Boratastilbene: Synthesis, Structural Characterization, and Photophysics

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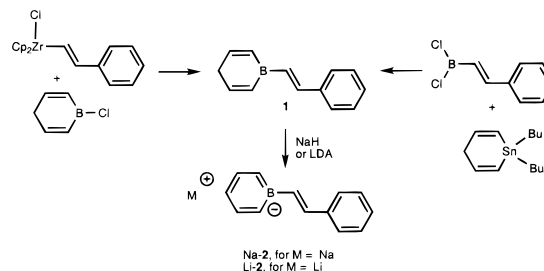Santa Barbara, California 93106*

Interest in the chemistry of boracycloalkenes, boraarenes, and borataarenes stems from the concepts of π-electron aromaticity and conjugation across sp²-hybridized boron.[1] Boratabenzene, the most representative example of this class of compounds, was initially observed as a ligand coordinated to transition metals, and several catalysts have been designed that are based on this fragment.[2] Less attention has been focused on how the B⁻-for-C substitution influences the photophysics and photochemistry of organic chromophores. This isoelectronic replacement maintains the total number of electrons constant and the overall structural features intact within a given molecular fragment. The study of boron-containing chromophores should therefore give insight into the effect of an additional negative charge and an asymmetric charge distribution on the properties of photoexcited organic compounds. Additionally, boron-containing conjugated polymers are of current interest because of their potentially useful optoelectronic properties.[3] Understanding the behavior of the individual monomeric units provides a useful knowledge base for designing more complex conjugated structures.

Within the context of this idea, we chose *boratastilbene* as an attractive synthetic and study candidate since the photophysics of *stilbene* are well understood.[4] Singlet and triplet energy surfaces have been determined which account for photoisomerization efficiency and fluorescence quantum yield. The importance of the photochemistry of stilbenoid compounds in materials science is also well documented.[5] This communication reports the synthesis, characterization, and optical properties of sodium and lithium boratastilbene.

Transmetalation of the styryl fragment from Cp₂ZrCl(CH= CHPh)[6] (Cp = C₅H₅) to 1-chloro-1-boracyclohexa-2,5-diene[7] gives *trans*-1-styryl-1-boracyclohexa-2,5-diene (**1**, in Scheme 1). Extraction of **1** from Cp₂ZrCl₂ using pentane, followed by sublimation, affords **1** in 35% overall yield.[8] Alternatively, **1** can be prepared by reaction of 1,1-dibutyl-1-stannacyclohexa-2,5-diene with *trans*-styrylboron dichloride in essentially quantitative yield by ¹H NMR spectroscopy. However, **1** and Cl₂SnBu₂ have

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(3) (a) Matsumi, N.; Naka, K.; Chujo, Y. *J. Am. Chem. Soc.* **1998**, *120*, 5112. (b) Matsumi, N.; Naka, K.; Chujo, Y. *J. Am. Chem. Soc.* **1998**, *120*, 10776. (c) Corriu, R. J.-P.; Daforth, T.; Douglas, W. E.; Guerrero, G.; Siebert, W. S. *Chem. Commun.* **1998**, 963.
(4) Saltiel, J., Waller, A. S.; Sears, D. F., Jr.; Gareett, C. J. *J. Phys. Chem.* **1993**, *97*, 2516.
(5) (a) Meier, H. *Angew. Chem., Int. Ed. Engl.* **1992**, *31*, 1399. (b) Whitten, D. G.; Chen, L. H.; Geiger, H. C.; Perlstein, J.; Song, X. D. *J. Phys. Chem. B* **1998**, *102*, 10098. (c) Bazan, G. C.; Oldham, W. J., Jr.; Lachicotte, R. J.; Treticak, S.; Chernyak, V.; Mukamel, S. *J. Am. Chem. Soc.* **1998**, *120*, 9188.
(6) Harada, S.; Taguchi, T.; Tabuch, N.; Narita, K.; Hanzawa, Y. *Angew. Chem., Int. Ed. Engl.* **1998**, *37*, 1698.
(7) Maier, G.; Hankelmann, J.; Reisenauer, H. P. *Angew. Chem., Int. Ed. Engl.* **1985**, *24*, 1065.
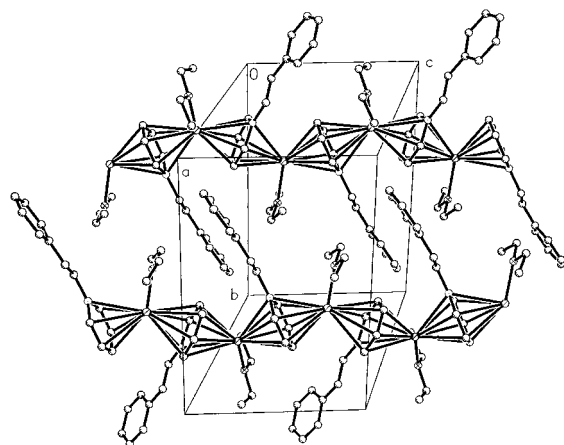
Scheme 1

