Valence Bonds in Planar and Quasi-Planar Boron Disks

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Abstract : Planar and quasi-planar boron clusters with a disk-like shape are investigated in search of common bonding characteristics. Methods used involve molecular orbital calculations based on Density Functional Theory (DFT), and valence bond partitioning using Adaptive natural Density Partitioning (AdNDP) analysis. For high-symmetry cases the proposed bonding schemes are confirmed using the group-theoretical induction method. The focus is on the electron occupation of delocalized in-plane 3-center and 4-center bonds. For disks consisting of concentric rings this inner electron count is found to be equal to a multiple of the vertex count of the inner polygon. For two concentric rings the multiplying factor is four, for three concentric rings it is eight. The appropriate bonding schemes are presented which explain these results. Some giant clusters with two hexagonal holes are also discussed.

Keywords : planar boron disk, multi-center bonds, valence bond theory, AdNDP, induced representations.

1. Introduction

Oligoclusters of boron display a bewildering variety of structures, ranging from planar or quasi-planar sheets, disks and stripes, to polyhedral cages and coreshell clusters ^[1]. To understand the chemical bonds at the origin of these structures constitutes a real challenge. Extensive Molecular Orbital calculations on a variety of structures demonstrate the delocalized nature of the boron-boron bonds, due to their inherent electron-deficiency. In the case of elongated and disk-like compounds the out-of-plane π -bonding closely follows free-electron models for resp. a particle in a rectangular box and an electron on a disk^[2]. Also, the in-plane or σ -orbitals display patterns that reflect these continuum models, albeit they are more dependent on the actual shapes. A more detailed analysis of this in-plane bonding requires the toolbox of Valence-Bond Theory (VBT), which deconvolutes the molecular orbitals in local bonds over two to several centers. Such an analysis has yielded a convincing model for the inner bonds in elongated stripes^[3]. The aim of the present study is to extend this model to the more general class of planar and quasi-planar disk-like clusters. The final objective is to obtain a set of rules that governs the distribution of inner σ electrons on a boron disk-shaped cluster. Our strategy will be based on a simple density functional theory (DFT) molecular calculation, complemented with the adaptive natural density partitioning analysis (AdNDP)^[4]. Use will also be made of the group-theoretical induction method^[5].

2. Computational details

Optimization of geometries was carried out in this work using DFT with the combined B3LYP exchange-energy correlation method ^[6-8] using the basis set 6-311G** implemented in Gaussian 09 program ^[9]. Additional single point Natural Bond orbital (NBO) calculations were done on the optimized structures with the same basis set. We have adopted in this work the AdNDP Analysis, which provides partitioning of electron density and gives rise to a quantitative and comprehensive bonding pattern in many chemical system. In previous studies, this tool has been successfully applied in order to analyse bonding pictures in a variety of molecules ^[10, 11]. The bonding pattern analysis was conducted using the AdNDP method implemented in Multiwfn package. [T. Lu

and F. Chen, Multiwfn: A Multifunctional Wavefunction Analyzer, J. Com. Chem., 2012, **33**, 580–592.]

The canonical molecular orbitals (CMO) and the AdNDP bonds were visualized with the Gaussview software. The molecular orbitals of the resulting ground states in each cluster are characterized according to the irreducible representations (irreps) of the structural point group symmetry.

3. Structures

An overview of the clusters considered is shown in Fig. 1. The smallest B_7^- cluster is the cornerstone which provides the primary insight into the bonding scheme that we will be using. The B_8 and B_9^- clusters represent analogous molecular wheels where the central boron is hepta- and octacoordinated. Then there is a series of disk-like clusters, with cluster sizes ranging from 12 up to 20. Six of these consist of two concentric rings, apart from B_{18} . This cluster has a different structure, and can be viewed as a tile





Fig. 1: Boron disk clusters [Add to this figure the optimized structures of B8, B9-, B21-]

of the hexagonal sheet. The B_{21}^- cluster is very similar to B_{19}^- with an additional cap of two boron atoms. The next clusters, with 30 and 36 boron atoms, consist of three concentric rings. Finally we also will consider the recently proposed cluster with 50 borons, which has two central holes^[12], and its congener B_{56} .

4. Analysis

a. Centered polygons

As a starting point we consider the single centered polygons: B_7^-, B_8, B_9^- . The electron counts are given in Table 1.

