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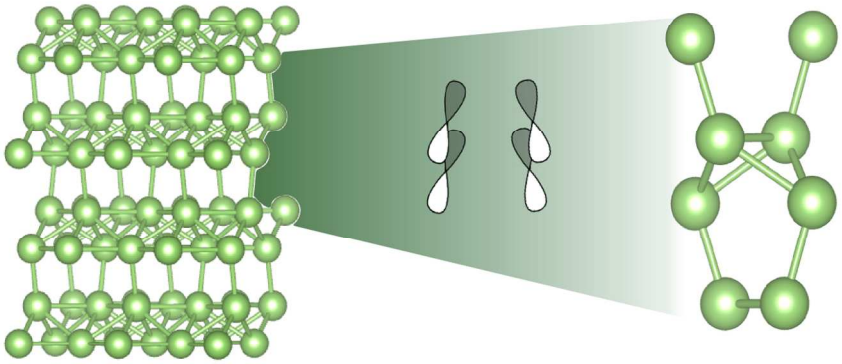

Analysis of the bonding between pairs of atoms in small gallium clusters gives insight into the structure of bulk alpha gallium, a 'molecular metal'.

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The dimeric nature of bonding in gallium: from small clusters to the α-gallium phase

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We consider the structural similarity of small gallium clusters to the bulk structure of α-gallium, which has been described as a molecular metal via density functional theory-based computations. Previous calculations have shown that the structures of the tetramer, hexamer, and octamer of gallium are all structurally similar to the α-phase. We perform an analysis of the bonding in these clusters in terms of the molecular orbitals and Atoms in Molecules description in order to assess whether we can see similarities at these sizes to the bonding pattern which is ascribed to the co-existence of covalent and metallic bonding in the bulk. The singlet Ga_4 and Ga_8 clusters can be constructed in a singlet ground state from the Ga-dimers in the first excited triplet state of the Ga_2-molecule, the $^3\Sigma_g^-$ state. Molecular orbital (MO) analysis confirms that the dimer is an essential building block in these small clusters. Comparison of the AIM characteristics of the bonds within the clusters to the bonds in the bulk α-phase supports the identification of the covalent bond in the bulk as related to the $^3\Sigma_g^-$ state of the dimer.

1 Introduction

Gallium is an unusual metal, exhibiting a rich phase diagram[1], in consideration of size effects,[2–5] temperature[6] and pressure dependent[7,8] modifications. Under standard conditions, it adopts the α-phase,[9,10] a rhombohedral lattice based on an 8-atom unit cell in which the atoms are arranged in pairs, sometimes referred to as a dimeric structure.[11–13] This description of the metal as a molecular solid gives some explanation of the low melting temperature, if the dimeric character remains in the liquid. However the evidence for this remains mixed; the liquid has been claimed to be more like the high-pressure phases Ga-II and Ga-III than dimeric,[14] or like the β-phase.[15] The presence of small clusters has been seen in other theoretical studies.[16,17] Some indirect experimental evidence of local solid-like structure, possibly attributable to clustering, is provided by the scattering behaviour of liquid Ga.[18]

It should be emphasised that the theoretical description of molecular solids is a known problem; in a system where there is apparent competition between molecular and metallic character, it is a basic requirement that an appropriate theoretical description must be able to describe both types of bonding on an equal footing. However, it is by no means clear how to best describe a coexistence of metallic and covalent bonding. That the electron density is high between pairs of atoms may be seen in any DFT calculation of the electronic structure of α-gallium; in the density of states there is a marked dip around the Fermi level[11] which has been associated with the participation of electrons in covalent bonds.

The experimental observation of the higher-than-bulk melting temperatures of gallium clusters[19–21] has provided dramatic evidence of the implications of the odd structure of gallium for a range of properties. Any explanation of this phenomenon seems to rely on the nature of bonding in these small clusters being significantly different to that of the bulk, and indeed, the dimeric character of the very small clusters is lost at sizes around 10 atoms, where the first internal atom is introduced.[22–26] Previous work has interpreted the electron localisation function (ELF) as quantification of covalent and metallic bonding in larger Ga clusters[27], though this interpretation is not unique[28] when considering the original interpretation of the ELF[29] and keeping in mind that chemical bonding is not an observable.