similar volatility and solubility properties, and we have been unable to isolate pure **1** by this method.

Deprotonation of **1** with NaH or LDA in THF affords the sodium and lithium salts of boratastilbene (Na-**2** and Li-**2**). Single crystals of Na-**2**·(Et₂O) suitable for X-ray diffraction studies were obtained by allowing an Et₂O/benzene (10:1) solution to stand at −35 °C for 15 h. The metrical parameters within the boratastilbene anion are in agreement with those of previously characterized boratabenzene lithium salts (average distances in Å, B−C$_\alpha$ = 1.514(2), C$_\alpha$−C$_\beta$ = 1.393(2), C$_\beta$−C$_\gamma$ = 1.396(2));[9] however, the intermolecular organization exhibits interesting features. The molecules arrange along the *c* axis as a polymeric contact ion pair chain. Within the chains each sodium ion is coordinated to two boratabenzene fragments and to an ether molecule (Figure 1). The boratastilbene anions are tilted away from each other at an angle of ∼49°. Li-**2** is obtained as microcrystals that are not suitable for X-ray diffraction.

As shown in Figure 2a, the absorption spectrum of Li-**2** in THF displays a λ_{max} at 348 nm ($\epsilon_{348} = 1.7 \times 10^5$ L mol⁻¹ cm⁻¹). Also noticeable is a "shoulder" in the 400−440 nm region, which becomes less pronounced with increasing concentration and is absent when the spectra are measured in Et₂O or toluene. The emission in THF (Figure 2b) lacks vibronic structure and has a maximum at ∼500 nm. The excitation spectrum (Figure 2c) is considerably different from the absorption spectrum ($\lambda_{max} = 403$ nm). Negligible emission is observed in Et₂O or toluene. These data suggest that in THF there is more than one species in solution and that most of the emission arises from the species absorbing in the "shoulder" region of the absorption spectrum. The dependence on solvent and concentration suggests that Li-**2** in THF is in equilibrium between an aggregated species, most likely a sandwich structure in which two boratastilbene units are coordinated to a lithium cation ([Li(THF)$_x$(**2**₂Li)], in eq 1), and a solvent-separated ion pair (Li(THF)$_x$//**2**).[10] Furthermore, we propose that Li(THF)$_x$//**2** is responsible for the absorption band centered at 403 nm and accounts for most of the emission.
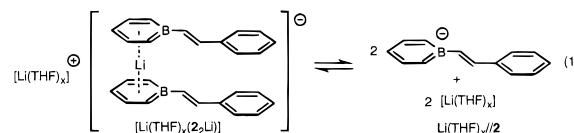
To test our hypothesis, we added an excess of 12-crown-4 to THF solutions of Li-**2**. Under these conditions the majority of the Li cations will be coordinated by the 12-crown-4, thereby

