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Ditopic Binding of Alkali Halide Ions to Trimethylboroxine

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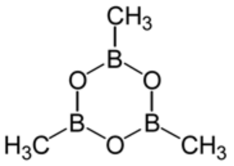
Abstract: Trimethylboroxine (TMB) is a six-membered ring compound containing Lewis acidic boron and Lewis basic oxygen atoms that can bind halide anion and alkali metal cation, respectively. We employed Fourier transform ion cyclotron resonance spectroscopy to study the gas-phase binding of $LiBrLi^+$ and $F^-(KF)_2$ to TMB. TMB forms association complexes with both $LiBrLi^+$ and $F^-(KF)_2$ at room temperature, providing direct evidence for the ditopic binding. Interestingly, the $TMB\cdot F^-(KF)_2$ anion complex is formed 33 times faster than the $TMB\cdot Li^+BrLi$ cation complex. To gain insight into the ditopic binding of an ion pair, we examined the structures and energetics of $TMB\cdot Li^+$, $TMB\cdot F^-$, $TMB\cdot LiF$ (the contact ion pair), and $Li^+\cdot TMB\cdot F^-$ (the separated ion pair) using Hartree–Fock and density functional theory. Theory suggests that F^- binds more strongly to TMB than Li^+ and the contact ion-pair binding ($TMB\cdot LiF$) is more stable than the separated ion-pair binding ($Li^+\cdot TMB\cdot F^-$).

Key words: Ditopic Ion-Pair Binding, Ion-Molecule Association, Trimethylboroxine, Lithium Fluoride

Introduction

The selective binding of either cation or anion to macrocycles has been widely used in constructing supramolecular assembly for molecular recognition.[1,2] Recently, the ion-pair binding[3] has attracted much attention because of the potential application in zwitterion recognition and/or selective extraction of zwitterionic species of environmental importance.[4,5] Both cation and anion co-operatively bind to the ditopic receptors that possess the separate binding site for each charge type; the binding of one charged species induces the subsequent binding of the counter ion.[6–10] The cation is typically bound by noncovalent interactions with Lewis basic oxygen or nitrogen atoms in crown ethers,[4,6–8] aza-crowns,[3] and esters,[9,10] whereas the anion is held either by electrostatic interactions with cation moieties,[7] or by hydrogen bonding with proton-rich amide groups,[3,4,8,9] or by coordinate covalent bonding with a Lewis acidic boron atom.[6]

In this regard, boroxine is an interesting molecule to test for ditopic binding, because this six-membered ring compound contains both oxygen and boron atoms. Although the boroxine ring is planar with six equivalent B–O bonds, the aromatic character is considered to be almost absent because p-electrons are mostly localized on oxygen atoms and boron atoms are electron-deficient.[11–13] Here, we present experimental and theoretical results that support the ditopic binding of alkali halide to trimethylboroxine (TMB, **1**).



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Scheme

In experiments, Fourier-transform ion cyclotron resonance (FT-ICR) mass spectrometry was employed to study the gas-phase association of TMB with alkali halide cations and anions in the ICR cell. The rate constant for the association reaction was measured from the reaction time plot. After confirming the binding of both cation and anion to TMB by mass spectrometry (MS), we carried out ab initio calculations to examine the ion-pair binding to TMB, because MS did not yield a signal for neutral charge-state complexes. In theory, the structures and energetics of the contact ion-pair binding complexes as well as the separated ion-pair binding complexes were examined.

Experimental Section

FT-ICR mass spectrometry was employed to measure the rate constant for the binding of the mass-selected $LiBrLi^+$ cation or $K_2F_3^-$ anion to TMB. Experimental details have been described previously.[14–16] In brief, we prepared $LiBrLi^+$ and $K_2F_3^-$ in the ICR cell by matrix-assisted laser desorption ionization (MALDI) of a mixture of lithium bromide and potassium fluoride salts with dibenzo-18-crown-6, respectively. The MALDI sample was loaded on a Teflon substrate. The 355-nm laser output was used for MALDI. TMB vapor was leaked into the ICR chamber at room temperature through a leak valve, and its partial pressure measured by ion gauge was in the $1.5–10.0 \times 10^{-7}$ Torr range. All chemicals were purchased from Sigma Aldrich. Liquid TMB was used after several freeze-pump-thaw cycles.

