

## The hydrogen bonding characteristic of $(\text{H}_2\text{O})_n$ ( $n=14-17$ ): quantum theory of atoms in molecules

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The hydrogen bonding characteristics of water clusters  $(\text{H}_2\text{O})_n$  ( $n=14-17$ ) are investigated by using Quantum Theory of Atoms in Molecules (QTAIM). The stabilities of the water clusters are related to the strength and number of hydrogen bonding. The strength of hydrogen bonding is primarily concerned with the characteristic of the donor molecule. The electron densities of bonding critical points of hydrogen bonding formed by DAA, DDAA and DDA molecule as hydrogen-donor (H-donor) are about 0.045 a.u., 0.035 a.u. and 0.025 a.u. respectively. The strength of hydrogen bonding formed by DAA as H-donor is the strongest, and that formed by DDA as H-donor is the weakest. The strength of hydrogen bonding in pentagonal rings is stronger than that in the cubes.

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### 1. Introduction

Atomic and molecular clusters show many special properties in superconductivity, information storage, catalysis, energy storage and so on. The special properties of the clusters make their use a promising in advanced materials manufacturing. As a simple and stable molecular cluster, water molecular clusters have attracted more and more attention. There are a lot of researches on the structures and stabilities of water clusters both in experiment and theory. Experimentally, the infrared laser spectroscopic and the vibrational intramolecular O-H stretching spectra studies for smaller water clusters were used for the structural confirmation [1-5]. Theoretically, a great number of studies are reported on the global minima for water molecules clusters [6-9]. Xantheas et.al. have been conducted a significant amount of research on water clusters and reviewed their structures and energetics [10-15].

The water molecules are linked through the hydrogen bonding in water clusters. Most physical, chemical and biological properties of water are determined by its hydrogen bonding network. As an essential interaction in nature, hydrogen bonding plays a crucial role in many biological processes and material formations [16-18], which leads to the further research in the future. Revealing the natures of the hydrogen bonding network in water clusters is one of the important scientific researches. Stipkin et. al. [19] reported a combined experimental and theoretical study of the hydrogen bonding at the air-water interface using surface selective heterodyne detected vibrational sum frequency spectroscopy. Iwata [20] investigated the

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charge-transfer and dispersion terms for every pair of water molecule (donor and acceptor water molecules) in the water clusters  $(\text{H}_2\text{O})_{20}$  and  $(\text{H}_2\text{O})_{25}$ . Tokmachev et. al. [21] calculated the spatial and electronic structure of all hydrogen bonding configurations for three systems: idealized cage  $(\text{H}_2\text{O})_{20}$  and defect cages with one or two hydrogen bonds broken. Cole et. al. [22] presented the results of using the time evolution method to extract the tunneling lifetimes for motions that break and reform the hydrogen bond for the water dimer, trimer, and pentamer. Using isotopically labeled cold cluster ions, Yang et. al [23] reported the spectral signatures of a single, intact  $\text{H}_2\text{O}$  molecule embedded at various sites in the  $\text{Cs}^+(\text{D}_2\text{O})_{20}$  ion. Pérez et. al. [24] reported the hydrogen bond cooperativity and the three-dimensional structures of water nonamers and decamers. The isomers for each cluster size have the same nominal geometry but differ in the arrangement of their hydrogen bond networks.

The diversity of the hydrogen bonding network leads to numerous configurations of water clusters. The total number of possible hydrogen bonding network is very large even for medium sized water clusters. Jenkins et. al. [25] investigated the structural and chemical properties of the small water clusters  $(\text{H}_2\text{O})_4$ ,  $(\text{H}_2\text{O})_5$  and  $(\text{H}_2\text{O})_6$  by using the quantum theory of atoms and molecules (QTAIM). Kumar et. al. [26] analyzed the topological diversity of the isomers of water clusters  $(\text{H}_2\text{O})_n$  ( $n=7-10$ ) employing the scalar fields of total electronic charge density and the molecular electrostatic potential (MESP). In this paper, the characters of hydrogen bonding of  $(\text{H}_2\text{O})_{14}$ ,  $(\text{H}_2\text{O})_{15}$ ,  $(\text{H}_2\text{O})_{16}$  and  $(\text{H}_2\text{O})_{17}$  clusters are studied by using QTAIM. We use W14, W15, W16 and W17 to denote the corresponding water clusters. Two isomers are investigated for each cluster. The geometric structures are optimized by using high-precision theoretical method MP2/aug-cc-pVDZ. The critical points and electron densities of hydrogen bonding are analyzed in detail. Our studies may light on the understanding the hydrogen bonding in water clusters.