The varied nature of bonding in gallium has been further demonstrated by the synthesis of metalloid clusters which exhibit structural motifs familiar from the bulk modifications. These are obtained through the use of different ligands which can be said to fine-tune the gallium-gallium interactions through a combination of changes in density and effective charge.[31–33] Also in its cluster chemistry, gallium adopts structures which range from icosahedral, dimeric, fcc-like and other compact structures related to the high-pressure phases.[34] There has been a demonstrated correlation between volume constraints due to the ligand shell and the structural phase rep-

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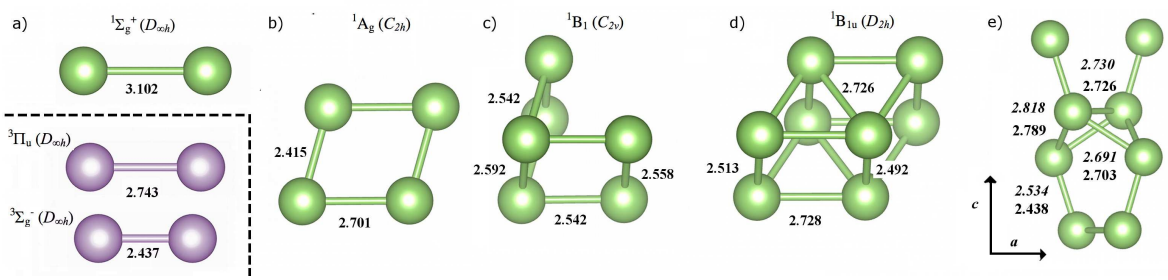

Fig. 1 a) The structures of the three lowest lying states of Ga_2, the lowest lying singlet states of b) Ga_4, c) Ga_6, and d) Ga_8, and e) unit cell of the α-gallium phase are presented. For the clusters, the bond lengths given (in Å) are those calculated with BP86/TZ2P in this study; for α-gallium, both calculated[30] and experimental[10] (in italics) values are given.

resented by the cluster; however, the subtleties of changes in electronic structure have been less well studied. The flexibility of the nature of the gallium-gallium bond is therefore a matter of real current interest, with fascinating synthetic implications.

Our goal in this study is to examine the electronic structure of the series of clusters Ga_4, Ga_6, and Ga_8, with respect to the gallium dimer, as they exhibit the most striking structural similarity to the α-gallium phase. While the triplet and singlet states are very close in energy for each of these small clusters, they show clear structural differences, with the triplet states of notably higher symmetry. The singlet isomers exhibit a symmetry breaking leading to an alternation of bond lengths which will be discussed in detail below. We restrict our analysis to the lowest energy singlet state of each cluster, for comparability with the bulk. This restriction also removes the need to deal with degeneracies present in the more symmetric structures found for the triplet states. We first discuss the structural progression of these small clusters, then consider the nature of the frontier molecular orbitals as the clusters increase in size. Finally, we consider an Atoms in Molecules (AIM) analysis of the evolution of the nature of the bonds in the clusters with size, and compare directly to a model of the α-phase.

2 Method

Density functional theory was used as implemented in the ADF code.[35] Structural optimizations were carried out applying the BP86 functional[36,37] together with a TZ2P basis set.[38] Relativistic effects were considered within the zeroth order relativistic approximation (ZORA).[39] The wavefunction data for AIM calculations were computed with the same functional and the def2-TZVPP basis set[40] using Gaussian09 C.01[41] and analysed with the AIMAll[42] package.

3 Results

3.1 Structures

The structures are summarised in Fig. 1. Here, the structures of Ga_4, Ga_6, and Ga_8 clusters in the lowest lying singlet states calculated at BP86/TZ2P are given. These are in good agreement with previous calculations.[22,23] Additionally, the three lowest lying electronic states of Ga_2 (Fig. 1a) are given and the unit cell of the α-Ga phase with computed[30] and experimental[10] values (Fig 1e).