Table 1: Centered polygons: valence electron counts, with partitioning over π -, outer and inner σ -bonds

\mathbf{B}_m^{-q}	N _{tot}	N_{π}	$N_{\sigma o}$	$N_{\sigma i}$	polygon
\mathbf{B}_7^-	22	4	12	6	hexagon
B ₈	24	4	14	6	heptagon
B_9^-	28	6	16	6	octagon

The primary cluster in the table is the 7-atom cluster in its anionic state. According to Alexandrova et al.^[13], the structure is slightly pyramidal and has

two competing ground states, depending on spin. In the triplet ground state the symmetry is C_{6v} , while in the singlet state the structure is distorted to C_{2v} . The anionic cluster has 22 valence electrons. The MO analysis shows that in this molecule four electrons reside in *out-of-plane* π -orbitals while the remaining 18 electrons occupy *in-plane* σ -orbitals. There are three out-of-plane orbitals transforming as the familiar aromatic triad σ +2 π . Occupation with four electrons gives rise to the configuration: $(\sigma)^2(\pi_x,\pi_y)^2$. The half-filled π -orbitals give rise to a biradical character that explains the competing ground states. In the triplet state equal occupation of π_x and π_y is fixed and the sixfold symmetry is thus conserved. In the singlet state energy can be gained by doubly occupying either π_x or π_y , which by a vibronic mechanism leads to symmetry lowering.

Our main focus is however on the σ -shell and here the AdNDP analysis shows the way. The cluster invests not less than 12 electrons to form a completely bonding outer ring. This is a general conclusion from the work of the Boldyrev group ^[14], which has been established for every single planar or quasi-planar boron cluster, irrespective of its shape. We call this set of bonds the *outer* σ *bonds*. Remains thus a set of six valence electrons which are involved in the inner bonding inside the disk. AdNDP analysis allocates these to 3c-2e bonds on alternating inner triangles. Since there are six triangles all together, which require equal occupation, the conclusion is that we must consider a resonating system of triangular bonds. As for traditional Lewis structures, resonance must also be imposed by AdNDP schemes, whenever equivalent descriptions exist. ^[15] The resulting bonding description is as follows:



An alternative way is to distribute the inner electrons over 4c-2e bonds, covering two adjacent triangles. Again there are two resonating ways to realize this:



From either point of view the 7-cluster can be correctly assigned as σ -aromatic. Both schemes are possible, but the occupation numbers (ON) of the 4c-2e bonds are 1.94 |e|, as compared to 1.79 |e| for the 3c-2e bonds. Moreover, our previous analysis of elongated clusters ^[3] has shown that the 4c-2e bonds are consistent with the electron counting in a full family of extended structures, as opposed to the 3c-2e bonds.

The hepta- and octacoordinated clusters follow exactly the same inner σ bonding pattern. [H. J. Zhai, A. N. Alexandrova, K. A. Birch, A. I. Boldyrev, L.-S. Wang, Hepta- en octacoordinated boron in molecular wheels of eight- and nine-atom boron clusters: observation and confirmation, *Angew. Chem. Int. Ed.*, 2003, **42**, 6004-6008.] This may also be demonstrated by a group-theoretical analysis. The π - and inner σ -orbitals form aromatic triads, which in the group D_{8h} transform as follows:

$$\pi : A_{2u} + E_{1u}$$

i- $\sigma : A_{1g} + E_{1g}$

The symmetries of the outer bonds along the periphery of the wheel can be found by the induction method. Let $\Gamma(\gamma H\uparrow G)$ denote the representation in the molecular point group G, based on a set of functions which transform according to the irreducible representation γ in the site group H. This resulting representation is called the induced representation. In the present case the site group of a peripheral bond is $C_{2\nu}$ with the C_2 axis through an edge of the polygon. This direction is conventionally denoted as C_2 ." The symmetry of the 2c bond on the edge in this site group is a₁. Hence the peripheral bonding is induced as $\Gamma(a_1C_{2\nu}^{**}\uparrow D_{8h})$:

$$0 - \sigma : \Gamma \left(a_1 C_{2\nu} \uparrow D_{8h} \right) = A_{1g} + B_{2g} + E_{1g} + E_{2g} + E_{3g}$$

