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Synthesis and Fluoride Binding Properties of Tris-pyridinium Borane

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A novel multi-cationic borane, tri-*N*-methylpyridinium substituted triarylborane, $[BAr^N_3]I_3$ ([**2**]I_3) (Ar^N = 4-(4-C_5H_4N-Me)-2,6-Me_2-C_6H_2) was prepared from the corresponding neutral tris-pyridyl borane, BAr_3 (**2a**) (Ar = 4-(4-C_5H_4N)-2,6-Me_2-C_6H_2). The crystal structure of **2a** determined by X-ray diffraction study reveals the presence of tri-coordinate boron center with peripheral pyridyl moieties. The fluoride ion affinity of the cationic borane, [**2**]I_3 was investigated by UV-vis absorption titrations and was compared with that of neutral **2a**. While **2a** binds fluoride with the binding constant of 1.9×10^2 M^{-1} in THF/H_2O (9:1 v/v) mixture, [**2**]I_3 shows a very high binding constant ($K = 1.0 \times 10^8$ M^{-1}) that is greater by six orders of magnitude than that of **2a** in the same medium. This result indicates that the fluorophilicity of triarylborane can be drastically enhanced by multiple pyridinium substitutions.

Key Words : Triarylborane, Pyridinium, Fluoride, Chemosensor

Introduction

The selective recognition of fluoride ions is of great interest owing to the harmful effects of fluorides in physiological and environmental systems. Despite the important roles of fluorides in dental health and in treating osteoporosis,[1] taking excessive fluorides may lead to fluorosis.[2] To prevent such detrimental effects of fluoride, the selective detection of fluorides has recently received considerable attention. Among the receptors for the detection of fluorides developed to date, triarylborane compounds are shown to be one of the most effective molecular platforms due to their high Lewis acidity, as well as high selectivity provided by the steric protection of the boron center with *ortho*-substituents on the aryl group.[3] Although most triarylborane receptors have successfully operated in organic media with high binding affinity,[4-6] they showed a limited binding ability in the presence of water, which interferes with the fluoride binding. Since fluoride is present in abundance in aqueous media, detection of fluoride in aqueous or water-compatible media is of great importance in real applications. Many efforts have thus been focused on enhancing the Lewis acidity of a boron center by introducing strong electron-withdrawing groups into the triarylboranes.[7-14] Among such approaches, the cationic triarylboranes have been shown to largely increase the fluoride affinity of the boron center enough to be operating in aqueous media, due to the Coulombic and inductive effects of cationic groups that assist B-F dative interactions.[5,7,9-13]

Gabbaï and co-workers have reported various types of mono- and multi-cationic triarylboranes which can bind fluoride in aqueous solution (Chart 1).

For example, the mono-ammonium[13] and phosphonium boranes[11] ([**I**]$^+$) are shown to selectively bind fluoride in

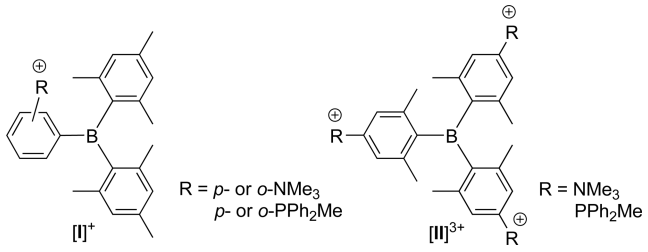


Chart 1

aqueous solution. Furthermore, it was shown that the Lewis acidity can be enhanced by the introduction of multiple cationic moieties.[7,12] The tri-ammonium and phosphonium boranes ([**II**]$^{3+}$) showed higher binding affinity than the mono- and di-cationic derivatives in water.[7] These results attested that while retaining the steric protection of the boron center by *ortho*-Me groups, the peripheral introduction of multiple cationic moieties into triarylborane can significantly enhance the Lewis acidity of a boron center and has an additive effect on the Lewis acidity enhancement due to the increased Coulombic and inductive effects of cationic groups.

