Why Does Disubstituted Hexamolybdate with Arylimido Prefer to Form an Orthogonal Derivative? Analysis of Stability, Bonding Character, and Electronic Properties on Molybdate Derivatives by Density Functional Theory (DFT) Study

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The bonding character of arylimido molybdate derivatives has been investigated, using density functional theory (DFT). The natural bond orbital analysis reveals that the Mo≡N triple bond in the arylimido molybdate derivatives is comprised of a σ-bond and two π-bonds. The energy analysis of 2,6-dimethylaniline disubstituted molybdate derivatives $[Mo_6O_{17}R_2]^{2-}$ (where R = 2,6-dimethylaniline group) has been performed. The results show that orthogonal $[Mo_6O_{17}R_2]^{2-}$ is more stable than diagonal $[Mo_6O_{17}R_2]^{2-}$. The bonding capability of the $Mo_6O_{17}R$ fragment with arylimido group R is strong for orthogonal $[Mo_6O_{17}R_2]^{2-}$. 2,6-Dimethylaniline disubstituted hexamolybdate derivative prefers to form an orthogonal derivative. The analysis of geometrical and electronic properties provides further support. The arylimido effectively modifies the occupied molecular orbitals and extends its organic π-electrons to the polyoxometalate skeleton. The major contributors to the highest occupied molecular orbital (HOMO) are p orbitals centered on the C atoms and N atoms, and d_{yz} orbitals centered on Mo atoms linked with the N atom of the organoimido group. The present investigation provides important insight into polyanion−organoimido interactions.

1. Introduction

Polyoxometalates (POMs) constitute an immense class of compounds and exhibit remarkable chemical and physical properties, which have been applied in a variety of fields, including catalysis, medicine, biology, analytical chemistry, and materials science.[1−6] Recently, numerous novel POM functional materials have been produced. Among them, the POMs with covalently bonded organic species in their surfaces generate new multifunctional hybrid materials with fascinating structural, electrochemical, and photophysical properties, and this has become a focus of the synthesis chemistry of POMs.[7−13]

In 1992, Judeinstein reported the first POM−polymer hybrid material in which Keggin POM cluster was covalently linked to a polystyrene or polymethacrylate backbone through Si−O bonds.[14] Lalot and co-workers subsequently synthesized POM−polymer cross-linked networks.[15−17] Stein and co-workers prepared macroporous silica materials with POM.[18,19] Maatta and co-workers reported organic polymers bearing polyoxometalates pendants.[20,21] The chemistry of POMs has gained great interest and led to promising applications. Among many organic derivatives of POMs, organoimido derivatives have attracted a particular interest. Recently, a large number of imido derivatives of the hexamolybdate anion have been synthesized continuously. Peng and co-workers prepared monofunctionalized, bifunction-

alized, and dumbbell hybrid materials by means of a palladium-catalyzed coupling of a POM cluster with organoimido,[11,12,22,23] and they synthesized a high-purity disubstituted orthogonal hexamolybdate derivative by reacting α-$[Mo_8O_{26}]^{2-}$ with organoimido.[13]

Although POM chemistry is an extremely rich area of experimental research, calculations on POMs have been relatively scarce. Bénard and co-workers have investigated the properties of a variety of systems, such as electronic properties, redox properties, host−guest interactions, and the relative basicities of oxygen sites, using the ab initio Hartree−Fock and the density functional theory (DFT) method.[24−27] Poblet and co-workers have reported a series of theoretical investigations on the electronic and magnetic properties and relative stability.[28−35] Bridgeman and co-workers have reported DFT investigations that involved the molecular and electronic structures of isopolyanions and heteropolyanions.[36−39] Borshch have investigated the electron delocalization in substituted polyanions.[40−42] Others have made significant contributions as well.[43−45] Recently, DFT has been widely used in computational chemistry; in particular, it has been used to simulate transition metal complexes.[46,47] These works have shown that DFT is the optimal choice to investigate complicated transition metal systems including POMs.