For the gallium dimer (Fig. 1a), we confirm $^3\Pi_u$ being the electronic ground state, with a bond length of 2.743 Å, which agrees reasonably with the experimental value of 2.75 Å[43]. Experimental data on the structures of the larger clusters is, to the best of our knowledge, not available. In addition, we present the first excited $^3\Sigma_g^-$ triplet state (+4.9 kJ mol^{-1}) and the $^1\Sigma_g^+$singlet state (+49.1 kJ mol^{-1}). Notably, the bond lengths found for the triplet states (2.437 Å and 2.743 Å) are rediscovered not only in the solid-state phase (Fig. 1e) as stated previously[22,23] but can also be found in the clusters investigated here.

For Ga_4 (Fig. 1b), we show the structure of the ^1A_g state which is 37.1 kJ mol^{-1} higher in energy compared to the D_{4h} symmetric triplet ground state at the computational level applied here. The cluster exhibits a rhomboid structure with bond lengths of 2.415 and 2.701 Å, very close to the first and second nearest neighbour distances in the bulk. For Ga_6 (Fig. 1c), the picture is less clear. The $^1B_1$ state shown here is only very slightly higher in energy (0.2 kJ mol^{-1}) compared to the D_{3h} symmetric triplet ground state.[44] The bond lengths in the cluster do not enable a clear identification of closer and distant pairs with 2.542, 2.558 and 2.592 $\AA$ bond distances. Consequently, the bond lengths observed are between the values for the two triplet states of the gallium dimer. The largest cluster investigated here (Ga_8, Fig. 1d) already exhibits a singlet ($^1B_{1u}$) ground state. The structure shown allows a clear iden-

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tification of close (2.492 Å and 2.513 Å) and distant (2.726 Å and 2.728 Å) pairs.

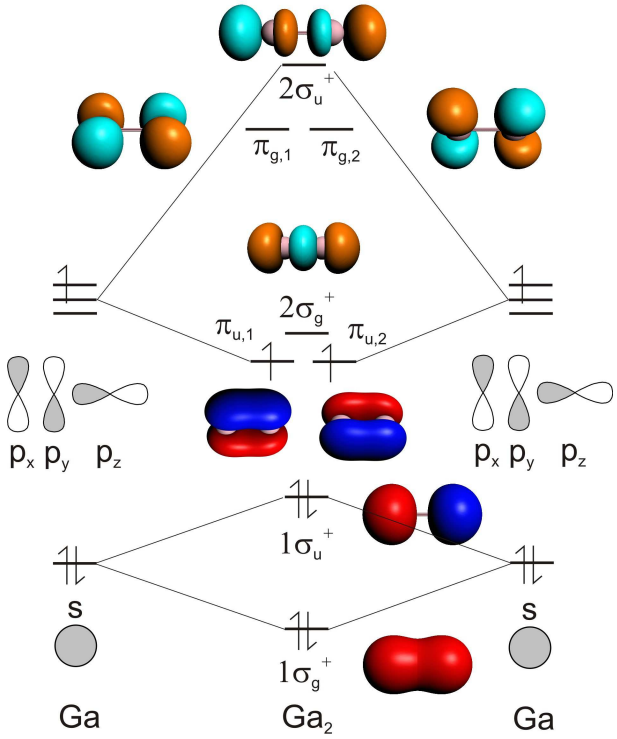

Fig. 2 Molecular orbital diagram for Ga_2 from BP86/TZ2P. Energy ordering and occupation numbers given for the $^3\Sigma_g^-$ state.

3.2 Molecular orbitals

Starting from the insights gained by investigating the molecular structures, we begin our analysis of the electronic structure of the clusters by recalling the molecular orbital (MO) diagram of the gallium dimer.[45] Figure 2 presents the ordering of the MOs observed in the ground state, where the valence p-orbitals combine to form one σ orbital ($2\sigma_g^+$), and two π-orbitals (π_u) from the combination of p_y or p_x orbitals. In the $^3\Pi_u$ ground state, one of the π_u-orbitals is singly occupied, as is the $2\sigma_g^+$-orbital. As it is well-known,[45] the exact energy ordering of the $2\sigma_g^+$ and the π_u-orbitals is the result of a delicate balance of orbital overlap and electron correlation. The other possibility for arriving at a triplet state is that both π_u-orbitals are singly occupied and the $2\sigma_g^+$ is empty: This indeed corresponds to the $^3\Sigma_g^-$ state, which is essential for understanding the cluster structures as we will show later on. The orbital energies and occupations found in the current study are compared to literature results in Tab. 1. We confirm the previously found good agreement between DFT results and high-level coupled cluster calculations.