The total valence shell thus must transform as:

$$\Gamma_{\rm MO} = 2A_{1g} + B_{2g} + 2E_{1g} + E_{2g} + E_{3g} + A_{2u} + E_{1u}$$

in line with the computational results. The high coordination number for the central boron in these compounds indicates that for the subsequent analysis of the clusters we must search for valence bond pictures that involve bonds that could extend over several centers and are compatible with the symmetry of the cluster, involving resonance when two complementary schemes arise.

b. Double concentric disks

The disks, listed in Table 2, are made up of two concentric rings. A special feature of these systems is that, with the exception of B_{12} , an almost barrierless rotation of the inner ring versus the outer ring is observed ^[16]. This motion could be triggered by photons to yield a 'molecular Wankel motor ^[17,18]. It indicates that the bonding in these systems is delocalized and covers all centers irrespective of their detailed connectivity.

Our analysis is based on the total number of valence electrons in the cluster, N_{tot} , which is equal to 3m+q where *m* and *-q* represent respectively the number of boron atoms and the cluster charge (0, -1 and -2). By applying a reverse engineering method ^[3], which consists to remove the π - and outer σ -electrons, we obtain the number of inner σ -electrons. These numbers are denoted resp. as N_{π} , $N_{\sigma o}$, and $N_{\sigma i}$. The resulting counts are given in Table 2.

\mathbf{B}_m^{-q}	N _{tot}	N_{π}	$N_{\sigma o}$	N _{oi}	polygon
B ₁₂	36	6	18	12=4x3	triangle
B ⁺ ₁₃	38	6	20	12=4x3	triangle
B_{13}^{-}	40	8	20	12=4x3	triangle
B ⁻ ₁₅	46	8	22	16=4x4	quadrilateral
B_{19}^{-}	58	12	26	20=4x5	pentagon
B_{20}^{2-}	62	12	26	24=4x6	hexagon
B_{21}^{-}	64	12	28	24	

Table 2: Double concentric clusters: valence electron counts, with partitioning over π -, outer and inner σ -bonds

The number of π -electrons increases steadily with the diameter of the cluster and closely follows the spectrum of a particle confined to a disk ^[19]. The sequence of these orbitals is: $1\sigma < 1\pi < 1\delta < 2\sigma$... where the numerical factor refers to the radial quantum number (which is one more than the number of radial nodes), and the Greek symbols denote the number of angular nodes. Closure of the disk orbitals will thus lead to a sequence: 2, 6, 10, 12... Examples with 6 electrons are

 B_{12} and B_{13}^+ , which gain extra stability from π -aromaticity. ^[21] [G. Martinez-Guajardo, A. P. Sergeeva, A. I. Boldyrev, T. Heine, J. M. Ugalde and G. Merino, Unravelling phenomenon of internal rotation in B⁺₁₃ through chemical bonding analysis, Chem. Commun., 2011, 47, 6242-6244.] In contrast, the clusters B_{13}^{-} and B_{15}^{-} with $N_{\pi}\!\!=\!\!8$ fall in between two aromatic numbers, which predicts that they would have competing spin states and be subject to symmetry lowering. This is indeed verified by ab initio calculations. ^[20] The B_{19}^{-} and B_{20}^{2-} clusters with 12 π -electrons are disk-aromatic^[19,22] [J. O. C. Jimnez-Halla, R. Islas, T. Heine, and G. Merino, B₁₉: An aromatic Wankel motor, Angew. Chem. Int. Ed. 2010, 49, 5668 – 5671.] When the photoelectron spectrum of the B_{19}^- was characterized for the first time, it was suggested that this cluster was doubly aromatic because of the presence of 12 π -electrons^[23]. It is clear though that double aromaticity and disk aromaticity are not identical concepts as they yield different symmetry representations : two concentric aromatic rings would be described by $1\sigma + 1\pi + 2\sigma + 2\pi$, while a 12-electron aromatic disk is characterized by $1\sigma + 1\pi + 1\delta + 2\sigma$, as we have indicated above. Only the latter scheme is correct for the B_{19}^- and B_{20}^{2-} clusters.