To elucidate more the Lewis acidity enhancement of triarylboranes by multiple substitutions of cationic moieties, we designed a tri-pyridinium substituted triarylborane in this study. Since the recent report on mono-pyridinium boranes demonstrated that pyridinium moiety can enhance the Lewis acidity enough to extract fluorides in water/$CHCl_3$ mixture,[10] it can be expected that the introduction of tri-pyridinium moieties will show a large increase in the Lewis acidity of triarylborane. In this report, we prepared a tris-*N*-methylpyridinium borane and compared its fluoride binding affinity with that of the neutral tris-pyridyl borane. Details of synthesis, characterization, and the fluoride binding properties

of the tris-pyridinium borane are described.

Experimental Section

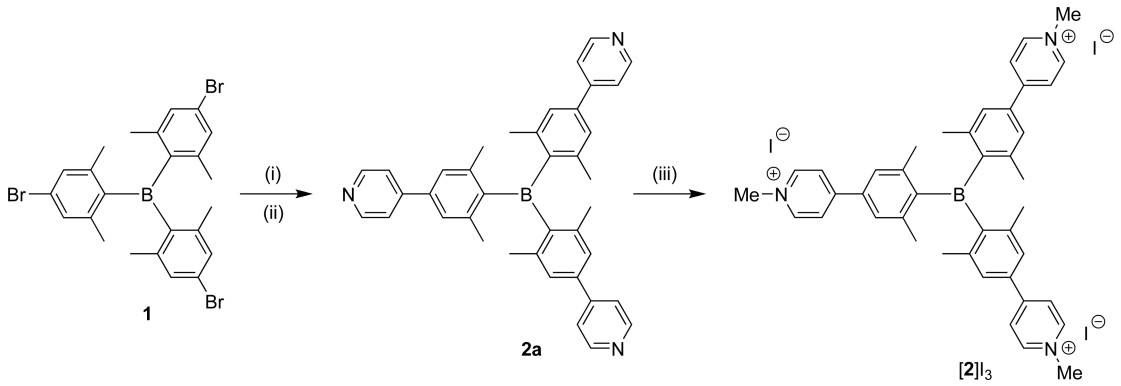
General Considerations. All operations were performed under an inert nitrogen atmosphere using standard Schlenk and glove box techniques. Anhydrous grade solvents (Aldrich) were dried by passing them through an activated alumina column and stored over activated molecular sieves (5 Å). Spectrophotometric grade THF (Aldrich) was used as received. Commercial reagents were used without any further purification after purchasing from Aldrich (*n*-BuLi (2.5 M solution in hexane), $BF_3{\cdot}OEt_2$, trimethyl borate ($B(OMe)_3$), $Pd(PPh_3)_4$, Na_2CO_3, MeI, 4-bromopyridine hydrochloride, tetra-*n*-butylammonium fluoride (TBAF)). Tris(4-bromo-2,6-dimethylphenyl)borane (**1**)[15] was prepared according to the reported procedures. Deuterated solvents from Cambridge Isotope Laboratories were used. NMR spectra were recorded on a Bruker Avance 400 spectrometer (400.13 MHz for ^1H, 100.62 MHz for ^{13}C, 128.38 MHz for ^{11}B) at ambient temperature. Chemical shifts are given in ppm, and are referenced against external Me_4Si (^1H, ^{13}C) and $BF_3{\cdot}OEt_2$ (^{11}B). Elemental analyses were performed on an EA1110 (FISONS Instruments) by the Environmental Analysis Laboratory at KAIST. UV-vis absorption spectra were recorded on a Jasco V-530 spectrophotometer.