We turn to examine the bonding of Ga_4, Ga_6, and Ga_8 in light of the results for Ga_2. The occupied orbitals are presented in Fig. 3. At left we see the two singly occupied orbitals of the $^3\Sigma_g^-$ triplet state, which has the short bond length characteristic of the dimeric bond in the α-phase.

To the right of the Ga_2 orbitals in Fig. 3 are presented the relevant occupied and unoccupied MOs for the singlet state of Ga_4. The two occupied MOs are, on inspection, constructed from side on combinations of the occupied MOs of the ground state of the gallium dimer. The interpretation of each MO in terms of the overlap of the MOs of the dimer $^3\Sigma_g^-$ state is sketched at right. The HOMO-1 is equally clearly built from the orbitals of the dimers, aligned end on. The bond length alternation is consistent with the orientation of the dimer MOs. The LUMO is a combination of the unoccupied $2\sigma_g^+$ orbitals of the Ga_2 dimers.

For Ga_6, we know from the structural parameters that we do not have significant bond alternation, and we see the basis for this in the MO diagram. Only the HOMO can be interpreted as due to the overlap of dimer MOs on each pair of atoms. The two lower MOs are constructed in a centrosymmetric fashion from the atomic p-orbitals. Thus only one of the three occupied orbitals in the six-atom cluster corresponds to a bonding picture built from the dimers. An alternative view of the HOMO-2 in Ga_6 leads to the hypothesis, that this MO is constructed from overlapping $2\sigma_g^+$ orbitals of the constituent dimers which have a more favorable spatial arrangement for overlap compared to the second set of π_u orbitals. Similarly to Ga_2, the (partial) occupation of the $2\sigma_g^+$ orbitals leads to a lengthening of the intra-pair bonds (2.558 and 2.592 Å, in comparison to 2.415 Å in Ga_4). This leads to all bonds being comparable in length, close to intra-pair bonds which is also reflected in the similar AIM values (as discussed below).[46]

In contrast, Ga_8 has an MO diagram strongly reminiscent of that which we saw for Ga_4. The p-electrons are split between four MOs, the lowest energy of which looks much like the overlap of two Ga_4 HOMOs; due to the π-overlap of the four MOs of the constituent dimers. The next MO in Ga_8 provides overlap of the p-orbitals oriented along the edges of the rhombohedron, while the third explains the distortion of the cluster away from cubic symmetry, by overlapping the MOs on the two central dimers of the cluster (the atoms which have four nearest neighbours). However, the HOMO also helps to understand the alternation in bond lengths: the four pair bonds are again short in the direction perpendicular to the end on overlap of the dimer MOs.

In summary, the description of the bonding of the clusters in terms of the orbitals of the $^3\Sigma_g^-$ dimer provides an intuitive understanding of the bond length alternation observed in the singlet states of the Ga_4 and Ga_8 clusters. In contrast, the higher symmetries found for the triplet states of these clusters[23] may be expected to result from the occupation of AO-based MOs

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Table 1 Orbital energies (eV) and occupation numbers according to figure 2 and relative energies for different electronic states (in kJ mol^{-1}) of Ga_2 in comparison to reference data.

State	Orbital energy and Occupation			BP86/TZ2P	B3LYP	BP86	CCSD(T)/QZVPP	CCSD(T)/aug-
	$\pi_{u,1}$	$\pi_{u,2}$	$2\sigma_g^+$	(this work)	/DZP++[25]	/DZP++[25]	//PBE/SVP[23]	PP-cc-pVTZ[22]
$^3\Pi_u$	-3.770 (1)	-3.583 (0)	-3.917 (1)	0.0	0.0	0.0	0.0	0.0
$^3\Sigma_g^-$	-4.092 (1)	-4.092 (1)	-3.914 (0)	4.9	15.2	5.9	5.0	9.6
$^1\Sigma_g^+$	-3.018 (0)	-3.018 (0)	-3.075 (2)	49.1	35.1	43.9	-	52.1