## 2. Computational methods

The geometric structures of  $W_n$  ( $n=14-17$ ) were extracted from our previous work [27]. Those structures were optimized by using second order perturbation theory MP2 with double zeta basis with polarization function 6-31G(d,p). In this paper, we re-optimize those structures by using the MP2 with high-level basis sets the augmented correlation-consistent polarized valence double-zeta aug-cc-pVDZ. When the basis sets change from 6-31G(d,p) to aug-cc-pVDZ, the basis functions per  $\text{H}_2\text{O}$  molecule increase from 25 to 41.

QTAIM provides a powerful method for the study of bonding using the electron density distribution [28, 29]. The critical point (CP) in the total electron density is a position in which  $\nabla\rho(\mathbf{r})=0$ . The CP is divided into different types according to the properties of the Hessian matrix of  $\rho(\mathbf{r})$ . The eigenvalues of this matrix are given in the order  $\lambda_1<\lambda_2<\lambda_3$ . The critical points are labeled using the notation  $(\omega, \sigma)$ , where  $\omega$  is the rank and  $\sigma$  is the signature (the rank is the number of non-zero curvatures of  $\rho(\mathbf{r})$ , the signature is the algebraic sum of the signs of the eigenvalues). In three dimensions, there are four types of stable critical points. They are denoted as (3, -3) (local maxima, usually corresponding to nuclear positions, called nuclear critical points (NCPs)), (3, -1) and (3,+1) (saddle points, called bond critical points (BCPs) and ring critical

points (RCPs), respectively), and (3, +3) (local minimum, corresponding to a cage, called cage critical points (CCPs)). For the clusters, the relation of the numbers of NCPs, BCPs, RCPs and CCPs is expressed as:

$$n_{\text{NCP}} - n_{\text{BCP}} + n_{\text{RCP}} - n_{\text{CCP}} = 1$$

The structural optimization is carried out by using the Gaussian 09 program [30]. The critical points and electron densities are calculated using AIMQB program within the AIMAll package [31].

### 3. Results and discussion

#### 3.1. Geometrical structures and stabilities of W14, W15, W16 and W17

For each species, the two isomers which have typical structure characteristics are selected, and the geometrical structures are displayed in Fig.1. The structure of W14-a is a double-layer structure composed of shared tetramer and pentamer. The structures of W15-a and W16-a are stacked pentamers and cubes respectively. The structures of W14-b and W16-b is a cage structure composed of pentamers and tetramers. The structure of W15-b is constructed by capping an additional water molecule on the side edge of W14-a. The isomer W17-a is an “internally-solvated” structure (one water molecule at the center of the cluster). The isomer W17-b is a “all-surface” structure (all water molecule on the surface of the cluster).

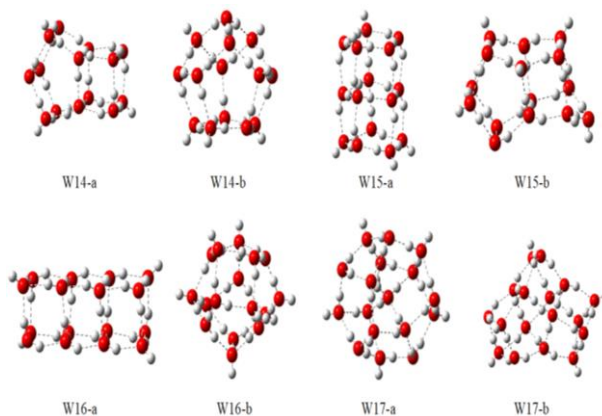


Fig. 1. The isomers of W14, W15, W16 and W17 clusters, addressed in this investigation.

