Supramolecular Chemistry

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# Tetraanionic Organoborate Squares Glued Together by Cations To Generate Nanotubular Stacks**

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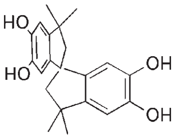

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3,3,3′,3′-Tetramethyl-1,1′-spirobisindane-5,5′,6,6′-tetrol (**1**; hereafter $LH_4$), which is easily obtained in racemic form, is an attractive building block for the construction of functional solids, because of its ready availability, its rigid angularity, and its chirality. Shea and co-workers have reported that reaction of $LH_4$ with phenyltriethoxysilane under basic conditions generates tetraanionic molecular squares of composition $[(C_6H_5Si)_4L_4]^{4-}$, in which the silicon centers have five-coordinate environments that are probably close to square pyramidal with a square $O_4$ base defined by two $L^{4-}$ units.[1] Although no X-ray crystallographic data are available, NMR spectroscopy indicates that a single diastereoisomer with $C_{2h}$ symmetry containing the two $L^{4-}$ enantiomers in equal numbers is selectively formed. Duhme and co-workers isolated $Na_4[(MoO_2)_2L_2]$ from the reaction of $LH_4$ with sodium molybdate.[2] In this case, X-ray crystallography revealed a macrocycle with a 2:2 rather than a 4:4 ligand/metal ratio, the two $L^{4-}$ units being of the same chirality. Herein, we describe some organoborate solids containing $[B_4L_4]^{4-}$ molecular squares, in which all four of the $L^{4-}$ components are of the same chirality. These squares, which contain a large central hole, are stacked one on top of another

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and “glued” together by cations to form infinite columns. Large channels of roughly square cross section and of roughly nanometer dimensions run through the centers of the columns.

Reaction of $LH_4$ with $B(OMe)_3$ and triethylamine ($Et_3N$) in methanol in a sealed tube at 160 °C generates crystals of solvated $(Et_3NH)_4[B_4L_4]$.[3a,4a] The crystal structure contains discrete molecular $[B_4L_4]^{4-}$ squares, shown in Figure 1, in which all four $L^{4-}$ units have the same handedness. The B···B separation across the center of the squares is 13.22 Å. The organoborate squares, all of the same chirality, stack one on top of another in the direction perpendicular to the $B_4$ plane (that is, the *c* direction), with the negatively charged boron centers of one square vertically above and below those of adjacent squares. The $[Et_3NH]^+$ ions are located between pairs of anionic boron centers. A combination of electrostatic anion–cation attraction (Figure 2 a) and hydrogen bonding (Figure 2 b) aligns the components of the stack to produce a tubular structure. As is indicated in Figure 2 b, all the N–H vectors point in the same direction and form significant hydrogen bonds to two ligand oxygen atoms (N–H···O 2.939(4) and 3.018(4) Å).

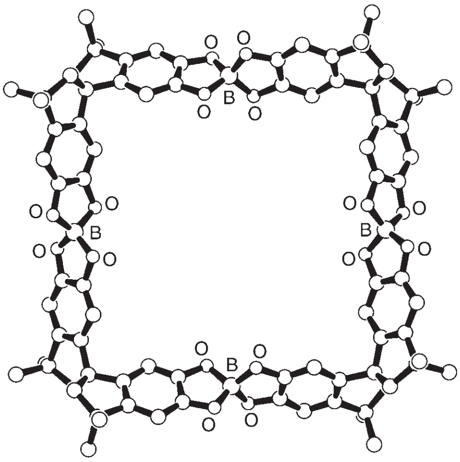

***Figure 1.*** A $[B_4L_4]^{4-}$ square in the structure of solvated $(Et_3NH)_4[B_4L_4]$. Hydrogen atoms are omitted for clarity.

All the columns in the structure are parallel and are packed as shown in Figure 3. Any column of a given chirality makes contact with four columns of opposite chirality. The tubes contain disordered solvent, which is very easily removed without disruption of the tubular structure (see below). This structure is reminiscent of the cyclic peptide nanotubes described by Ghadiri et al.,[5] which also consist of stacks of macrocycles hydrogen bonded together to generate tubular structures. However, in the present example of $(Et_3NH)_4[B_4L_4]$, anion–cation attraction provides a powerful additional tube-forming influence.