Synthesis of Tris(2,6-dimethyl-4-(4-pyridyl)-phenyl)-borane (2a). A hexane solution of *n*-BuLi (2.5 M, 1.3 mL, 3.3 mmol) was added to a THF (20 mL) solution of **1** (0.56 g, 1.0 mmol) at –78 °C. After stirring for 1 h at this temperature, the cold mixture was transferred into a solution of $B(OMe)_3$ (0.9 mL, 10 equiv) in THF (20 mL) *via* cannula at –78 °C. The mixture was stirred for another 1 h and then was allowed to warm to room temperature. After stirring overnight, the reaction was quenched with saturated aqueous NH_4Cl (30 mL). The aqueous layer was extracted with CH_2Cl_2 (2 × 20 mL) and the organic layer was separated. The combined organic layers were dried over $MgSO_4$ and the solvents were evaporated under reduced pressure. Next, the crude boronic acid (0.39 g, 0.85 mmol) was diluted in 20 mL of degassed EtOH and was added slowly to a mixture of 4-bromopyridine hydrochloride (0.74 g, 3.83 mmol), $Pd(PPh_3)_4$ (0.10 g, 0.088 mmol), and Na_2CO_3 (1.50 g) in toluene (40 mL) at room temperature. Degassed distilled water (20 mL) was subsequently added to the mixture. After stirring for 15 min at room temperature, the reaction mixture was heated at reflux for 24 h. After cooling the mixture to room temperature, the organic layer was separated and the aqueous layer was extracted with CH_2Cl_2 (3 × 30 mL). The combined organic layers were dried over $MgSO_4$ and the solvents were removed under reduced pressure. Purification of the crude product by column chromatography (eluent: EtOAc) afforded **2a** as an ivory powder. Yield = 0.16 g (34%). Single crystals suitable for X-ray diffraction study were grown from vapor diffusion of ether into a THF solution of **2a**. ^1H NMR ($CDCl_3$) δ 8.63 (dd, J = 6.1, 3.0 Hz, 6H), 7.53 (dd, J = 6.2, 3.0 Hz, 6H), 7.24 (s, 6H), 2.14 (s, 18H). ^{13}C NMR ($CDCl_3$) δ 150.07, 147.85, 147.14, 141.41, 139.00, 126.37, 121.37, 23.17. ^{11}B NMR ($CDCl_3$) δ 84 (br s). Anal. Calcd for $C_{39}H_{36}BN_3$: C, 84.02; H, 6.51; N, 7.54; Found: C, 84.04; H, 6.66; N, 7.75.

Synthesis of Tris(2,6-dimethyl-4-(4-*N*-methylpyridinium)-phenyl)borane triiodide ([2]I_3). To a solution of **2a** (30 mg, 54 mmol) in CH_3CN (30 mL) was added excess MeI (10 equiv) at room temperature. The mixture was then refluxed for 24 h. After cooling to room temperature, the solvent was evaporated under reduced pressure. The solid residue was washed with CH_2Cl_2 (10 mL) and dried under vacuum. Yield = 32 mg (60%). ^1H NMR (DMSO-d_6) δ 8.99 (d, J = 6.8 Hz, 6H), 8.52 (d, J = 6.8 Hz, 6H), 7.80 (s, 6H), 4.31 (s, 9H, *N-Me*), 2.14 (s, 18H). ^{13}C NMR (DMSO-d_6) δ 153.90, 149.47, 146.03, 141.91, 135.05, 127.61, 124.32, 47.57 (*N-Me*), 22.97. ^{11}B signal was not observed. Anal. Calcd for $C_{42}H_{45}BI_3N_3$: C, 51.30; H, 4.61; N, 4.27; Found: C, 51.01; H, 4.88; N, 4.75.

UV-vis Titration Experiments. UV-vis titrations of fluoride ions were performed in THF or THF/H_2O (9:1 v/v) with a 1-cm quartz cuvette at ambient temperature. Typically, a solution of triarylborane (3.0 mL) was titrated with incremental amounts of fluoride. The absorbance data obtained were fitted to a 1:1 binding isotherm. The detailed conditions are given in the Figure captions.

X-ray Crystallography. Single crystals of **2a** was coated with Paratone oil and mounted onto a glass capillary. The



Scheme 1. (i) *n*-BuLi (3 equiv), $B(OMe)_3$ (10 equiv), THF, –78 °C. (ii) 4-Bromopyridine hydrochloride (3 equiv), $Pd(PPh_3)_4$, Na_2CO_3, toluene/EtOH/H_2O (2:1:1, v/v), reflux, 24 h, 34%. (iii) MeI (10 equiv), CH_3CN, reflux, 24 h, 60%.

crystallographic measurement was performed on a Bruker SMART Apex II CCD area detector diffractometer with a graphite-monochromated Mo-Kα radiation (λ = 0.71073 Å). The structure was solved by direct methods and all non-hydrogen atoms were subjected to anisotropic refinement by full-matrix least-squares on F^2 by using the SHELXTL/PC package. Hydrogen atoms were placed at their geometrically calculated positions and refined riding on the corresponding carbon atoms with isotropic thermal parameters. The detailed crystallographic data are given in Table S1 (see Supporting Information). Crystallographic data for the structure reported here has been deposited with CCDC (Deposition No. CCDC-930416 (**2a**)). These data can be obtained free of charge *via* http://www.ccdc.cam.ac.uk/conts/retrieving.html or from CCDC, 12 Union Road, Cambridge CB2 1EZ, UK, E-mail: deposit@ccdc.cam.ac.uk.