The number and strength of the hydrogen bonding are important factor to determine the stability of the water cluster. For the pair-wise water molecules, one of them provides the H atom for hydrogen bonding and is called hydrogen-donor (H-donor) molecule, and the other one is called hydrogen-acceptor (H-acceptor) molecule. In hydrogen bonding network, the H<sub>2</sub>O molecule can be divided into three types: The H<sub>2</sub>O molecule participates to form four hydrogen bondings as two H-bond donors and two H-bond acceptors, which is called DDAA molecule; The H<sub>2</sub>O molecule participates to form three hydrogen bondings as two H-bond donors and one H-bond

acceptors, which is called DDA molecule; The H<sub>2</sub>O molecule participates to form three hydrogen bondings as one H-bond donors and two H-bond acceptors, which is called DAA molecule. The number of hydrogen bonding in water cluster can be expressed as formula:

$$n_{(\text{O}\cdots\text{H})} = 2 \times (n_{\text{DDAA}} + n_{\text{DDA}}) + n_{\text{DAA}}$$

The  $n_{(\text{O}\cdots\text{H})}$ ,  $n_{\text{DDAA}}$  and  $n_{\text{DDA}}$  are the number of the hydrogen bonding, DDAA molecule and DDA molecule respectively. The molecule numbers of different types are also listed in Table 1.

*Table 1. The number of the different type of water molecule, the binding energies (eV), the strength of hydrogen bonding (eV), the number of the different type of critical point.*

Cluster	$n_{\text{DAA}}$	$n_{\text{DDA}}$	$n_{\text{DDAA}}$	$E_b$	$E_b/n_{(\text{O}\cdots\text{H})}$	$n_{\text{BCP}}$		$n_{\text{RCP}}$	$n_{\text{CCP}}$
						$n_{\text{O}\cdots\text{H}}$	$n_{\text{O-H}}$		
W14-a	5	5	4	-6.47	-0.281	23	28	12	2
W14-b	7	7	0	-6.28	-0.299	21	28	9	1
W15-a	5	5	5	-6.96	-0.278	25	30	13	2
W15-b	7	6	2	-6.83	-0.297	23	30	12	3
W16-a	4	4	8	-7.52	-0.269	28	32	16	3
W16-b	8	0	8	-7.27	-0.303	24	32	10	1
W17-a	6	6	5	-8.08	-0.289	28	34	17	4
W17-b	5	5	7	-8.00	-0.276	29	34	16	3

The binding energy of water clusters is defined as the difference in the energies of the cluster and the water molecules, and calculated by using the following expression:

$$E_b = E(\text{Wn}) - nE(\text{H}_2\text{O})$$

where the  $E(\text{Wn})$  is the total energies of the water clusters, the  $E(\text{H}_2\text{O})$  is the energy of the water molecule, the  $n$  is the number of the water molecule. The binding energies are listed in Table 1. The strength of hydrogen bonding is defined as binding energy per hydrogen bonding ( $E_b/n_{(\text{O}\cdots\text{H})}$ ). The strengths of hydrogen bonding are also given in Table 1 and presented in Fig. 2. It can be seen that the strength of hydrogen bonding in W16-b is the strongest, in W14-b and W15-b are stronger, in W17-a are third. The strength of hydrogen bonding in W16-a is the weakest, that in W14-a, W15-a and W17-a are weaker. We note that the more DAA molecule is related to stronger hydrogen bonding strength.