Reactions under conditions similar to those above, but with benzyldiethylamine ($BzEt_2N$) replacing triethylamine, yield crystals of composition $(BzEt_2NH)_4[B_4L_4]\cdot 4\,MeOH$.[3b,4b] The crystal structure is very similar to that of solvated $(Et_3NH)_4[B_4L_4]$. Stacks of $[B_4L_4]^{4-}$ squares, all of the same chirality, are glued together by the $[BzEt_2NH]^+$ ions in much the same way. However, in $(BzEt_2NH)_4[B_4L_4]\cdot 4\,MeOH$, the benzyl groups project into the channels, as was our intention, making edge-to-face phenyl contacts, as shown in Figure 4. Four methanol molecules, trapped in the spaces above and below the quartets of benzyl groups, are securely imprisoned, as indicated by thermogravimetric measurements described below.

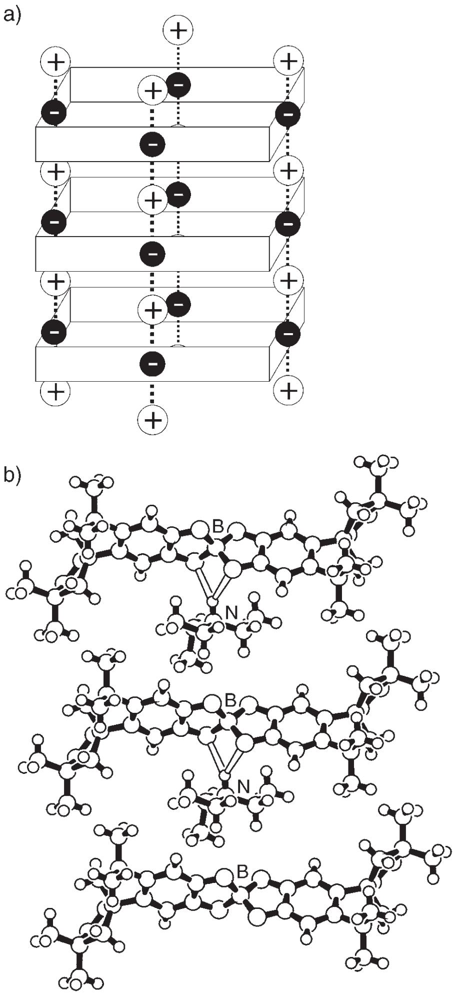

***Figure 2.*** a) Schematic representation of the stacking of tetraanionic squares, electrostatically glued together by monocations. Negative charges correspond to boron centers. b) Section of the crystal structure of solvated $(Et_3NH)_4[B_4L_4]$, showing the location of the $[Et_3NH]^+$ ions between anionic boron centers. Hydrogen bonds are indicated by the open connections.

We wondered if it might also be possible to use appropriate diamines in place of triethylamine. When doubly protonated, the diamines could potentially tether column to column, in addition to binding square to square. Reaction of $LH_4$ with $B(OMe)_3$ and 1,3-di(aminomethyl)-benzene (amb) under conditions similar to those employed above with triethylamine, yields crystals of solvated $(Me_2ambH_2)_2[B_4L_4]$ (in which $[Me_2ambH_2]^{2+}$ represents the diprotonated form of 1,3-di(methylaminomethyl)benzene, that is, $(MeNH_2{}^+CH_2)_2C_6H_4$).[3c,4c] Evidently, N-methylation of the amino groups of amb by methanol has occurred under

