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Receptors

Sulfonium Boranes for the Selective Capture of Cyanide Ions in Water**

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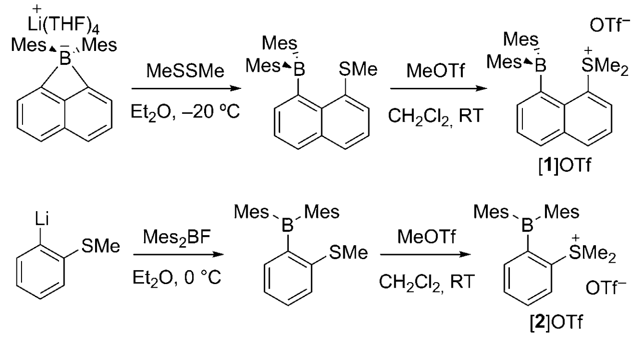
Owing to the presence of low lying σ* orbitals, sulfonium ions are inherently Lewis acidic and can interact with electron-rich substrates to form donor–acceptor complexes. Although this phenomenon has been documented,[1] efforts to use sulfonium ions as a binding site in Lewis acidic hosts have not been reported. As part of our fundamental interest in the chemistry of polydentate Lewis acidic boranes,[2] we have become interested in probing the synthesis and properties of anion receptors containing accessible sulfonium ions. As an added motivation for these studies, we anticipated that the anion binding properties of sulfonium boranes would also benefit from attractive Coulombic effects similar to those occurring in other cationic boron-based anion receptors.[3,4]

To test the validity of the aforementioned concepts, we synthesized the cationic boranes $[\mathbf{1}]^+$ and $[\mathbf{2}]^+$ which feature adjacent sulfonium and boryl moieties connected by a 1,8-naphthalenediyl or *o*-phenylene linker, respectively (Scheme 1). The salt [**1**]OTf was obtained by reaction of the tetrakis(THF)lithium salt of dimesityl-1,8-naphthalenediylborate[5] with dimethyldisulfide and subsequent methylation of the resulting sulfide with MeOTf (Scheme 1). The salt [**2**]OTf could also be conveniently prepared in two steps by reaction of *o*-lithiothioanisole[6] with dimesitylboron fluoride and subsequent methylation with MeOTf.



Scheme 1. Syntheses of [**1**]OTf and [**2**]OTf.

Both [**1**]OTf and [**2**]OTf have been isolated in an analytically pure form and characterized by multinuclear NMR spectroscopy, UV/Vis spectroscopy, and single-crystal X-ray diffraction. The detection of a ^{11}B NMR resonance near $\delta = 70$ ppm ($\delta = 67$ ppm for $[\mathbf{1}]^+$ or $\delta = 77$ ppm for $[\mathbf{2}]^+$) and the presence of a low energy UV/Vis absorption band at 340 nm in MeOH for both $[\mathbf{1}]^+$ ($\varepsilon = 16350\,\mathrm{M}^{-1}\mathrm{cm}^{-1}$) and $[\mathbf{2}]^+$ ($\varepsilon = 9300\,\mathrm{M}^{-1}\mathrm{cm}^{-1}$) indicate the presence of a coordinatively unsaturated boron center, which mediates π conjugation of the aromatic ligands.[7] The resulting boron-centered chromophores are fluorescent and give rise to a broad emission band at 464 nm for $[\mathbf{1}]^+$ ($\phi = 0.02$) and 450 nm for $[\mathbf{2}]^+$ ($\phi = 0.12$) when excited at 350 and 340 nm in MeOH, respectively. As reported for other sulfonium salts,[8] $[\mathbf{1}]^+$ and $[\mathbf{2}]^+$ are sensitive to UV light and should therefore not be irradiated for extended periods of time. The crystal structures of these salts clearly show that: 1) the boron center adopts a trigonal-planar coordination geometry ($\Sigma_{(\text{C-B-C})} = 359.6°$ for $[\mathbf{1}]^+$ and $360.0°$ for $[\mathbf{2}]^+$); 2) that the boron–sulfur separation in $[\mathbf{1}]^+$ (3.07 Å) is slightly shorter than in $[\mathbf{2}]^+$ (3.12 Å) (Figure 1).[9] Despite the similarity of this boron–sulfur separation, the two cationic boranes differ by the respective disposition of the boryl and sulfonio moieties which are oriented in a more convergent fashion in $[\mathbf{1}]^+$. A natural bond orbital (NBO) analysis carried out at the density functional theory (DFT) optimized geometry of $[\mathbf{1}]^+$ indicates the presence of a lp(S)→p(B) donor–acceptor interaction (Figure 1) whose deletion leads to an increase of the total energy of the molecule by $E_{\text{del}} = 6.8\,\text{kcal mol}^{-1}$. Therefore, in addition to being more sterically crowded, the boron center of $[\mathbf{1}]^+$ experiences electron donation from the neighboring sulfur atom, a phenomenon which would be expected to reduce its electron deficiency. Analogous computations on $[\mathbf{2}]^+$ show that this lp(S)→p(B) interaction (Figure 1), although present, is much weaker ($E_{\text{del}} = 2.3\,\text{kcal mol}^{-1}$), which is in agreement with the more divergent orientation of the lp(S) and p(B) orbitals. Altogether, this analysis shows that $[\mathbf{2}]^+$ features a more accessible and electron-deficient boron atom.

