Unusual Fluorescence Red Shifts in (TICT)-Forming Boranes

Claudia Corneliβen[1] and Wolfgang Rettig[2]

Pyrrole substituted mesitylboranes and benzonitriles show highly solvent sensitive forbidden emission. In twisted model compounds, both fluorescence red shift and forbiddenness are increased.

INTRODUCTION

Compounds which form TICT (twisted intramolecular charge transfer) excited states [1–4] are known to be potential candidates for fluorescence probe molecules both sensing free volume effects [5,6] and exhibiting very large Stokes shifts. Although the emission process from a TICT state is, in principle, forbidden due to the near-orthogonal geometric arrangement of the chromophores [7], exceptions have been described with large TICT fluorescence quantum yields [8,9], which provide a new access to highly brilliant fluorescence probes with large Stokes shifts.

As the first step, we want to focus on the large Stokes shift property alone and disregard the problem of the allowedness of the emissive transition for the moment. Borane compounds with exceptionally large Stokes shifts are described which are closely related to the prototype TICT system, aminoborane, the states of which can be described within the biradicaloid (BR) model, a generalization of the TICT model [4,8,10,11]. The aim of this investigation was the classification of the elec-

tronic character and relative state energies of S_0, S_1, and T_1 as a function of the twist angle within the framework of the model of BR states. The following electronic characteristics have been derived for these prototype TICT systems.

(a) S_1 possesses an energetic minimum at a twist angle of 90° where donor and acceptor subunits are perpendicular to each other.

(b) The wavefunction of the S_1 state possesses a strong charge transfer (CT) character for this twisted geometry.

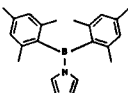(c) Nearly degenerate singlet and triplet energies are found for the TICT minimum.
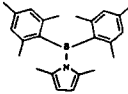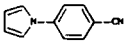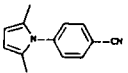
Such states have been of special spectroscopic interest, because the phenomena of dual fluorescence could be explained as competing reactions of FC (Frank–Condon-type) emission and adiabatic photoreaction into a TICT minimum.

In this paper, we present the spectroscopic features of the B,B-bis(mesityl)pyrroloboranes I and II [12], with a pyrrole group as the donor and a strong borane acceptor group (Table I). These compounds are analogous to aminoborane. For comparison, the spectroscopic behavior of the TICT-forming pyrrole compounds III and IV, with a different acceptor group (4-cyanophenyl), was investigated too. The latter compounds have a close relationship to the "parent molecule" of the TICT phe-

[1] I. N. Stranski Institute, Technical University, Berlin, Strasse des 17. Juni 112, D-10623 Berlin, Germany.
[2] W. Nernst Institute for Physical and Theoretical Chemistry, Humboldt-University, Berlin, Bunsenstr. 1, D-10117 Berlin, Germany.

Table I. Spectral and Photophysical Parameters of the Investigated Pyrroloboranes and Pyrrolobenzonitriles

Compound		Solvent	λ^F_{max} (nm)	$\Delta\nu_{st}$ (cm^{-1})	ϕ_f	τ_f (ns)	k_f (s^{-1})
I		Hexane	428	13,100	0.015	7.4	$2.0\cdot10^6$
		Diethyl ether	474	15,270	0.038	30	$1.3\cdot10^6$
		Acetonitrile	510	16,760	0.018	16	$1.1\cdot10^6$
II		Hexane	538	15,900	0.012	13.6	$8.8\cdot10^5$
		Diethyl ether	580	17,240	0.004	5.5	$8.0\cdot10^5$
		Acetonitrile	No fluorescence observable at 298 K				
III		Hexane	348	7,630	0.030	2.4	$1.2\cdot10^7$
		Diethyl ether	404	11,610	0.023	3.8	$0.6\cdot10^7$
		Acetonitrile	482	15,616	0.038	8.2	$0.4\cdot10^7$
IV		Hexane	420	12,550	0.006	2.9	$2.1\cdot10^6$
		Diethyl ether	480	15,530	0.019	12.2	$1.4\cdot10^6$
		Acetonitrile	No fluorescence observable at 298 K				

nomenon, namely, DMABN (4-N,N-dimethylaminobenzonitrile) [13].

RESULTS

Absorption and corrected fluorescence spectra for I to IV in nonpolar hexane and medium polar diethyl ether are displayed in Figs. 1 and 2, and the relevant photophysical data are summarized in Table I. From the red shift of the fluorescence maximum, which increases with increasing solvent polarity, and from the fact that this red shift is substantially stronger for the 2,5-dimethyl-substituted pyrrolocompounds (II and IV compared to I and III), it can be concluded [14,15,17] that the emission originates from an excited state with a high-charge transfer character.

The average geometry of the 2,5-dimethyl compounds (II, IV) should be more strongly twisted in the fluorescent state than I and III, consistent with the significantly lower k_f values of II and IV in comparison with those of I and III, indicating a smaller overlap of the donor–acceptor unit.