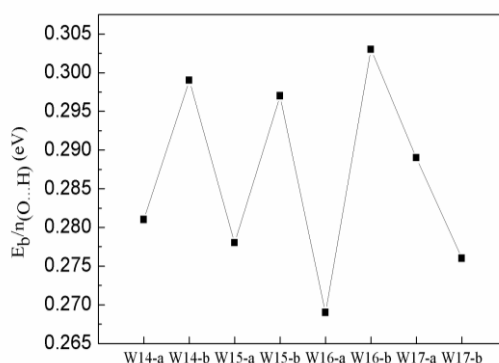


Fig. 2. The strength of hydrogen bonding of the  $W_n$  ( $n=14-17$ ) cluster.

### 3.2. The hydrogen bonding characteristics of W14, W15, W16 and W17

In order to further analyze the relationship between the strength of hydrogen bonding and the type of  $H_2O$  molecule which participates in the formation of hydrogen bonding. We calculated the QTAIM properties, where the critical point data are also given in Table 1. The more extensive tabulation of the electron density for each hydrogen bonding and the types of the H-donor molecule and H-acceptor molecule are given in supplementary material Table S1-S8. Figure 3 illustrates the electron density of the hydrogen bonding which formed by different type of  $H_2O$  molecule as H-donor. It is clearly shown that the DAA, DDAA and DDA molecule as H-donor, the electron densities of the hydrogen bonding are about 0.045 a.u., 0.035 a.u. and 0.025 a.u. respectively. This indicates that the hydrogen bonding is strongest when the DAA molecule acts as an H-donor, while the hydrogen bonding is weakest when the DDA molecule acts as an H-donor. There are no DDAA type water molecule in W14-b and W16-b. The  $2s2p$  orbitals of oxygen atom in  $H_2O$  molecule form  $sp^3$  hybrid orbitals. Two bonding  $\sigma$  orbitals of these form two intramolecular O-H bondings, and the remaining two nonbonding  $\sigma$  orbitals are occupied by two lone pair electrons. The overlap between the  $\sigma$  donor of O-H bonding in one  $H_2O$  molecule and the orbital of the lone pair electrons of O atom in another  $H_2O$  molecule plays a dominant role for the strength of hydrogen bonding. Good overlap corresponds to linear hydrogen bonding. The bond angle of water molecule is  $103.9^\circ$ . When two intramolecular O-H bondings of one water molecule are involved in the formation of hydrogen bondings, it is difficult to ensure that the two O-H bondings are well overlapped with the lone pair electrons of acceptor molecule. Therefore, the hydrogen bondings are stronger when only one O-H bonding is involved in the formation of hydrogen bonds, i.e., H-donor molecule is DAA. We also calculated the averages angles of hydrogen bondings O-H $\cdots$ O in pentagonal rings for the structure W15-a and in cubes for the structure W16-a. The average angles in pentagonal rings and cubes are  $172.71^\circ$  and  $167.10^\circ$  respectively. The angles of hydrogen bonding in pentagonal rings are closer to  $180^\circ$ , indicating the hydrogen bonding are closer linear. So the strength of hydrogen bonding in pentagonal rings is stronger than that in the cubes. The electron densities of BCPs in Table S3 and Table S5 also support that conclusion.