As indicated before the $N_{\sigma\sigma}$ count simply corresponds to twice the number of outer links. The intriguing result in the table is that the remaining delocalized inner σ -bonds give rise to an electron count $N_{\sigma i}$ which is a multiple of 4, and the multiplying factor is simply the vertex count of the inner polygon! This finding can be rationalized using the AdNDP bond analysis. In principle, many different polycenter bonding schemes are conceivable with varying electron occupations. However, high occupations can in all cases be reached by a straightforward distribution which covers the entire mesh. This is illustrated in the case of B_{15}^- in Fig. 2. It runs as follows: the central *n*-gon is always the meeting point of *n* radial bonds crossing its edges. In between these bonds there are a further multi-center tangent bonds between the inner and outer ring, curved along the vertices of the central polygon. Together these make up for 2*n* electrons pairs or 4*n* electrons. Even if the outer ring is stretched more extensively this scheme seems to be imposed, including more than 4 centers in the stretched areas.



Fig. 2: AdNDP analysis for B_{15}^- inner σ : four bonds across the edges of the rhombus in the center (left) + four bonds adjacent to its vertices (right).

The final example in Table 2 is the B_{21}^- cluster, which has been studied by Piazza et al. [Z. A. Piazza, W.-L. Li, C. Romanescu, A. P. Sergeeva, L.-S. Wang, A. I. Boldyrev, A photoelectron spectroscopy and ab initio study of B_{21}^- : negatively charged boron clusters continue to be planar at 21, *J. Chem. Phys.*, 2012, **136**, 104310.] There are several isomers within a few kcal/mol. The global minimum structure is presented in Fig. 3. Together with the inner σ -bonds from AdNDP. One clearly observes the double ring of 10 bonds around the central pentagon, exactly as in the case of B_{19}^- , requiring 20 electrons. With $N_{\sigma i}$ equal to 24, this leaves four extra electrons for two bonds in the upper part of the structure.

Fig. 3: AdNDP analysis inner σ -bonding in B_{21}^{-} [new figure!]

It should be emphasized that the 4n rule, illustrated in Table 2, only applies to clusters which consist of two concentric rings. While clusters with nuclearities

between 10 and 21 are usually planar, they are not all doubly concentric disks. Clusters B_{10} and B_{11}^- are elongated stripes. They have a different valence bond structure, which has been discussed in a previous publication. ^[3] In contrast, the lowest isomer of B_{14} is non-planar but has a D_{2d} cage-like structure. [L. Cheng, B_{14} : an all-boron fullerene, *J. Chem. Phys.*, 2012, **136**, 104301.] The lowest energy isomer of B_{17}^- has an elongated C_{2v} structure. Its π -shell is comparable to the delocalized π -shell of naphthalene. ^[25]

c. **B**₁₈

The neutral B_{18} cluster considered here is one of the two nearly degenerate singlet isomers, with a C_{3v} structure ^[24]. It is characterized by a high barrier to internal rotation ^[17]. Electron count in B_{18} is as follows:

	N _{tot}	\mathbf{N}_{π}	$\mathrm{N}_{\sigma o}$	$N_{\sigma i}$
B ₁₈	54	12	24	18

Although of a similar shape as the clusters in Table 2, the inner- σ electron count in B₁₈ does not obey the rule of four. Clearly this cluster behaves differently as it doesn't have a perfect concentric structure. It rather corresponds to a tile of the hexagonal sheet. According to AdNDP the 18 inner- σ electrons can be allocated to three separate aromatic sextets, one on each apex of the triangular shape, forming a boron analogue of a Clar structure for the graphene sheet.



Fig. 4: the AdNDP analysis for B_{18} inner- σ bonds

The symmetries of the corresponding MO's can easily be predicted from group theory. The point group of a pyramidal B_{18} structure is C_{3v} . The site of each triangular apex has only C_s symmetry. On the periphery of the B_{18} cluster there

are three bonds which are totally symmetric in the C_s site group and thus will be induced by $\Gamma(a'C_s\uparrow C_{3v})$. There are also six bonds which are lying on sites which have no symmetry at all. The induction process in this case yields the so-called regular representation, Γ_{reg} , which corresponds to $\Gamma(aC_1\uparrow C_{3v})$. It contains all irreducible representation of the parent group with a multiplicity equal to their degeneracy. Hence, for C_{3v} the regular representation is given by:

$$\Gamma_{\text{reg}} = \Gamma\left(aC_1 \uparrow C_{3\nu}\right) = A_1 + A_2 + 2E$$