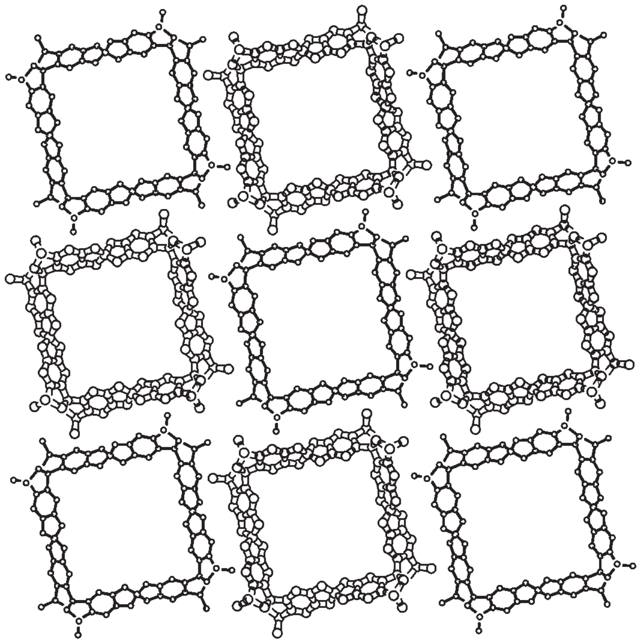

*Figure 3.* Packing of the "square stacks" in solvated $(Et_3NH)_4[B_4L_4]$. The stacks represented using small circles and thin closed bonds are all of the same chirality; the stacks represented using large circles and thick open bonds have the opposite chirality. Hydrogen atoms are omitted for clarity.

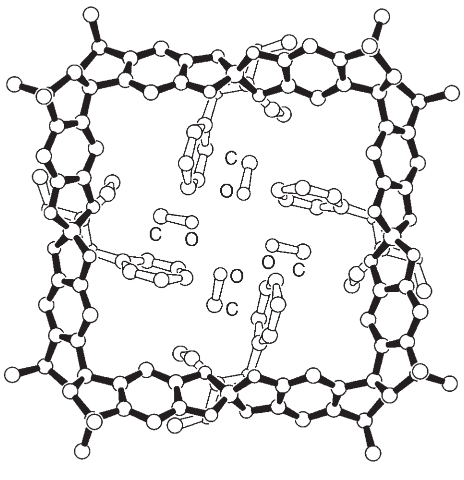

*Figure 4.* A $[B_4L_4]^{4-}$ square and four associated $[BzEt_2NH]^+$ ions in the structure of $(BzEt_2NH)_4[B_4L_4]\cdot 4\,MeOH$. The major orientations of the disordered methanol molecules are shown. Hydrogen atoms are omitted for clarity.

the forcing conditions used (160 °C in a sealed tube). Similar methylation reactions have been reported previously.[6] The presence of the $[Me_2ambH_2]^{2+}$ ion was independently indicated by electrospray mass spectrometry (ES/MS) on the solution obtained by decomposing the crystals of $(Me_2ambH_2)_2[B_4L_4]$ in aqueous acid. In the crystal structure of solvated $(Me_2ambH_2)_2[B_4L_4]$, $[B_4L_4]^{4-}$ squares, in which all the $L^{4-}$ units have the same chirality, are again present. Again, the squares stack one on top of another to generate tubelike columns, but now squares of opposite chirality alternate within a column, as shown in Figure 5a. Each square is rotated by approximately 20° around the tetragonal axis relative to its two nearest-neighbor squares of opposite chirality. This alternation within the stack leads to an approximate doubling of the $c$ parameter, compared to those of the other compounds,[4] in which all squares in a stack have the same chirality. As is shown in Figure 5b, the $[Me_2ambH_2]^{2+}$ ions are located between columns, as intended, where they do indeed serve as tethers. The two cationic nitrogen centers are electrostatically bonded to separate columns. The cation is disordered over two overlapping sets of sites related by a twofold axis. The two nitrogen atoms are hydrogen bonded to catechol oxygen atoms (N−H···O 2.983(8) Å at one nitrogen and 2.788(9) Å at the other).