(8) Approximately 5% of the conjugated isomer, *trans*-1-styryl-1-boracyclohexa-2,4-diene, is observed at this stage.
(9) For comparison against [Li(Me₂NCH₂CH₂NMe₂)][C₅H₅B-NMe₂], see: Herberich, G. E.; Schmidt, B.; Unglert, U.; Wagner, T. *Organometallics* **1993**, *12*, 2891. Na-**2** is the first sodium salt of a substituted boratabenzene to be structurally characterized.
(10) (a) Hoic, D. A.; Davis, W. M.; Fu, G. C. *J. Am. Chem. Soc.* **1995**, *117*, 8480. (b) Ashe, A. J., III; Kampf, J. W.; Müller, C.; Schneider, M. *Organometallics* **1996**, *15*, 386.

Figure 1. Molecular packing diagram of Na-**2** with a view down the *a* axis.
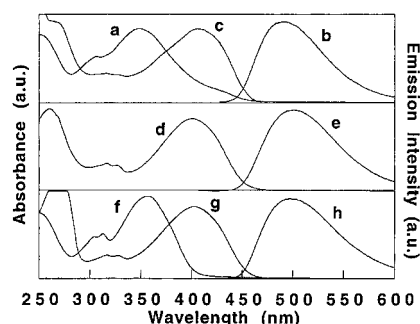

Figure 2. Spectra of Li-**2** and Na-**2** in THF: (a) absorption of Li-**2**; (b) emission of Li-**2**; (c) excitation of Li-**2**; (d) absorption of Li-**2** with 500 equiv of 12-crown-4; (e) emission of Li-**2** with 500 equiv of 12-crown-4; (f) absorption of Na-**2**; (g) absorption of Na-**2** with 2 equiv of dibenzo-18-crown-6; (h) emission of Na-**2** with 2 equiv of dibenzo-18-crown-6.

Figure 3. ORTEP drawing of Na(dibenzo-18-crown-6)-**2**.

Figure 4. HOMO and LUMO density surfaces for boratastilbene. The density value is 0.002 electrons/au^3. Gray surfaces indicate negative nodes while black surfaces indicate positive nodes.

increasing the concentration of noncoordinated boratastilbene.[11] The absorption of Li-**2**/12-crown-4 in THF (Figure 2d) is considerably red-shifted relative to that of Li-**2** in THF ($\epsilon_{400} = 1.6 \times 10^5$ L mol^{-1} cm^{-1}), and matches the excitation spectrum in Figure 2c. The emission (Figure 2e) is also similar to that of Li-**2** and, the excitation spectrum of Li-**2**/12-crown-4 is identical to Figure 2d. The fluorescence quantum yield (Φ_{PL}) from Li-**2**/12-crown-4 solutions in THF was calculated to be 0.60(3).

As shown in Figure 2f, the Na-**2** absorption spectrum in THF shows a λ_{max} at 357 nm ($\epsilon_{357} = 1.9 \times 10^5$ L mol^{-1} cm^{-1}) and moderate emission ($\Phi_{PL} = 0.16(3)$). Upon addition of 2 equiv of dibenzo-18-crown-6, the absorption spectrum (Figure 2g) red shifts ~50 nm ($\epsilon_{403} = 1.6 \times 10^5$ L mol^{-1} cm^{-1}) and the solution becomes considerably more emissive ($\Phi_{PL} = 0.68(3)$). Figure 2h shows that the emission of Na-**2**/dibenzo-18-crown-6 is identical to those of Li-**2**/12-crown-4 and Li-**2** in THF. The molecular structure determined from a single crystal grown from a Na-**2**/dibenzo-18-crown-6 solution in THF shows that each sodium ion is coordinated by the cyclic ether and two THF molecules. The ions are therefore insulated from the boratastilbene chromophore (Figure 3). Altogether, these observations are consistent with a breakup of a weakly emissive Na-**2** aggregate by dibenzo-18-crown-6 to give a strongly fluorescent, solvent-separated **2**.