Next, we decided to compare the Lewis acidity of these boranes by studying their behavior in aqueous solution as a function of pH. Since hydroxide binding to the boron center is expected to interrupt the π conjugation mediated by the vacant *p*-orbital on the boron atom,[10] we monitored the absorbance of the boron-centered chromophore as a function of pH in MeOH/H_2O (5:95 v/v; see the Supporting Information) and observed that $[\mathbf{1}]^+$ and $[\mathbf{2}]^+$ are stable up to pH 9.5 and 7.0, respectively. These experiments indicate that $[\mathbf{2}]^+$ is more acidic than $[\mathbf{1}]^+$ by at least two orders of magnitudes.

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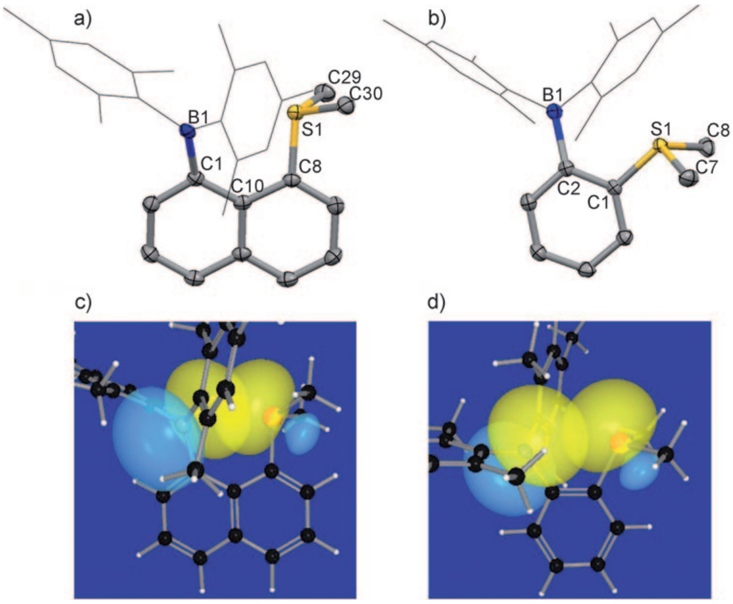

Figure 1. Top: Crystal structures of [**1**]OTf (a) and [**2**]OTf (b). The triflate anions and hydrogen atoms are omitted for clarity. Pertinent metrical parameters can be found in the text and the Supporting Information. Bottom: partial view of the molecule of [**1**]$^+$ (c) and [**2**]$^+$ (d) showing the contours of the NBOs involved in the lp(S)→p(B) donor–acceptor interaction.

Hydroxide binding to [**2**]$^+$ is reversible as confirmed by the observed revival of the absorbance of the boron-centered chromophore upon acidification of the solution. In the case of [**1**]$^+$, hydroxide binding is very slow and accompanied by decomposition.