Results and Discussion

Synthesis and Characterization. The synthetic procedures towards neutral tris-pyridyl borane, BAr_3 (**2a**) (Ar = 4-(4-C_5H_4N)-2,6-Me_2-C_6H_2) and its cationic derivative, $[BAr^N_3]I_3$ ([**2**]I_3) (Ar^N = 4-(4-C_5H_4N-Me)-2,6-Me_2-C_6H_2) are shown in Scheme 1. Lithiation of the starting bromo-triarylborane compound, tris(4-bromo-2,6-dimethylphenyl)-borane (**1**), with three equiv of *n*-BuLi, followed by reaction with $B(OMe)_3$ in THF afforded tris-boronic acid intermediate after aqueous work-up. The crude boronic acid was next subject to the Suzuki-Miyaura coupling reaction with three equiv of 4-bromopyridine hydrochloride, which produced the neutral borane **2a** after purification by column chromatography. The formation of **2a** was characterized by multinuclear NMR spectroscopy and elemental analysis. The ^{1}H NMR spectrum showed the expected resonances for the methyl groups at δ 2.14 ppm and the aromactic C-H protons of the Ar groups in the region of δ 8.6-7.2 ppm as two doublets (pyridyl) and one singlet (2,6-Me_2-C_6H_2) (Figure S1). Observation of one singlet proton resonance for the six methyl groups indicates that the three Ar groups in **2a** are chemically equivalent in solution. The broad ^{11}B NMR signal at δ 84 ppm confirms the presence of the trigonal boron atom. Furthermore an X-ray diffraction study revealed the molecular structure of **2a** (Figure 1 and Table S1). The central boron atom adopts a trigonal planar geometry ($\Sigma_{(C\text{-}B\text{-}C)}$ = 359.9°) and the three pyridyl moieties are attached at the *para*-positions of the Ar groups. The three Ar groups also form a propeller-like conformation due to steric repulsion between the six *ortho*-methyl groups around the boron atom.

The neutral borane **2a** was converted into the corresponding iodide salts of methylated pyridinium borane, [**2**]I_3 by refluxing it with excess MeI in acetonitrile (Scheme 1). The identity of [**2**]I_3 has been characterized by NMR spectroscopy and elemental analysis (Figure S2). Although ^{11}B NMR signal was not observed despite prolonged aquisition, the downfield shift of the C-H proton signals of the Ar^N groups to δ 9.0-7.8 ppm and the appearance of a new singlet peak at δ 4.3 ppm confirms methylation on the pyridy nitrogen atoms. As similarly observed in the neutral **2a**, the proton resonance for the six methyl groups appears as one singlet, pointing to the free rotation of the three Ar^N groups in solution.

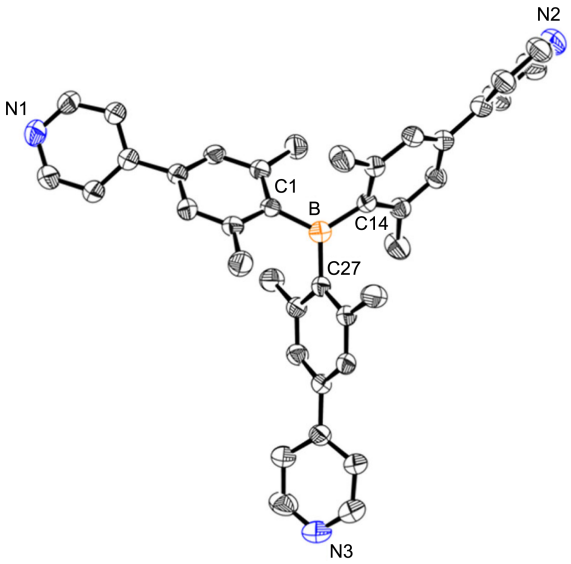


Figure 1. Crystal structure of **2a** (40% ellipsoid). H-atoms were omitted for clarity. Selected bond lengths (Å) and angles (deg): B-C(1) 1.583(4), B-C(14) 1.582(4), B-C(27) 1.585(4); C(1)-B-C(14) 121.1(2), C(1)-B-C(27) 117.6(2), C(14)-B-C(27) 121.2(2).

