band 1 emission to band 2.

new emission band (or series of bands) is observed which shifts to significantly longer wavelength as solvent polarity is increased. In all cases, the emission of **1b** is at longer wavelength than **1a** in the same solvent. The relative yield of the red emission (band 2) decreases compared to the short wavelength emission (band 1) as solvent polarity increases, and the total emission yield is qualitatively much smaller in polar solvents than in the nonpolar ones. Absolute emission yields were determined for **1a** and **1b** in *n*-hexane to be 0·038 and 0·023, respectively (emission lifetimes were obtained by single photon counting techniques, for a description of our apparatus see Reference 6). Lifetimes in the same solvent were 9·7 ns (320 nm) and 11·2 ns (430 nm) for **1a** and 11·3 ns (320 nm) and 14·0 ns (520 nm) for **1b**. We note that the lifetime determined is apparently independent of which emission band is monitored. TICT emission lifetimes are kinetically correlated (Reference 2, and references therein). Our lifetime data was adequately fitted to single exponential decays in the temperature range examined in this work. Further data will elaborate this point. We were unable to determine emission lifetimes for **1b** in any of the more polar solvents (too few counts in the red region for reasonable statistical photon counting). For **1a** we determined the following lifetimes: dioxane (480 nm), 30·5 ns; CH_2Cl_2 (530 nm), 49 ns; no lifetime could be determined in acetonitrile. We tentatively conclude that the lifetime is increasing with increasing polarity while the quantum yield for emission decreases.

The emission properties of pyrroloboranes **1** qualitatively support the theoretical treatment of Bonacic-Koutecky and Michl. The broad, longer wavelength emission is assigned to fluorescence from a twisted, dipolar excited state based on the following criteria. The emission exhibits a large Stokes shift, which implies that a large geometrical reorganization, such as a rotation, occurs on excitation. Second, the longer wavelength emission of **1b** is always observed to the red of that of **1a**, as would be expected for the more electron rich (lower ionization potential) dimethylpyrrole as a donor compared to pyrrole. Finally, each of **1a** and **1b** exhibits a strong red shift of the long wavelength emission as solvent polarity increases. From the solvent dependence of the emission maximum we roughly calculate that the excited state dipole moment of compounds **1** is 10–12 debye. The dipole moment calculation followed Lippert[7] and Mataga;[8] see also Reference 2, Figure 9. The value of the Onsager cavity radius was taken as 4 Å. This evidence supports the calculated picture[4] for the lowest excited singlet state of **1** as a perpendicular, charge separated dipole.

We note that compounds **1** also emit short wavelength fluorescence. We tentatively assign the nature of this emission to the initial Franck–Condon state (the planar state) produced on excitation of the species, although we can not rule out emission from an upper state such as a locally excited aromatic (mesityl) chromophore. We consider the latter explanation unlikely based on precedent. The fact that emission yields decrease in polar solvents is to be expected for a TICT process, but would not be anticipated *a priori* for the short wavelength emission if it originated from a locally excited state such as a π–π^* mesityl chromophore.

The pyrroloboranes **1** provide ample experimental support for the theoretical treatment of twisted internal charge transfer derived by Michl[4] for simple aminoboranes. They also provide a new example of materials which exhibit TICT processes outside the classes of simple hydrocarbons observed to date.[1,2]

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