Having established the pH stability range of these two novel cationic boranes, we decided to compare their anion affinity in aqueous solutions. Bearing in mind that anion binding to the boron center should results in a quenching of the low-energy band observed in the spectra of the boranes, these studies were monitored by UV/Vis spectroscopy. The addition of 15 equivalents of Cl^-, Br^-, I^-, NO_3^-, HSO_4^-, $H_2PO_4^-$, and $CH_3CO_2^-$ to a 32 μM solution of [**1**]$^+$ or [**2**]$^+$ in H_2O/MeOH (95:5 v/v) at pH 7 did not result in any changes of the absorption spectrum, indicating the absence of any significant interactions. A similar observation was made for [**1**]$^+$ in the presence of F^- or CN^-. Unlike [**1**]$^+$, [**2**]$^+$ gave a small but noticeable response in the presence of fluoride as indicated by the 4% absorption quenching measured upon the addition of 15 equivalents of F^-. A much more drastic response was observed in the presence of CN^-. Indeed, addition of only 0.2 equivalents of CN^- to a solution of [**2**]$^+$ (32 μM) resulted in the formation of a precipitate which was identified as [**2**(CN)]. Increasing the amount of cyanide led to higher yields of [**2**(CN)] (Figures 2 and 3). The precipitation of [**2**(CN)] precluded the determination of the cyanide binding constant of [**2**]$^+$ under these titration conditions. Nevertheless, a titration carried out in H_2O/MeOH (60:40 v/v) at pH 7, conditions under which [**2**(CN)] does not precipitate, showed that the binding constant under these conditions exceeds $10^8\,M^{-1}$. The identity of [**2**(CN)] has been firmly established by using conventional characterization techniques. Some of its salient spectroscopic features include: 1) a ^{11}B NMR resonance at $\delta = -14.7$ ppm indicating the presence of a four-coordinate boron center; 2) an intense IR band at 2162 cm^{-1} confirming the presence of the boron-bound cyano group.[4,11]

[**2**(CN)] has also been analyzed by single-crystal X-ray diffraction.[9] The B(1)-C(27) bond connecting the carbon atom of the cyanide anion to the boron center (1.636(5) Å) is comparable to those typically found in triarylcyanoborate anions[12] such as $[Ph_3BCN]^-$ (1.65 Å).[13] The sum of the C_{aryl}-B-C_{aryl} angles ($\Sigma_{(C\text{-}B\text{-}C)} = 337.7°$) indicates substantial pyramidalization of the boron atom. The B(1)-C(2)-C(1) angle of 122.4(3)° is close to the ideal value of 120° indicating that the structure is sterically unhindered. Finally, the centroid of the C(27)-N(1) (Ct_{CN}) bond is separated from the sulfur atom by only 3.03 Å and forms a Ct_{CN}-S(1)-C(8) angle of 164.2°. To investigate the presence of a possible interaction between the sulfur atom and the cyanide group, we carried out an NBO analysis of the DFT optimized structure. This analysis reveals the presence of a $\pi(C{\equiv}N)\rightarrow\sigma^*(S{-}C)$ donor–acceptor interaction unexpectedly complemented by a back-bonding $lp(S)\rightarrow\pi^*(C{\equiv}N)$ component. The concomitant deletion of these two interactions leads to an increase of the total energy of the molecule by 4.1 kcal mol^{-1}, an energy comparable to that of a strong hydrogen bond.[14] In addition to providing some energetic stabilization to the complex through formation of the aforementioned interactions, the sulfonium moiety flanks one side of the boron-bound cyanide anion thus providing steric protection against water molecules.

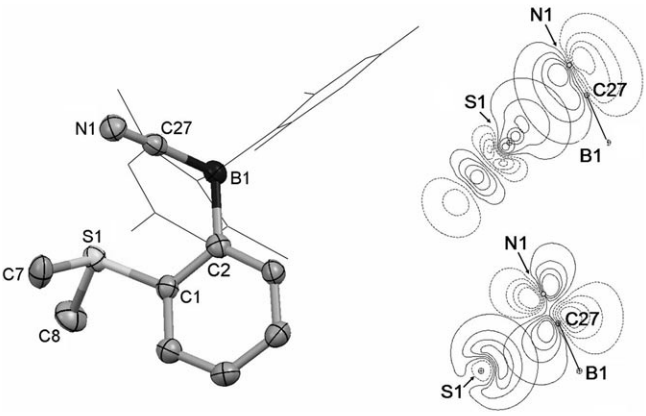

Figure 2. Left: Crystal structure of [**2**(CN)]. Hydrogen atoms omitted for clarity. Pertinent metrical parameters can be found in the text and the Supporting Information. Right: NBO contour plots showing $\pi(C{\equiv}N)\rightarrow\sigma^*(S{-}C)$ (top) and $lp(S)\rightarrow\pi^*(C{\equiv}N)$ (bottom) interactions.