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We also carried out Hartree–Fock (HF) and density functional theory (DFT) calculations with 6-311G(d,p) and 6-311+(2d,p) basis sets. Becke-3–Lee–Yang–Parr (B3LYP) functionals were used for DFT. The structures were optimized using a Gaussian-03 program and the binding energies were corrected for both the basis set superposition errors[17] and zero-point energies[18].

Results and Discussion

Reaction time plot of the $LiBrLi^+$ triple ion with TMB is shown in Figure 1a. TMB either abstracts Li^+ from $LiBrLi^+$ to yield TMB·Li^+ or forms a TMB·$LiBrLi^+$ adduct. The relative abundance (*I/total I*) of $LiBrLi^+$ decays exponentially with the rate constant of 2×10^{-11} cm^3 $molecule^{-1}$ s^{-1}. Both TMB·Li^+ and TMB·$LiBrLi^+$ are solvated by another TMB to yield $(TMB)_2$·Li^+ and $(TMB)_2$·$LiBrLi^+$, respectively. No third solvation of TMB is observed. Apparently, both the Li^+ and $LiBrLi^+$ cations bind to TMB. The final abundance ratio of $(TMB)_2$·$LiBrLi^+$ to $(TMB)_2$·Li^+ is about 3.

Reaction time plot of $K_2F_3^-$ with TMB is displayed in Figure 1b. TMB forms a TMB·$K_2F_3^-$ adduct exclusively. Neither F^- abstraction nor further solvation of TMB·$K_2F_3^-$ is observed. The rate constant for the anion association is 6.6×10^{-10} cm^3 $molecule^{-1}$ s^{-1}, which is ~33 times greater than that for the cation association. Meanwhile, the reaction of hot FKF^- ions with TMB has resulted in TMB·F^- with loss of KF (data not shown). Obviously, both the $K_2F_3^-$ and F^- anions bind to TMB. *These experimental results strongly suggest the ditopic binding of both cation and anion to TMB.*

To gain insight into the ion-pair binding to TMB, we studied the structures and energetics of TMB (**1**), TMB·Li^+ (**2**), TMB·F^- (**3**), the separated ion-pair complex Li^+·TMB·F^- (**4**, **5**), and the contact ion-pair complex TMB·LiF (**6**–**9**). The structures optimized at the B3LYP/6-311+G(2d,p) level are shown in Figure 2 for **1**–**3** and Figure 3 for **4**–**9**. The calculated binding energies are listed in Table 1.

Although **1** shows an equal B–O bond length (1.381 Å), the O–B–O bond angle (121.6°) is slightly greater than 120°, whereas the B–O–B bond angle (118.4°) is slightly less than 120° (Figure 2), indicating that p-electrons are not conjugated like an aromatic ring. The binding of Li^+ to one of oxygen atoms yields a planar complex **2** with the Li–O distance of 1.825 Å, whereas the F^- binding to one of boron atoms results in a tetrahedral boron complex **3** with the B–F distance of 1.429 Å (Figure 2). Neither a bidentate coordination of Li^+ to two oxygen atoms nor a tridentate coordination of F^- to three boron atoms yields a local minimum. The best estimate for the binding energy is $D_0(\mathbf{1} - Li^+) = 35.1$ kcal mol^{-1} and $D_0(\mathbf{1} - F^-) = 57.2$ kcal mol^{-1} at the B3LYP/6-311+G(2d,p) level. The coordinate covalent B–F^- bond is 22 kcal mol^{-1} stronger than the noncovalent O–Li^+ bond, in line with the greater association rate constant for $K_2F_3^-$ than for $LiBrLi^+$.