The experimental investigations have shown that organoimido is an effective template to synthesize inorganic−organic hybrid

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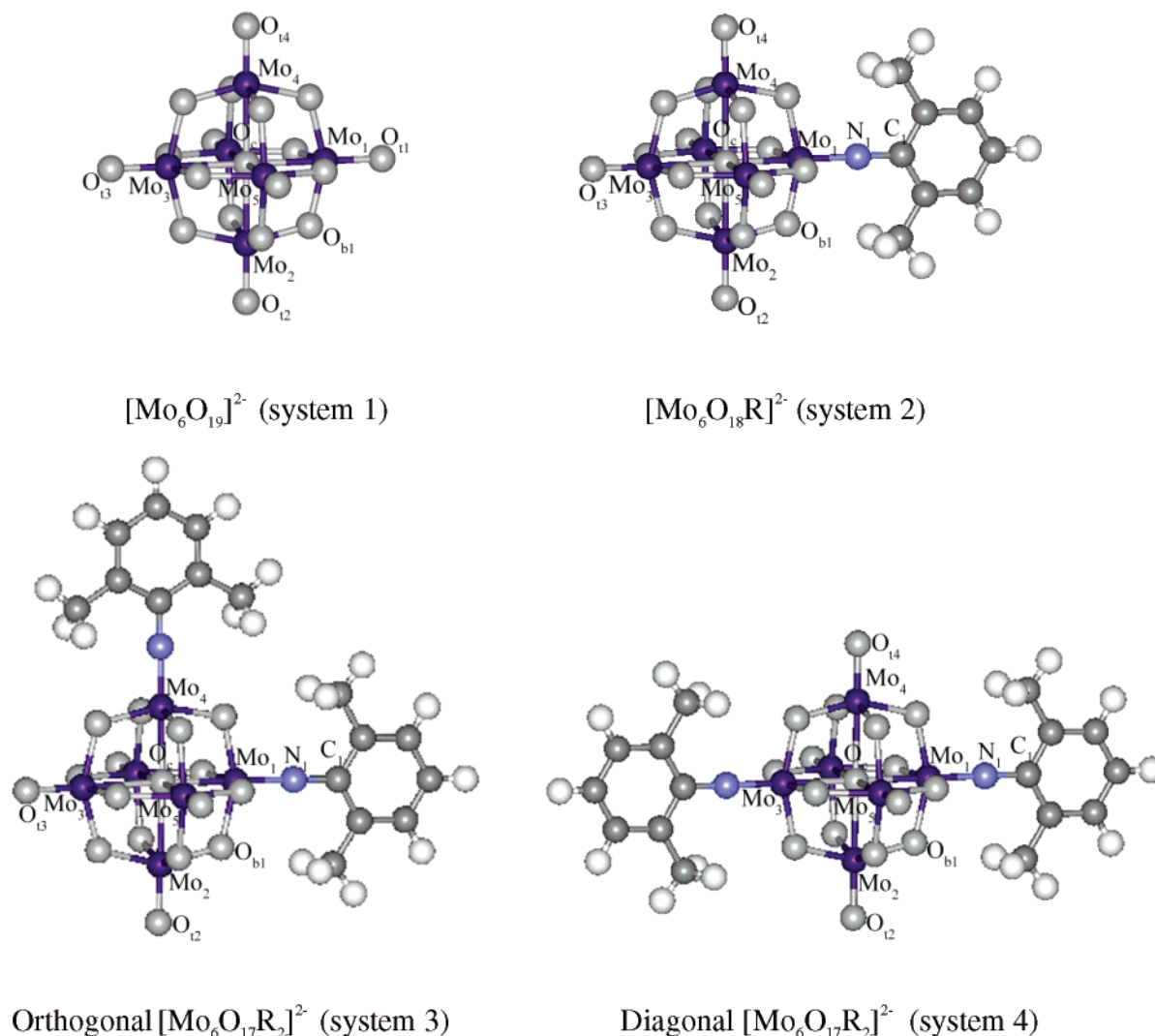
$[Mo_6O_{19}]^{2-}$ (system 1)

$[Mo_6O_{18}R]^{2-}$ (system 2)

Orthogonal $[Mo_6O_{17}R_2]^{2-}$ (system 3)

Diagonal $[Mo_6O_{17}R_2]^{2-}$ (system 4)

Figure 1. Calculation models.