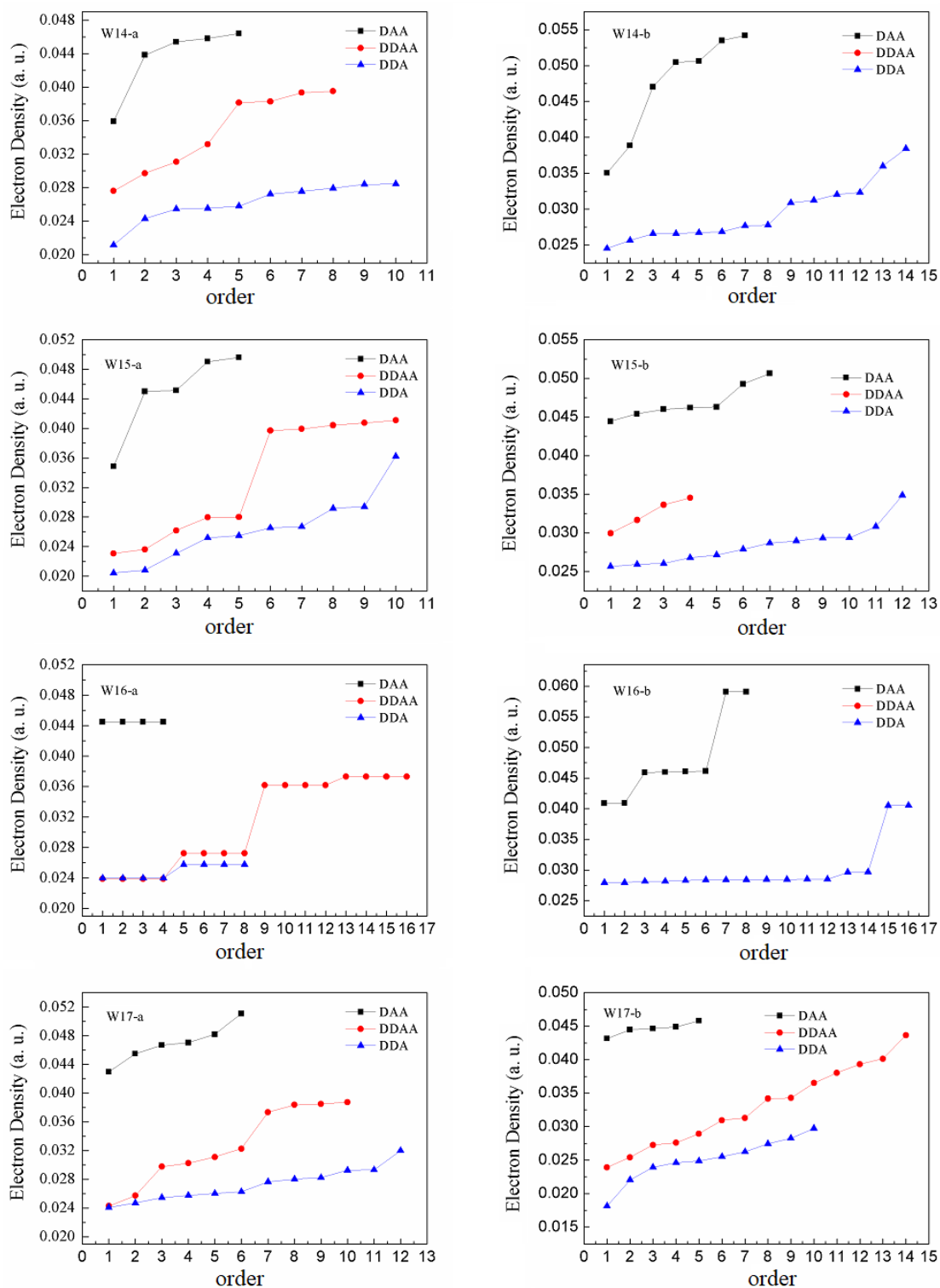


Fig. 3. The electron density of the different type of water molecule as H-donor (arranged in order of increasing of electron density).

The comparisons of the electron density of hydrogen bonding in the two isomers of  $W_n$  ( $n=14-17$ ) cluster are presented in Fig 4. For W14, W15 and W16 clusters, Fig.4 shows that the

averages of electron density in isomers -b are larger than that in isomers -a. It indicates that the averages of hydrogen bonding strength in isomers -b are stronger than that in isomers -a as shown in Fig.1, while the numbers of hydrogen bonding of isomers -a are more than that of isomers -b. The number and strength of hydrogen bonding determine that the isomers -a are more stable than the isomers -b for W14, W15 and W16 clusters. For the “internally-solvated” of W17 cluster structure, the number of hydrogen bonding is less than that of “all-surface” structure, but strengths of hydrogen bonding are stronger. Therefore, the “internally-solvated” structure is more stable.