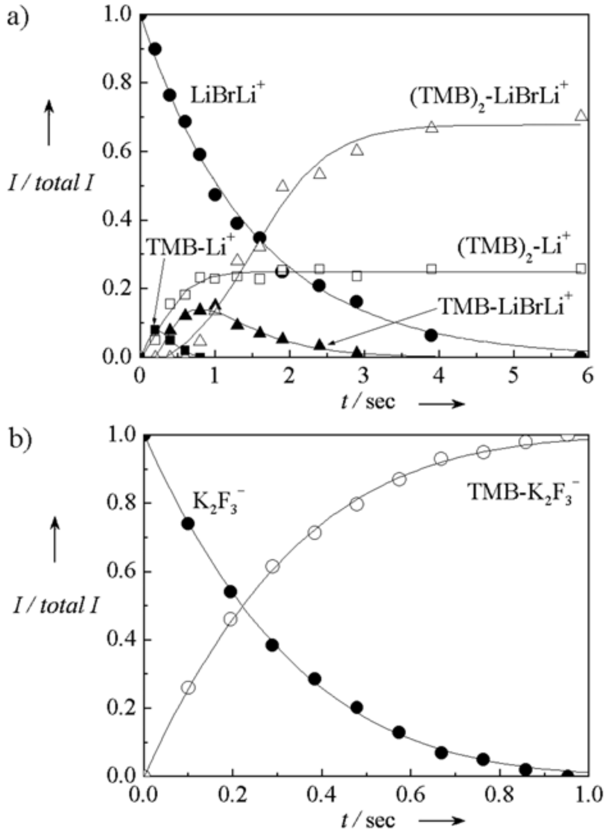

Figure 1. a) Reaction time plot of $LiBrLi^+$ with trimethylboroxine (TMB) at 1.0×10^{-6} Torr, $k_{obs} = 2 \times 10^{-11}$ cm^3 $molecule^{-1}$ s^{-1}; b) Reaction time plot of $K_2F_3^-$ with TMB at 1.5×10^{-7} Torr, $k_{obs} = 6.6 \times 10^{-10}$ cm^3 $molecule^{-1}$ s^{-1}.

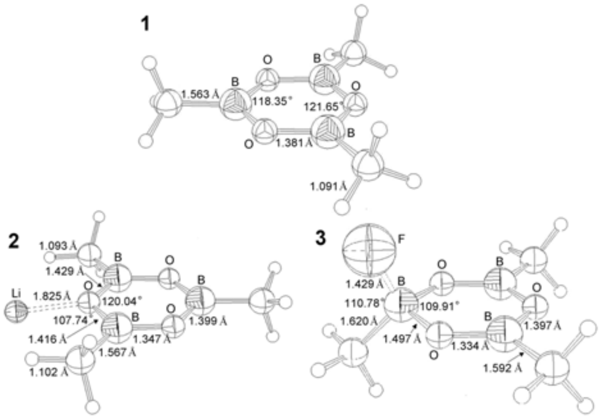

Figure 2. Structures of trimethylboroxine (**1**), **1**·Li^+ (**2**), and **1**·F^- (**3**) optimized at the B3LYP/6-311+G(d,p) level.

The structures of two separated ion-pair complexes (**4**, **5**) and four contact ion-pair complexes (**6**–**9**) are presented in Figure 3. In the case of **4**, F^- forms a tetrahedral boron complex with the B–F distance of 1.402 Å, while Li^+ binds to the oxygen atom with the Li–O distance of 1.758 Å in the *para* position from the tetrahedral boron. Meanwhile, the boroxine ring remains planar. In **5**, F^- also forms a tetrahedral boron complex with the B–F distance of 1.308 Å, while Li^+ binds

Table 1. Binding Energies of **1**·Li$^+$ (**2**), **1**·F$^-$ (**3**), Li$^+$·**1**·F$^-$ (**4**,**5**), **1**·LiF (**6**–**9**), and LiF at 0 K^a.

method	**2**	**3**	**4**	**5**	**6**	**7**	**8**	**9**	LiF
HF/6-311G(d,p)	33.7	61.1	176.7	192.1	193.5	201.0	198.8	205.3	205.7
B3LYP/6-311G(d,p)	35.7	63.7	183.3	196.3	195.7	200.6	201.0	206.3	220.0
HF/6-311+G(2d,p)	33.4	57.2	172.2	188.8	192.4	197.4	197.6	204.2	184.7
B3LYP/6-311+G(2d,p)	35.1	57.2	175.5	189.5	193.3	196.5	198.2	204.0	185.0
Thermochemical Data^b									184.4

^{a}The dissociation limits are **1** + Li$^+$ for **2**, **1** + F$^-$ for **3**, **1** + Li$^+$ + F$^-$ for **4**–**9**, and Li$^+$ + F$^-$ for LiF.
^{b}Taken from ref 19.