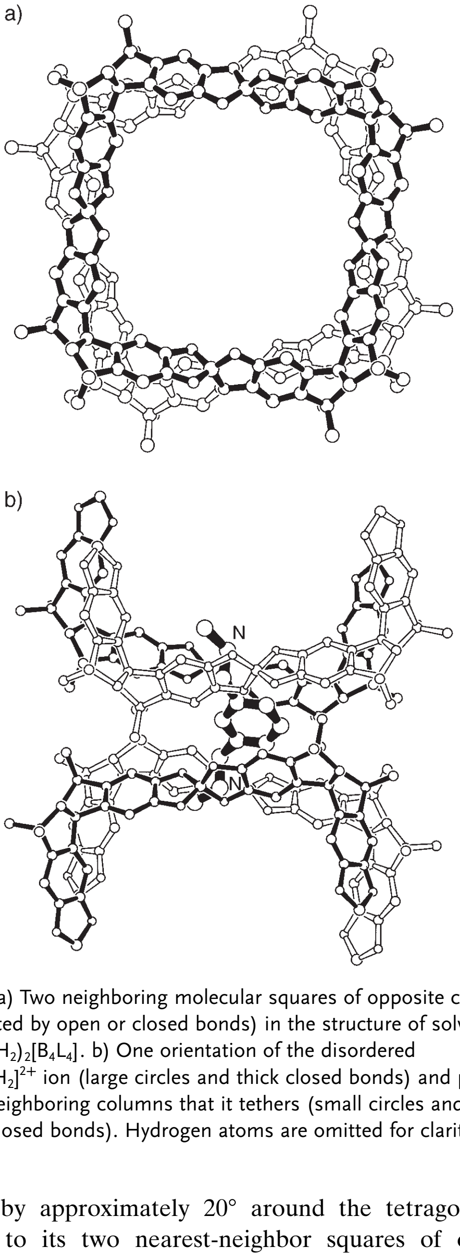

*Figure 5.* a) Two neighboring molecular squares of opposite chirality (represented by open or closed bonds) in the structure of solvated $(Me_2ambH_2)_2[B_4L_4]$. b) One orientation of the disordered $[Me_2ambH_2]^{2+}$ ion (large circles and thick closed bonds) and parts of the two neighboring columns that it tethers (small circles and thin open or closed bonds). Hydrogen atoms are omitted for clarity.

If the channels in the structures of solvated $(Et_3NH)_4[B_4L_4]$ and $(Me_2ambH_2)_2[B_4L_4]$ are regarded as tubes of constant square section, the edges of the squares, taking van der Waals surfaces into account, are estimated to be 7.5 and 9.8 Å, in each of the compounds, respectively.

When a sample of solvated $(Et_3NH)_4[B_4L_4]$ on the pan of the thermogravimetric instrument is exposed to a stream of nitrogen, it loses all its solvent, prior to any heating. The resulting mass of the sample remains essentially unchanged when the sample is subsequently heated to 270 °C, beyond which decomposition occurs (see Supporting Information). Thermogravimetric analysis of $(BzEt_2NH)_4[B_4L_4]\cdot 4\,MeOH$ indicates insignificant weight loss up to 270 °C; evidently, the methanol molecules remain trapped in the structure. Thermogravimetric analysis of solvated $(Me_2ambH_2)_2[B_4L_4]$ reveals relatively slow weight loss up to approximately 150 °C, whereafter little weight loss occurs until 270 °C; evidently, in this case, the solvent is held more tenaciously than in $(Et_3NH)_4[B_4L_4]$.

When suspended in water, ethanol, or chloroform for one week, crystals of solvated $(Et_3NH)_4[B_4L_4]$ and $(Me_2ambH_2)_2[B_4L_4]$ show no signs of either dissolution or deterioration. After the compounds are collected, dried under vacuum, and exposed to the atmosphere, their powder X-ray diffraction (XRD) patterns remain unchanged. Their powder XRD patterns also remain unchanged after the compounds are held at 200 °C for 90 minutes in a stream of nitrogen. Such stability to solvent loss is not rare in coordination polymers, but the present cases are exceptional in that electrostatic anion–cation attractive forces, in concert with secondary bonding interactions, are responsible for preserving the crystallinity.