Encouraged by the results of our initial anion binding studies, we decided to investigate the use of [**2**]$^+$ for the detection of cyanide near the maximum allowable concentration of 50 ppb (1.9 μM) recommended by the European Union (EU) for drinking water.[15] To this end, we monitored the fluorescence at 460 nm ($\lambda_{ex} = 300$ nm) of a 4.0 μM solution of [**2**]$^+$ in pure water upon addition of CN^-. Remarkably,

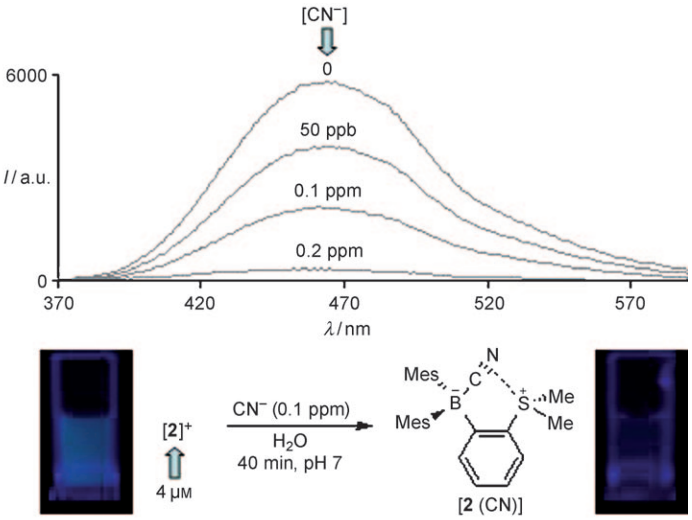

Figure 3. Top: Fluorescence spectrum of [**2**]$^+$ (4.0 μM) in pure water at pH 7 (HEPES 10 mM) before and after addition of cyanide. Bottom: Visible fluorescence changes (under a hand-held UV-lamp) accompanying the formation of [**2**(CN)]. The reaction conditions are provided in the figure.

addition of 50 ppb of CN$^-$ resulted in a 33% quenching of the fluorescence after one hour (Figure 3). Next, we decided to test the behavior of [**2**]$^+$ in the presence of 0.2 ppm (7.7 μM) of cyanide, which corresponds to the maximum contaminant level set by the US Environmental Protection Agency.[16] Under these conditions, an almost complete quenching of the fluorescence was observed after one hour (Figure 3). The naked-eye observation of this fluorescence quenching can be readily observed when 0.1 ppm of cyanide is added to a 4 μM solution of [**2**]$^+$ as shown in Figure 3. Thus, [**2**]$^+$ is one of the rare molecular systems competent for cyanide sensing at the sub-parts per million level in water.[17]

In conclusion, we report the synthesis of a sulfonium borane ([**2**]$^+$) which can be used in pure water for the fluorescence detection of cyanide near the EU maximum allowable concentration. The high affinity of this borane arises from favorable Coulombic effects which serve to stabilize the cyanoborate complex against dissociation. Last, but not least, the sulfonium moiety interacts with the cyanide guest through both a bonding and back-bonding interaction, thus enhancing the unusual affinity of [**2**]$^+$ toward cyanide.

Experimental Section

Synthesis of [**2**]OTf: 2-Bromothioanisole (0.83 g, 4.1 mmol) was allowed to react with *n*BuLi (1.95 mL, 4.3 mmol, 2.2 M in hexanes) in diethyl ether (20 mL) at 0 °C. After stirring the reaction mixture for 1 h at 0 °C, dimesitylboron fluoride (1.2 g, 4.5 mmol) was added to the resulting solution. The reaction mixture was warmed to room temperature and stirred overnight. The reaction was quenched with water (10 mL). The organic layer was separated, dried over $MgSO_4$, filtered, and concentrated in vacuo to afford a yellow solid. This solid was washed with hexanes (7 mL) to afford 1-dimesitylboryl-2-methylthio-benzene as a pale-yellow solid (1.01 g, 66% yield). ^{1}H NMR (400 MHz, $CDCl_3$) $\delta = 2.01$ (s, 12H; Mes-CH_3), 2.27 (s, 3H; S-CH_3), 2.29 (s, 6H; Mes-CH_3), 6.77 (s, 4H; Mes-CH), 7.05 (t, $J =$ 7.2 Hz, 1H; phenyl-CH), 7.12–7.18 (m, 2H; phenyl-CH), 7.33 ppm (t, $J = 7.2$ Hz, 1H; phenyl-CH); ^{13}C NMR (100 MHz, $CDCl_3$) $\delta = 16.61$, 21.45, 23.10, 124.50, 124.72, 128.30, 130.95, 134.41, 139.23, 140.94, 142.78, 143.98, 148.00 ppm; ^{11}B NMR (128 MHz, $CDCl_3$) $\delta = 74.94$ ppm (bs).