Examination of the HOMO and the LUMO of boratastilbene (Figure 4)[12] indicates that photoexcitation results in a net charge transfer from the boratabenzene ring to the phenyl ring. In stilbene, excitation leads to a twisted biradicaloid structure which is close in energy to the ground-state energy surface. This small energy gap allows for fast radiationless decay to a mixture of cis and trans isomers.[13] The availability of the charge-transfer transition for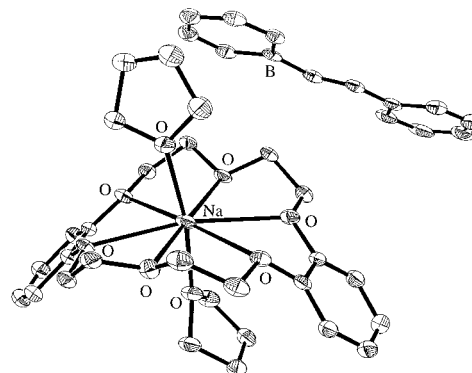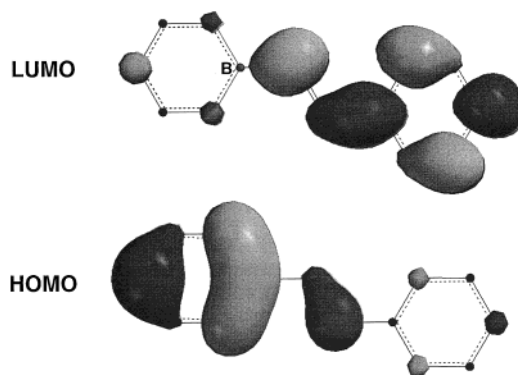 boratastilbene accounts for the higher fluorescence quantum yield, the lack of vibronic structure in the emission spectrum, and the fact that we failed to detect photoisomerization processes. It is also likely that upon aggregation the HOMO becomes involved in bonding (either covalent or ionic) to the metal ions, as in Figure 1, and is less available for charge transfer. Other, less well-defined deactivation processes become available in the larger structures.

In summary, we disclose here the synthesis of boratastilbene. The anionic charge results in aggregation-dependent photophysics. Nonpolar solvents encourage dimeric or oligomeric structures which are nonemissive or weakly emissive. Solvent-separated boratastilbene is highly emissive, relative to stilbene, because the inequivalent charge density of the two rings leads to intramolecular charge transfer.[14] This intrinsic difference should be considered in the design of materials targeted for specific applications.

Supporting Information Available: Complete details for the synthesis of all compounds and the crystallographic studies of Na-**2** and Na-(dibenzo-18-crown-6)-**2** (PDF). This material is available free of charge via the Internet at http://pubs.acs.org.

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(11) *Crown Ethers and Analogues*; Patai, S., Rappoport, Z., Eds.; Wiley & Sons: New York, 1989.

(12) Calculated using the Spartan Package: Hehre, W. J. *Practical Strategies for Electronic Structure Calculations*; Wavefunction: Irvine, CA, 1995; p 205. The molecular orbital surfaces were created after calculation of ab initio (HF) single-point energies employing the 3-21G* basis set.

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(14) Electron-rich stilbene derivatives show higher emission quantum yields than stilbene, albeit because of a different mechanism. See, for example: (a) Smit, K. J.; Ghiggino, D. P. *Chem. Phys. Lett.* **1985**, *122*, 369. (b) Zeglinski, D. M.; Waldeck, D. H. *J. Phys. Chem.* **1988**, *92*, 692. We also recognize the electronic relationship between boratastilbene and styrylpyridium. For selected examples, see: (c) Huang, W.; Helvenstone, M. *Langmuir* **1999**, *15*, 6510. (d) Kawai, H.; Nagamura, T. *J. Chem. Soc., Faraday Trans.* **1988**, *94*, 3581. (e) Takagi, K.; Aoshima, K.; Sawaki, Y.; Iwamura, H. *J. Am. Chem. Soc.* **1985**, *107*, 47.