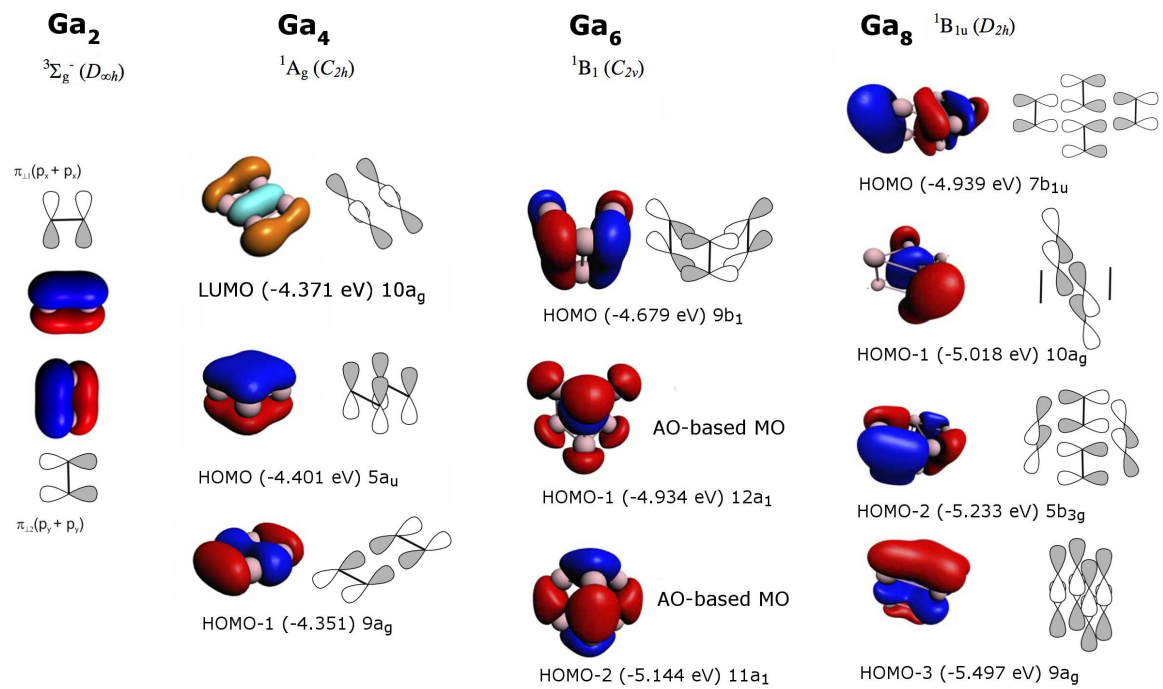

Fig. 3 The MOs of the Ga_4, Ga_6, and Ga_8 clusters in the singlet state are related to the orbitals of the dimer, demonstrating the oligomeric nature of the clusters where the Ga_2 dimer in the $^3\Sigma_g^-$ triplet state is the basic building block.

and/or occupation of the $2\sigma_g^+$ orbitals, as discussed above for Ga_6.

3.3 Electron densities and bonding

In addition to the analysis of orbitals, we also analyzed the electron densities of the compounds investigated. To this end we carried out AIM analyses on the BP86/def2-TZVPP level of approximation based on the BP86/TZ2P structures for the Ga clusters as well as a cluster model of the α-Ga phase (conventional unit cell of 8 atoms, with the bond lengths labelled in Fig. 1e, computed as a singlet state). The trends of the electron densities and the ellipticities at the bond critical points between close and distant pairs of Ga atoms are summarized in Fig. 4. It becomes clear that the electron density is considerably higher for the Ga atoms forming close dimers (pair bonds) compared to distant dimers (inter-pair bond) indicating a stronger interaction. At the same time, the ellipticity of the respective bonds is clearly smaller for the pair bonds. This is in line with the MO picture showing orbitals between close pairs often exhibiting stronger overlap. We can compare the cluster data to the values found for the $^3\Sigma_g^-$ state of the dimer and the cluster model of the solid-state phase which point toward the conclusion that the bonding between dimers in the clusters indeed provides a model for the dimer interactions in the bulk based on these indicators. Noteably, the Ga_6 cluster exhibits only a small difference in electron density between pair and inter-pair bonds, in line with the very similar bond lengths and atomic orbital (AO) based MO picture discussed above. In Fig. 4b, a correlation is found between the distance