Fluoride Binding Studies. To investigate an effect of multiple pyridinium moieties on the Lewis acidity enhancement of triarylborane, UV-vis titration experiments with fluoride were carried out using **2a** and [**2**]I_3. Fluoride binding property of the neutral **2a** was first examined in THF. **2a** features two absorption bands centered at 265 and 345 nm (Figure 2). Upon addition of incremental amounts of fluoride

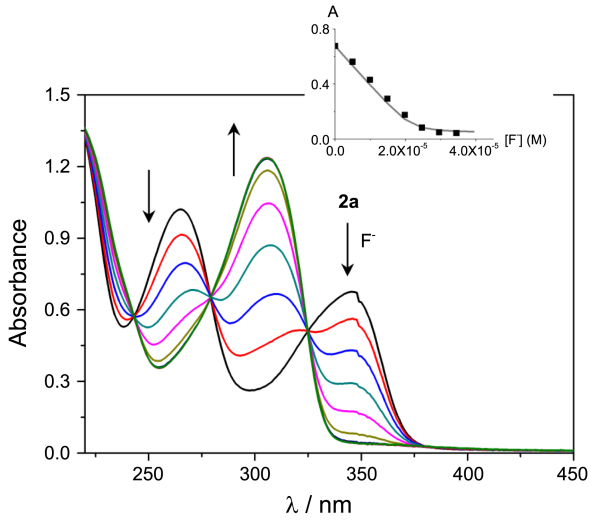


Figure 2. Spectral changes in the UV-vis absorption of a solution of **2a** in THF (2.19×10^{-5} M) upon addition of TBAF (3.0×10^{-3} M, 0-2.0 equiv). The inset shows the absorbance at 345 nm as a function of [F^-]. The line corresponds to the binding isotherm calculated with $K = 3.5 \times 10^6$ M^{-1}.