It is interesting to consider how the rigid angularity and chirality of the $L^{4-}$ ligand, together with the stereochemical preferences of the associated metal or metalloid center (for example, molybdenum,[2] silicon,[1] or boron, herein) influence the composition and geometrical features of the aggregates they form. The strong preference of the $\{MoO_2\}^{2+}$ moiety for a *cis* dioxo arrangement imposes a *cis* configuration upon the two chelating catechol donors, which strongly inclines them towards one another, predisposing the system to form a "small ring" 2:2 association. When the two locally chiral doubly chelated molybdenum centers in $[(MoO_2)_2L_2]^{4-}$ have the same absolute configuration, and when the two $L^{4-}$ units are of the same chirality, a relatively strain-free 2:2 association is formed.[2] On the other hand, the two catechol units associated with each silicon center in $[(C_6H_5Si)_4L_4]^{4-}$ and with each boron center in $[B_4L_4]^{4-}$ are nearly diametrically opposed to each other. The two catechol groups are essentially coplanar in the case of $[(C_6H_5Si)_4L_4]^{4-}$, thereby providing the $O_4$ base of a square pyramidal coordination environment, and are essentially orthogonal in the case of $[B_4L_4]^{4-}$, forming a tetrahedral coordination environment. As can be seen in Figure 1, boron's requirement for a tetrahedral environment is nicely satisfied in the 4:4 association $[B_4L_4]^{4-}$, when all four $L^{4-}$ units have the same chirality. In contrast, the square pyramidal coordination geometry of the silicon centers in the $[(C_6H_5Si)_4L_4]^{4-}$ squares is more easily attained by two $L^{4-}$ units of one chirality and two of the other.[1]

Preliminary synthetic and structural exploration indicates that many nitrogen bases, upon reaction with $LH_4$ and $B(OMe)_3$, yield tetragonal crystalline products, in which either all squares in a column have the same chirality (given by $Et_3N$, $Me_3N$, $Me_2NCH_2CH_2NH_2$, $Et_2NCH_2CH_2OH$, $BzEt_2N$, and piperazine) or squares of opposite chirality alternate within a column (given by $NH_2(CH_2)_nNH_2$ ($n = 2$, 3, or 6), $NH_3$, $N_2H_4$, $Et_2NOH$, and triethylenetetramine). Thus, the basic structure, consisting of chiral squares electrostatically cemented together by cations to form nanotubes that are packed parallel to one another, appears to be strongly preferred. Similar tubular structures are expected to be obtainable with a wide range of other nitrogen bases.

In summary, we report herein the first members of an extended family of easily accessible solids with spacious tubular structures. In the structures, chiral anionic macrocycles containing a large square central hole are cemented together by cations. The basic tubular structure is preserved after solvent removal, and these compounds have the potential to show interesting sorption properties. The fact that no atom within the structure is heavier than oxygen may be beneficial in practical applications where low density is important, for example, the storage of gases, such as hydrogen.

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[3] a) Preparation of $(Et_3NH)_4[B_4L_4]\cdot 12\,H_2O$: $B(OMe)_3$ (0.0296 g, 0.293 mmol) in methanol (2.5 mL) was added to a solution of $LH_4$ (0.0870 g, 0.256 mmol) in methanol/$Et_3N$ (2.5 mL/1 mL). The solution was heated in a sealed tube at 160 °C for two days. Colorless crystals were collected, washed with methanol, and allowed to air dry. Yield: 0.0673 g, 53 %. Elemental analysis (%) calcd for $(Et_3NH)_4[B_4L_4]\cdot 12\,H_2O$ ($C_{108}H_{168}B_4N_4O_{28}$): C 64.4, H 8.4, N 2.8; found for air-dried sample: C 64.3, H 7.8, N 2.9; calcd for $(Et_3NH)_4[B_4L_4]\cdot 5\,H_2O$ ($C_{108}H_{154}B_4N_4O_{21}$): C 68.7, H 8.2, N 3.0; found for room-temperature vacuum-dried sample: C 68.9, H 8.1, N 3.0. b) Preparation of $(BzEt_2NH)_4[B_4L_4]\cdot 4\,MeOH$: $B(OMe)_3$ (0.0170 g, 0.169 mmol) in methanol (0.5 mL) was added to a solution of $LH_4$ (0.05 g, 0.1 mmol) in methanol/$BzEt_2N$ (0.5 mL/0.3 mL). The solution was heated in a sealed tube at 160 °C for two days. Colorless crystals were collected, washed with methanol, and allowed to air dry. Yield: 0.0347 g, 62 %. Elemental analysis (%) calcd for $C_{132}H_{168}B_4N_4O_{20}$: C 72.9, H 7.8, N 2.6; found: C 72.8, H 7.4, N 2.8. c) Preparation of $(Me_2ambH_2)_2[B_4L_4]\cdot 10\,H_2O$: $B(OMe)_3$ (0.25 g, 2.5 mmol) was added to a solution of $LH_4$ (0.86 g, 2.5 mmol) and amb (0.08 g, 0.6 mmol) in methanol (5 mL). The solution was heated in a sealed tube at 160 °C for two days. Colorless crystals were collected, washed with methanol, and allowed to air dry. Yield: 0.468 g, 41 %. Elemental analysis (%) calcd for $C_{104}H_{146}B_4N_4O_{26}$: C 65.7, H 7.2, N 2.9; found: C 65.8, H 6.8, N 3.3.