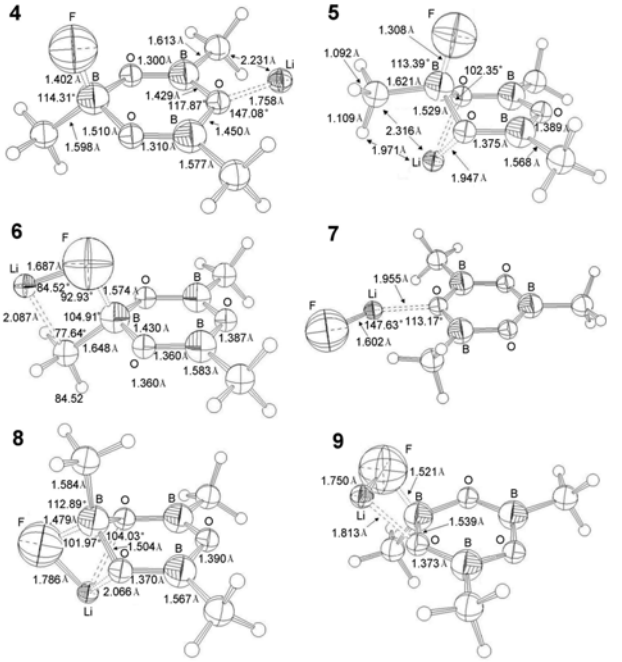

Figure 3. Structures of the separated ion-pair complexes Li$^+$·**1**·F$^-$ (**4**, **5**) and the contact ion-pair complexes **1**·LiF (**6**–**9**) optimized at the B3LYP/6-311+G(d,p) level.

to the two oxygen atoms bonded to the tetrahedral boron with the Li–O distance of 1.947 Å. The tetrahedral boron is puckered out of the plane and F$^-$ is located in an axial position. The contraction of the Li–O bond length from 1.825 Å in **2** to 1.758 Å in **4** and the concomitant contraction of the B–F bond length from 1.429 Å in **3** to 1.402 Å in **4** suggest the co-operative binding of both cation and anion to TMB. The ion-pair binding energies of 176 and 190 kcal mol^{-1} for **4** and **5** are 83 and 97 kcal mol^{-1} higher than the sum (92 kcal mol^{-1}) of D_0(**1** – Li$^+$) and D_0(**1** – F$^-$), respectively, indicating the synergic effect of co-operative ion-pair binding. Between the two complexes, **5** is 14 kcal mol^{-1} more stable than **4** at the B3LYP/6-311+G(2d,p) level. Notably, the binding energy of **5** is 4.5 kcal mol^{-1} greater than the heterolytic bond dissociation energy of LiF [D_0(Li$^+$ – F$^-$) = 185.0 kcal mol^{-1} and D_{exp}(Li$^+$ – F$^-$)^{19} = 184.4 kcal mol^{-1}].

For the contact ion-pair complexes **6** and **7**, either Li$^+$ or F$^-$ of LiF binds to TMB. In **6**, F$^-$ is bound to a boron atom and Li$^+$ is away from the ring to align with the methyl carbon atom attached to the tetrahedral boron atom. In **7**, Li$^+$ is bound to an oxygen atom in a plane and F$^-$ is uncoordinated. In the cases of **8** and **9**, both Li$^+$ and F$^-$ of LiF bind to TMB: In **8**, F$^-$ is coordinated to a boron atom, while Li$^+$ is bound to two adjacent oxygen atoms. The boron atom is puckered out of the plane with F$^-$ at an equatorial position and the Li–F bond dissects the puckered O–B–O angle. In **9**, both Li$^+$ and F$^-$ are coordinated to the adjacent boron and oxygen atoms, respectively, from the same side. The boroxine ring remains planar in **6**, **7**, and **9**. Of the contact ion-pair complexes, **9** is the most stable, whereas **6** is the least stable. The monodentate coordination of Li$^+$ (**9**) is energetically favored over the bidentate coordination (**8**) due to the puckering of a ring in the latter. The binding energy of **9** is 19.0 kcal mol^{-1} relative to the dissociation limit of **1** + LiF. Interestingly, the separated ion-pair complexes (**4**, **5**) are less stable than the contact ion-pair complexes (**6**–**9**). These theoretical results manifest the ditopic binding of an ion pair to TMB.

Conclusions

Trimethylboroxine is a simple ditopic receptor where both lithium cation and fluoride anion bind. F$^-$ binds more strongly to trimethylboroxine than Li$^+$, as F$^-$ forms a coordinate covalent bond with a Lewis acidic boron atom, whereas Li$^+$ forms a noncovalent bond with a Lewis basic oxygen atom. The fluoride-bound tetrahedral boron atom puckers out of the plane in boroxine. Both the contact ion pair and the separated ion pair co-operatively bind to trimethylboroxine; however, TMB favors the binding of the contact ion pair over the separated ion pair.

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