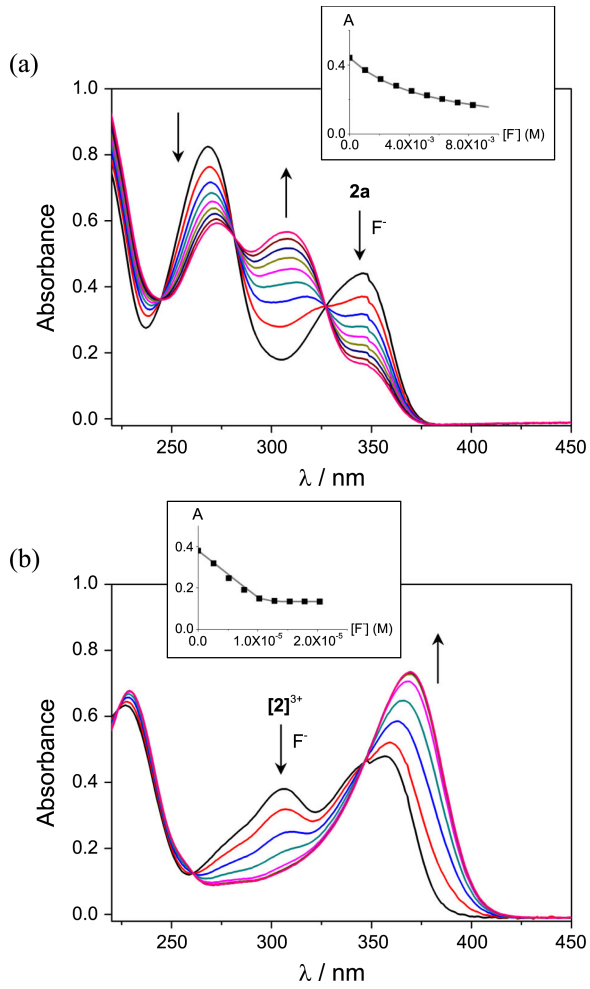


Figure 3. Spectral changes in the UV-vis absorption of a solution of (a) **2a** and (b) [**2**]I_3 in THF/H_2O (9:1 v/v, 1.97×10^{-5} M for **2a** and 1.09×10^{-5} M for [**2**]I_3) upon addition of TBAF (6.29×10^{-1} M, 0-382 equiv for **2a** and 1.55×10^{-3} M, 0-1.9 equiv for [**2**]I_3). The insets show the absorbance at 346 nm for **2a** and 306 nm for [**2**]I_3, respectively, as a function of [F^-]. The line corresponds to the binding isotherm calculated with $K = 1.9 \times 10^2$ M^{-1} for **2a** and 1.0×10^8 M^{-1} for [**2**]I_3.

(0-2.0 equiv in Figure 2), both bands were gradually quenched while a new absorption band at 305 nm was induced. Because the empty p_π(B) orbital occupies LUMO in the usual triarylboranes, the quenching of the lower-energy band at 345 nm can be attributed to the fluoride binding to the boron center. Based on the absorbance change at 345 nm, the fluoride binding constant (K) was estimated to be 3.5×10^6 M^{-1} from the 1:1 binding isotherms. It is notable that the K value is greater by one order of magnitude than that of Mes_3B ($K = 3.3(\pm 0.5) \times 10^5$ M^{-1} in THF) which has a similar steric environment around the boron center.[6,14] This result indicates that the introduction of pyridyl groups enhances fluorophilicity of triarylborane probably due to the extended conjugation, as well as the electron-withdrawing effect of pyridyl group.

Next, fluoride ion affinity of the pyridinuim borane, [**2**]I_3 was investigated and compared with that of neutral **2a**. Because it is well known that cationic boranes have very high fluoride ion affinities in organic media, the UV-vis titrations were carried out in more competing medium, such as THF/H_2O (9:1 v/v) mixture to discriminate the binding constants between **2a** and [**2**]$^{3+}$ (Figure 3). **2a** shows two absorption bands centered at 268 and 346 nm, which is very similar to the absorption feature in THF. However, both bands were quenched when a large excess of fluoride was added (0-382 equiv in Figure 3). The fluoride binding constant was calculated to be $K = 1.9 \times 10^2$ M^{-1}, which is lower than that obtained in THF by four orders of magnitude. On the other hand, the cationic [**2**]$^{3+}$ exhibits major absorption bands centered at 306 and 357 nm in THF/H_2O (9:1 v/v). The overall red shift of the absorption bands including the absorption onset position indicates that the HOMO-LUMO band gap of **2a** decreased after changing to the cationic form, suggesting the larger stabilization of LUMO than HOMO by cationic moiety. Upon addition of incremental amounts of fluoride (0-1.9 equiv in Figure 3), the high-energy band at 306 nm was gradually quenched while the low-energy band at 357 nm increases in intensity with a slight red shift to 369 nm. The red shift could be consequence of the formation of fluoroborate species, because the increased electron density may raise more the HOMO level than LUMO, resulting in the reduction of a band gap. Based on the absorbance change at 306 nm, the fluoride binding constant was calculated to be $K = 1.0 \times 10^8$ M^{-1}. Comparison of this K value with that of **2a** shows a drastic increase in the binding constant of [**2**]$^{3+}$ by six orders of magnitude. This result thus clearly demonstrates that the introduction of multiple pyridinium moieties into the triarylborane significantly enhances the Lewis acidity of the boron atom probably due to the favorable Coulombic and inductive effects of pyridinium groups, as similarly shown in other multi-cationic boranes.[7]

Conclusion

We have synthesized a tri-*N*-methylpyridinium substituted triarylborane, [**2**]$^{3+}$ from the corresponding neutral borane **2a**. It was shown by absorption titrations with fluoride ions in THF/H_2O (9:1 v/v) mixture that the fluoride binding constant of **2a** can be drastically enhanced upon changing to the cationic derivative [**2**]$^{3+}$ by six orders of magnitude. The present result thus indicates that the introduction of multiple pyridinium moieties into the triarylborane significantly enhances the Lewis acidity of a boron center probably due to the Coulombic and inductive effects of pyridinium groups, holding promise of [**2**]$^{3+}$ for the sensing of fluoride ions.

Supporting Information. Table for the crystallographic data and NMR spectra of compounds.

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