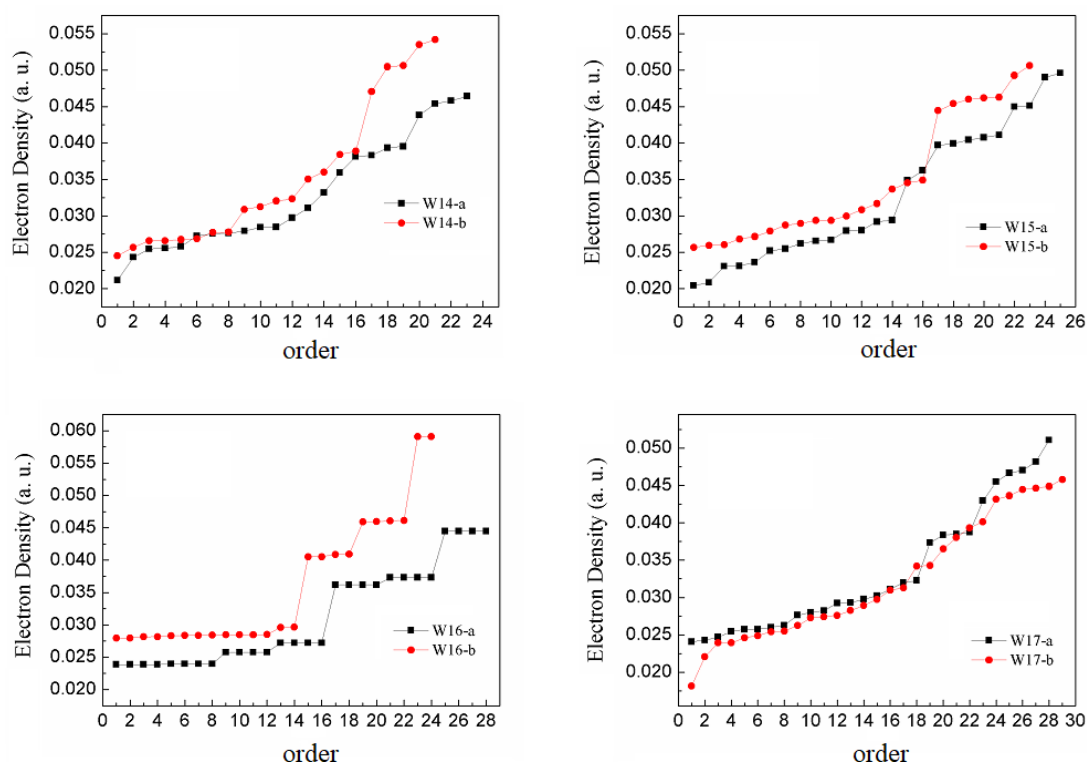


Fig. 4. The comparisons of the electron density of hydrogen bonding in the two isomers of  $W_n$  ( $n=14-17$ ) cluster (arranged in order of increasing of electron density).

#### 4. Conclusions

In this paper, the geometric structures of water clusters W14, W15, W16 and W17 are optimized by using the MP2 with the basis sets aug-cc-pVDZ. The hydrogen bonding characteristics are investigated with the Quantum Theory of Atoms in Molecules (QTAIM). The lowest energy isomer of the W14-a is composed of tetramer and pentamer, the W15-a and W16-a are stacked pentamers and cubes, the W17-a is “internally-solvated” structure. The stabilities of the water clusters are related to both the number and strength of hydrogen bonding. The number of hydrogen bonding in water cluster is calculated using formula  $n_{(O\cdots H)}=2\times(n_{DDAA}+n_{DDA})+n_{DAA}$ . The strength of hydrogen bonding is primarily concerned with the characteristics of the donor molecule. The electron densities of the hydrogen bonding formed by DAA molecule as H-donor are about

0.045 a.u., and the strength of hydrogen bonding is the strongest. The electron densities of the hydrogen bonding formed by DDA are about 0.035 a.u., and the strength of hydrogen bonding is the weakest. The angles of hydrogen bondings O-H $\cdots$ O and electron densities of BCPs show the strength of hydrogen bonding in pentagonal rings is stronger than that in the cubes.

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