Without additional purification, 1-dimesitylboryl-2-methylthio-benzene (0.3 g, 0.81 mmol) was allowed to react with methyl triflate (0.92 mL, 8.1 mmol) in dichloromethane (10 mL). The resulting mixture was heated to reflux, stirred overnight, and then cooled to room temperature. The solvent was removed in vacuo to yield a foamy solid which was dissolved in diethyl ether (5 mL). Addition of hexanes (5 mL) to the resulting solution and subsequent cooling to −40 °C led to precipitation of a solid which was isolated by filtration and washed with hexanes to afford [**2**]OTf (0.38 g, 88% yield). ^{1}H NMR (400 MHz, $CDCl_3$) $\delta = 2.04$ (bs, 12H; Mes-CH_3), 2.30 (s, 6H; Mes-CH_3), 3.00 (bs, 6H; S-CH_3), 6.85 (s, 4H; Mes-CH), 7.46 (d, $J = 7.4$ Hz, 1H; phenyl-CH), 7.67 (t, $J = 7.4$ Hz, 1H; phenyl-CH) 7.85 (t, $J = 7.4$ Hz, 1H; phenyl-CH), 8.39 ppm (d, $J = 7.4$ Hz, 1H; phenyl-CH); ^{13}C NMR (100 MHz, $CDCl_3$) $\delta =$ 21.40, 23.02, 28.82, 118.91, 122.09, 129.32, 129.96, 133.97, 134.26, 134.88, 141.28, 141.80, 153.95 ppm; ^{11}B NMR (128 MHz, $CDCl_3$) $\delta = 77$ ppm (bs); Anal. Calcd for $C_{27}H_{32}BF_3O_3S_2$ ([**2**]OTf): C, 60.45; H, 6.01. Found: C, 60.15; H, 6.00.

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[9] Crystal data:[**1**][OTf]-$(CH_2Cl_2)_{0.5}$: 0.20 × 0.10 × 0.10 mm, $C_{31.5}H_{35}BClF_3O_3S_2$, $M_r=628.98$, triclinic, space group $P\bar{1}$, $a=8.5182(17)$, $b=10.144(2)$, $c=18.638(4)$ Å, $b=92.55(3)°$, $V=1513.0(5)$ Å^3, $Z=2$, $r_{calcd}=1.381$ Mg m^{-3}, $Mo_{K\alpha}$ radiation (l= 0.71073 Å), $T=110(2)$ K, 13329 measured reflections, 4735 unique, $R_{int}=0.0228$, $R_1=0.0508$, $wR_2=0.1268$ (all data). [**2**]-[OTf]: 0.35 × 0.13 × 0.13 mm, $C_{27}H_{32}BF_3O_3S_2$, $M_r=536.46$, monoclinic, space group $P2_1/c$, $a=8.5100(17)$, $b=23.287(5)$, $c=13.710(3)$ Å, $b=99.22(3)°$, $V=2681.8(9)$ Å^3, $Z=4$, $r_{calcd}=1.329$ Mg m^{-3}, $Mo_{K\alpha}$ radiation ($l=0.71073$ Å), $T=110(2)$ K, 61457 measured reflections, 6455 unique, $R_{int}=0.0322$, $R_1=0.0532$, $wR_2=0.1258$ (all data). **2**-CN: 0.31 × 0.08 × 0.05 mm, $C_{27}H_{32}BNS$, $M_r=413.41$, monoclinic, space group $P2_1/c$, $a=8.6248(17)$, $b=14.589(3)$, $c=18.030(4)$ Å, $b=96.42(3)°$, $V=2254.5(8)$ Å^3, $Z=4$, $r_{calcd}=1.218$ Mg m^{-3}, MoKa radiation ($l=0.71073$ Å), $T=110(2)$ K, 21259 measured reflections, 5433 unique, $R_{int}=0.0898$, $R_1=0.1361$, $wR_2=0.1696$ (all data). Specimens of suitable size and quality were selected and mounted onto 0.7 mm nylon loop with apiezon grease. The structures were solved by direct methods, which successfully located most of the non-hydrogen atoms. Subsequent refinement on F^2 using the SHELXTL/PC package (version 5.1) allowed location of the remaining non-hydrogen atoms. CCDC 722717 ([**1**]$^+$), 722718 ([**2**]$^+$), and 722719 ([**2**(CN)]) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

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