However, the main absorption band of the pyrrolobenzonitrile compounds III and IV does not correspond to a CT transition because there is no effect of solvent polarity on the absorption energy. The corresponding state is therefore S_2, with a dipole moment close to that of the ground state (≈4 D [16]), whereas the lower lying CT state (≈16 D according to ab initio CI calculations [17]) is hidden because of its forbidden character. For the pretwisted compounds II and IV, however, the weak long-wavelength shoulder in the absorption spectra could be assigned to $S_{1,CT}$.

DISCUSSION

All the compounds, I–IV, exhibit enormous Stokes shifts in polar solvents, and some of them even in nonpolar solvents. This phenomenon is likely to result from a geometrical rearrangement, i.e., TICT relaxation, within the lifetime of the excited state. An alternative explanation is simply given by a $S_2\rightarrow S_1$ relaxation process (i.e., internal conversion), consistent with the small shoulder in the red edge of the absorption spectra of II and IV. Most probably, both relaxation processes occur simultaneously.

Although the Stokes shifts are large, the fluorescence quantum yields of compounds I–IV are rather low, which make them unattractive for use as fluorescence probes in practice. However, during our studies on related strong donor–acceptor compounds, we found other B,B-bis(mesityl)boranes [18] which possess a dialkylaniline donor unit and show both a high sensitivity to solvent polarity, similar to the compounds studied here, and large fluorescence quantum yields (Table II). The forbiddenness of the TICT radiative emission can therefore be overcome, while keeping the advantage of the large Stokes shift. Other recent examples of allowed TICT emission have been reported for 4,4'-dimethylaminocyanostilbene [8] and 5,5'-biperylenyl [9].

ACKNOWLEDGMENTS

a)

b)

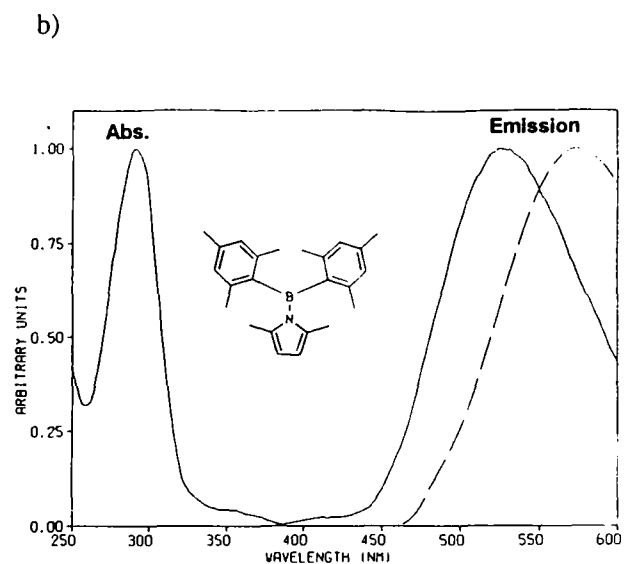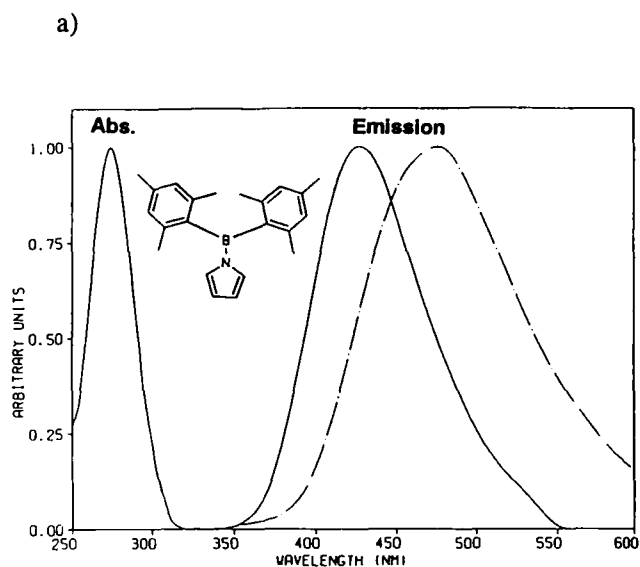
Fig. 1. Absorption and fluorescence spectra of I (a) and II (b) in *n*-hexane (——) and diethyl ether (- - -) at room temperature.

a)

b)

Fig. 2. Absorption and fluorescence spectra of III (a) and IV (b) in *n*-hexane (——) and diethyl ether (- - -) at room temperature.