The results for the 12 outer- σ bonds thus read:

$$o - \sigma: 2\Gamma\left(a'C_s \uparrow C_{3\nu}\right) + \Gamma\left(aC_1 \uparrow C_{3\nu}\right) = 3A_1 + A_2 + 4E$$

For one aromatic sextet at an apex the three occupied orbitals span 2a'+a'' in the site group, requiring twice the induction from a' and once from a'', as also indicated below. This yields the symmetry of the inner- σ bonds.

i-
$$\sigma$$
: $2\Gamma(a'C_s \uparrow C_{3\nu}) + \Gamma(a''C_s \uparrow C_{3\nu}) = 2A_1 + A_2 + 3E$

By summing up outer and inner contributions we get a group-theoretical prediction of the symmetries of the 21 σ -type occupied MO's. There is an exact match between these and the MO symmetries resulting from the DFT calculation.

Sergeeva et al.^[25] studied the electronic properties of the B_{18}^- anion using photoelectron spectroscopy and ab initio calculations. They report nine 3c-2e bonds, with occupation numbers between 1.8 and 1.9 |e|, and which are indeed sited on the apical hexagons, as in our Fig. 4. As mentioned in the case of B_7^- , this set of 3c-2e bonds offers an alternative description for σ -aromatic hexagons, albeit with smaller ON's. The extra unpaired electron of the anion is seen to occupy the central triangle in Fig. 4. [D. Moreno, S. Pan, L. L. Zeonjuk, R. Islas, E. Osorio, G. Martínez-Guajardo, P. K. Chattaraj, T. Heine and G. Merino, B_{18}^{2-} : a quasi-planar bowl member of the Wankel motor family, *Chem. Commun.*, 2014, **50**, 8140]

d. Triple concentric disks

To corroborate the above analysis we now concentrate on two clusters which consist of three concentric rings. The B_{30} boron cluster has a bowl shape with three concentric rings. It exhibits disk-aromaticity similar to that found for the doubly concentric clusters clusters^[26]. The B_{36} cluster has an analogous structure with a central hexagonal vacancy. It can be viewed as a repeating unit for boron monolayers, dubbed borophenes^[27,28]. The electron counts of these clusters are given in the Table 3.

Table 3: Triple conce	ntric clusters: v	alence electron	counts,	with partiti	oning
	over π , outer a	and inner- σ bond	ds		

\mathbf{B}_m^{-q}	N _{tot}	N_{π}	$N_{\sigma o}$	$N_{\sigma i}$	polygon
B ₃₀	90	20	30	40=8x5	pentagon
B ₃₆	108	24	36	48=8x6	hexagon

In these cases the inner- σ count is again a multiple of the degree of the central polygon, but now the multiplication factor is eight! This can easily be rationalized by AdNDP analysis. For a central *n*-gon, there are as before 4n electrons covering bonds for the first two concentric rings. A further 4n electrons are needed to occupy bonds between the second and third ring, as shown in Fig. 5.



Fig. 5: the AdNDP analysis for B_{30} inner- σ bonds

This analysis is confirmed independently by a group-theoretical induction. Since both clusters can be treated in an ideal C_{nv} symmetry, the irreducible representations of the bonds offer a detailed prediction of the symmetries of the

MO's involved. In the case of B_{36} a symmetry analysis based on C_{6v} yields the following results:

o-
$$\sigma$$
: $\Gamma\left(a'C_{s}^{d}\uparrow C_{6v}\right) + \Gamma\left(aC_{1}\uparrow C_{6v}\right) = A_{1} + B_{2} + E_{1} + E_{2} + \Gamma_{reg}$
i- σ : - central radial: $\Gamma\left(a'C_{s}^{d}\uparrow C_{6v}\right) = A_{1} + B_{2} + E_{1} + E_{2}$

- first concentric tangential: $\Gamma(a'C_s^{\nu}\uparrow C_{6\nu}) = A_1 + B_1 + E_1 + E_2$