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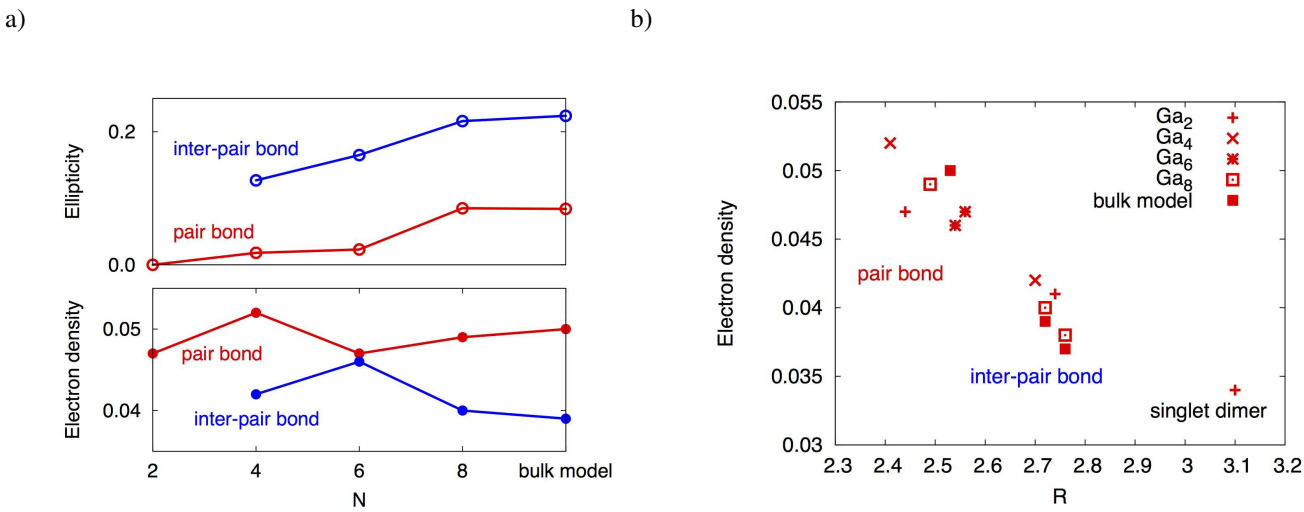

Fig. 4 a) The AIM electron densities and ellipticities of the pair and inter-pair bonds are plotted as a function of cluster size. b) The correlation between bond length and electron density at the bond critical point is shown.

of Ga atoms in the dimer, the clusters and the bulk model and the electron density value at the bond critical point. Three clusters of data are found: The pair bonds with high values for ρ, the inter-pair bonds with significantly smaller values and a much smaller value for the singlet state of the Ga-dimer. Thus, the AIM analysis supports the structural and orbital picture of dimeric features in the cluster and bulk structure.

4 Conclusions

In summary, the small gallium clusters Ga_4 and Ga_8 in their lowest lying singlet states can be understood as being composed of Ga-dimers in the first excited triplet state $^3\Sigma_g^-$ while Ga_6 exhibits less dimeric character. Molecular structure and bond lengths comparison give a first indication for this finding. Molecular orbital analysis confirms that the dimer orbitals make up the orbitals of the clusters, molecular orbitals being composed of atomic orbitals (as in Ga_6) can clearly be distinguished from dimer-derived orbitals. Comparison of the atoms-in-molecules characteristics of the bonds within the clusters to the bonds in the α-gallium bulk phase and the dimer support the identification of the covalent bond in the bulk as also being related to the $^3\Sigma_g^-$ state of the dimer.

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46 HOMO-1 could in principle also be interpreted as being composed of overlapping π_u orbitals. But in our view, the distortion from ideal dimer-type orbitals here (and to a lesser extent, in HOMO-2) is too large to support this hypothesis.

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