[4] a) Crystal data for $(Et_3NH)_4[B_4L_4]\cdot 6\,MeOH$: $0.03 \times 0.03 \times 0.15$ mm, tetragonal, $P4/n$, $a = 26.559(2)$, $c = 8.297(2)$ Å, $V = 5853(1)$ Å$^3$, $\rho_{calcd} = 1.129\ g\,cm^{-3}$, $\theta_{max} = 27.7°$, $Mo_{K\alpha}$ radiation, $\lambda = 0.71073$ Å, $T = 130$ K, no absorption correction applied, $\mu(Mo_{K\alpha}) = 0.076\ mm^{-1}$, 35805 reflections measured, 6761 unique, 372 parameters, $wR2$ (all data) $= 0.1863$, $R1$ $[I > 2\sigma(I)] = 0.0760$, max./min. residual electron density $= 0.494/-0.336\ e\,Å^{-3}$; b) Crystal data for $(BzEt_2NH)_4[B_4L_4]\cdot 4\,MeOH$: $0.13 \times 0.15 \times 0.50$ mm, tetragonal, $P4/n$, $a = 26.762(1)$, $c = 8.4339(8)$ Å, $V = 6040.5(7)$ Å$^3$, $\rho_{calcd} = 1.195\ g\,cm^{-3}$, $\theta_{max} = 27.5°$, $Mo_{K\alpha}$ radiation, $\lambda = 0.71073$ Å,

$T = 130$ K, no absorption correction applied, $\mu(\mathrm{Mo_{K\alpha}}) = 0.079\ \mathrm{mm^{-1}}$, 35117 reflections measured, 6865 unique, 394 parameters, $wR2$ (all data) $= 0.2398$, $R1$ $[I > 2\sigma(I)] = 0.0759$, max./min. residual electron density $= 0.598/-0.525\ \mathrm{e\,Å^{-3}}$; c) Crystal data for $(\mathrm{Me_2ambH_2})_2[\mathrm{B_4L_4}]\cdot 5\,\mathrm{MeOH}$: $0.30 \times 0.30 \times 0.55$ mm, tetragonal, $P4/ncc$, $a = 26.812(1)$, $c = 16.792(1)$ Å, $V = 12072(1)\ \mathrm{Å^3}$, $\rho_{\mathrm{calcd}} = 1.035\ \mathrm{g\,cm^{-3}}$, $\theta_{\max} = 27.6°$, $\mathrm{Mo_{K\alpha}}$ radiation, $\lambda = 0.71073$ Å, $T = 130$ K, no absorption correction applied, $\mu(\mathrm{Mo_{K\alpha}}) = 0.070\ \mathrm{mm^{-1}}$, 70228 reflections measured, 6949 unique, 373 parameters, $wR2$ (all data) $= 0.3113$, $R1$ $[I > 2\sigma(I)] = 0.0981$, max./min. residual electron density $= 1.188/-0.494\ \mathrm{e\,Å^{-3}}$. All structures were solved by direct methods and refined against $F^2$ using *SHELX*97.[7] CCDC-281956 ($(\mathrm{Et_3NH})_4[\mathrm{B_4L_4}]\cdot 6\,\mathrm{MeOH}$), CCDC-281957 ($(\mathrm{BzEt_2NH})_4[\mathrm{B_4L_4}]\cdot 4\,\mathrm{MeOH}$), and CCDC-281958 ($(\mathrm{Me_2ambH_2})_2[\mathrm{B_4L_4}]\cdot 5\,\mathrm{MeOH}$) 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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