REFERENCES

1. Z. R. Grabowski, K. Rotkiewicz, A. Siemiarczuk, D. J. Cowley, and W. Baumann (1979) *Nouv. J. Chim.* **3**, 443.
2. W. Rettig (1986) *Angew. Chem.* **98**, 969; *Angew. Chem. Int. Edit. Engl.* **25**, 971.
3. E. Lippert, W. Rettig, V. Bonačić-Koutecký, F. Heisel, and J. A. Miché (1987) *Adv. Chem. Phys.* **68**, 1.
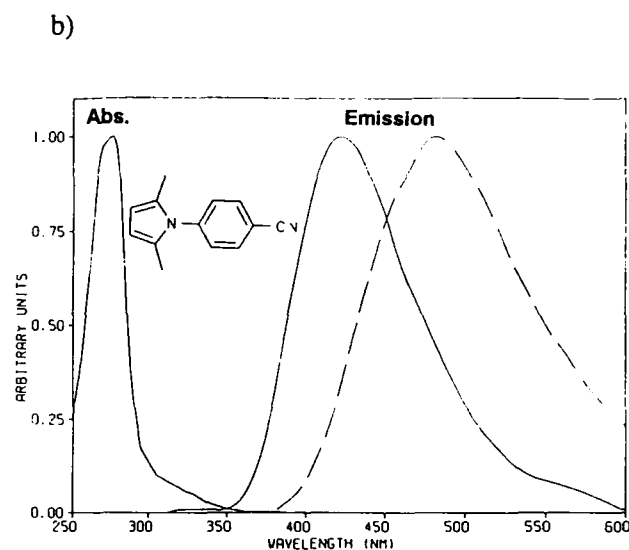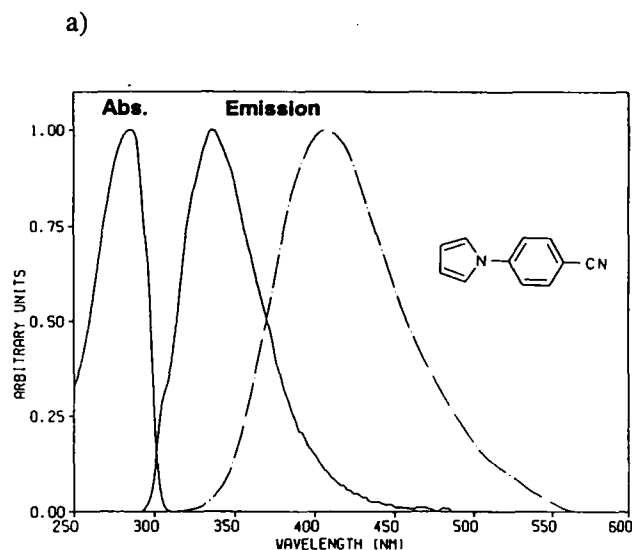
4. W. Rettig (1994) in J. Mattay (Ed.), *Topics in Current Chemistry, Photoinduced Electron Transfer*, Springer Verlag, Berlin, p. 253.
5. W. Rettig and W. Baumann (1992) in J. F. Rabek (Ed.), *Photochemistry and Photophysics, Vol. VI*, CRC Press, Boca Raton, FL, p. 79.
6. W. Rettig (1994) in J. R. Lakowicz (Ed.), *Topics in Fluorescence Spectroscopy IV: Probe Design and Chemical Sensing*, Plenum Press, New York (in press).
7. M. Van der Auweraer, Z. R. Grabowski, and W. Rettig (1991) *J. Phys. Chem.* **95**, 2083.
8. R. Lapouyade, K. Czeschka, W. Majenz, W. Rettig, E. Gilabert, and C. Rullière (1992) *J. Phys. Chem.* **96**, 9643.
9. J. Dobkowski, W. Rettig, B. Paeplow, K. H. Koch, K. Müllen, R. Lapouyade, and Z. R. Grabowski (1994) *New J. Chem.* (in press).

Table II. Fluorescence Quantum Yields and Red Shifts of Several DialkylanilinoBoranes [18]

Compound	Solvent	ϕ_f	λ_{Abs} (nm)	λ_{Em} (nm)	$\Delta\nu_{ST}$ (cm^{-1})
	c-Hexane	0.42	353	386	2420
	CH$_2$Cl$_2$	0.26	359	465	6350
	MeOH	0.05	358	512	8400
	c-Hexane	0.44	361	418	3780
	CH$_2$Cl$_2$	0.37	366	478	6400
	MeOH	0.34	364	520	8240
	c-Hexane	0.88	377	412	2250
	CH$_2$Cl$_2$	0.75	380	455	4340
	MeOH	0.55	376	474	5500

10. V. Bonačić-Koutecký and J. Michl (1985) J. Am. Chem. Soc. 107, 1765.
11. V. Bonačić-Koutecký, J. Koutecký, and J. Michl (1990) Electronic Aspects of Organic Photochemistry, J. Wiley & Sons, New York.
12. D. R. Britelli and D. Eaton (1989) J. Phys. Org. Chem. 2, 89.
13. E. Lippert, W. Lüder, and H. Boos (1962) in A. Mangini (Ed.), Advances in Molecular Spectroscopy, Pergamon Press, Oxford, p. 443.

14. W. Rettig and F. Marschner (1983) Nouv. J. Chim. 7, 425.
15. W. Rettig and F. Marschner (1990) New J. Chem. 14, 819.
16. H. Lumbroso, D. M. Bertin, and F. Marschner (1988) J. Mol. Struct. 178, 187.
17. C. Cornelißen, W. Rettig, and V. Bonačić-Koutecký (1992) unpublished results.
18. J. C. Doty, B. Babb, M. E. Glogowski, P. J. Grisdale, and J. L. R. Williams (1972) J. Organomet. Chem. 38, 229.