- second concentric tangential: Γ_{reg}

The sum of all these contributions yields:

$$\Gamma_{MO} = 5A_1 + 2A_2 + 3B_1 + 4B_2 + 7E_1 + 7E_2$$

We thus obtain the symmetries of the 42 occupied σ -MO's, accommodating 84 electrons. The predicted irreducible representations match exactly the symmetries of the calculated MO's. Our AdNDP analysis of the σ -bonding in this cluster coincides with the recent results of Li et al. ^[29] However, in that paper π -bonding is interpreted as a concentric 6π +18 π double aromaticity, which is at odds with our interpretation of aromaticity in these clusters as the modes of a particle on a disk. ^[19] In this model the spectrum π -shell follows the sequence:

$$1\sigma < 1\pi < 1\delta < 2\sigma < 1\varphi < 2\pi < 1\gamma < 2\delta < 1\eta < \dots$$

The 24 π -electrons in B₃₆ form a disk-aromatic system, corresponding to the closing of the 1 γ -level, with four vertical nodal planes. From a symmetry point of view a 6π +18 π double aromatic ring system would give rise to a scheme: 1σ +1 π +2 σ +2 π +1 δ +1 φ +1 γ . Unlike in the previously mentioned case of B⁻₁₉, in the present case the symmetries coincide, but the orbital ordering may be different. The calculation yields an orbital sequence which is almost perfectly in line with the predicted sequence of the disk model.

e. Giant disks with two central holes

The recently proposed large quasi-planar cluster B_{50} with two adjacent central holes still resemble the pattern of the triple concentric rings, except for some extra localized bonds in the center^[12]. The electron counts are given in Table 4.

Table 4: Giant disks with two adjacent central holes: valence electron counts, with partitioning over π , outer and inner σ ; *d* and *l* denote resp. delocalized and localized bonds.

\mathbf{B}_m^{-q}	N _{tot}	N_{π}	$N_{\sigma o}$	$N_{\sigma i}$
B ₅₀	150	32	44	72(d)+2(l)
B ₅₆	168	38	48	80(d)+2(l)

The AdNDP analysis for B_{50} is shown in Fig.6, and is clearly reminiscent of the triple concentric system.



Fig.6: the AdNDP analysis for B_{50} inner- σ

One recognizes 10 radial bonds in the center, 8 tangential bonds in the surrounding layer, and 16 further tangential bonds in the second layer. Extra bonds due to a deviation of the perfect ring system include a central 2c-2e bond and two more interstitial 4c-2e bonds.

Also noteworthy is the spectrum of the π -shell which is remarkably close to the sequence for a particle in a disk, forming the 32-electron aromatic series. up to the 1 η orbitals have five angular nodes as shown in the paper by Sai et al.^[12] Below thsi HOMO are the 2 δ orbitals having one radial and two angular nodes, as shown in Fig. 7.



Fig.7: the 2δ orbitals of B₅₀

The B_{56} cluster can be cut out of the α -sheet of boron with hexagonal holes. It was first studied by Rahane and Kumar ^[30]. Tian et al. recently presented the AdNDP analysis which confirms the presence of 82 inner- σ electrons, mostly arranged in concentric circles. ^[31]

5. Conclusion

Through multi-center bonding boron manages to realize a plethora of structures and shapes. Theoretical studies have been aiming at finding global or local minima for a large set of nuclearities. Apparently it was not possible to delineate a clear transition region between 2D and 3D structures. So for clusters with more than 40 atoms there seems to be a competition between core-shell, bilayer and quasi-planar structures. ^[12] The computational study of these clusters has also provided a wealth of information on molecular orbitals and the partitioning of electrons over the cluster. With the help of these data we started the search for patterns and rules that govern the distribution of the electrons and offer simple pictures of the delocalized bonds. Our previous study on elongated (essentially 1D) stripes^[3] is complemented here for 2D disk-like structures. The separation of the electron population in out-of-plane π -bonding, and inner and outer inplane σ -bonding appears to be the essential first step in the analysis. Understanding these structures really concentrates on the delocalized in-plane bonding inside the cluster. We have found that for concentric clusters the electron counts attributed to these bonds follow simple multiplicative rules, which can easily be explained with a precise number of delocalized bonds covering the entire mesh. In less symmetric clusters with two hexagonal holes, the concentric model still largely holds, with some extra local interstitial bonds between the holes. The B₁₈ cluster is not concentric, and offers an alternative pattern, which is partitioned in isolated aromatic sextets, with depleted regions in between.

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