materials. Organoimido derivatives can extend their organic π-electrons to the POM skeleton, and, in the meantime, the synergistic effect between inorganic clusters and organic segments would occur. Although several organoimido−POM derivatives have been synthesized, challenges remain. First, what is the nature of the bonding between the polyanion and the organoimido group? Second, why does the 2,6-dimethylaniline disubstituted hexamolybdate derivative prefer to form an orthogonal structure rather than a diagonal structure? Third, what is the function of the asymmetry of the central oxygen atom in the derivative? In this work, we attempt to address these problems, using the DFT method, and further provide useful guidelines for the rational design synthesis of this type of material and their three-dimension networks. Our work is the first study of the bonding characters and electronic properties on two isomers of disubstituted hexamolybdate derivatives $[Mo_6O_{17}R_2]^{2-}$ (where R = 2,6-dimethylaniline group). The preferable structures of two isomers have been examined, and the modified functions of organoimido have been interpreted. The deeper insight into the bonding nature of polyanions with organoimido groups has been gained, using natural bond orbital (NBO) analysis.

2. Theoretical Details

The DFT[48,49] calculations reported in this work were performed using the ADF2003.01 program.[50] The local density

approximation (LDA) characterized by the Vosko−Willk−Nusair (VWN)[51] parametrization is adopted for the correlation functional. In addition, gradient corrections of Beck[52] and Perdew[53] nonlocal corrections are used for the exchange and correlation functionals, respectively. Triple-ξ basis sets with added polarization functions were taken to describe the main group elements (C, N, O, H), whereas for the transition metal Mo atom, the approximation of a frozen core was used up to the 3d state. The relativistic effects were taken into account, using the zero-order regular approximation (ZORA).[54]

The calculation models of $[Mo_6O_{19}]^{2-}$ (system 1), monosubstituted $[Mo_6O_{18}R]^{2-}$ (system 2), and disubstituted $[Mo_6O_{17}R_2]^{2-}$ derivatives (where R = 2,6-dimethylaniline; the orthogonal derivative corresponds to system 3 and the diagonal derivative corresponds to system 4) are shown in Figure 1. The geometries of systems 1 and 2 were optimized under O_h and C_{2v} symmetry constraints, respectively. The geometry optimizations under the respective C_{2v} and D_{2h} symmetry constraints for systems 3 and 4 were also performed.

The total energies of disubstituted hexamolybdate derivatives $[Mo_6O_{17}R_2]^{2-}$ were extracted from single-point BP86 and B3LYP calculations with the Gaussian98 program.[55] To further ascertain the bonding between the arylimido and the molybdate cluster, we performed single-point calculation at the B3LYP level involving the effective core potential (ECP) on the Mo atom, using the Gaussian98 program. In all Gaussian98 calcula-
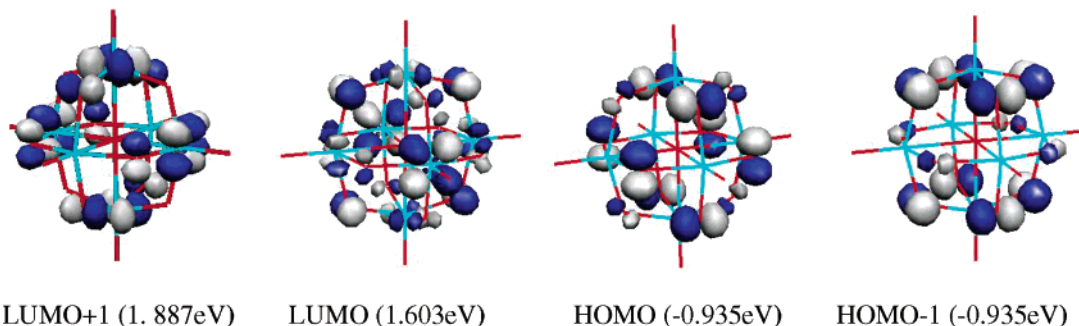
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LUMO+1 (1. 887eV)   LUMO (1.603eV)   HOMO (-0.935eV)   HOMO-1 (-0.935eV)

Figure 2. Schematic orbital diagrams of $[Mo_6O_{19}]^{2-}$ (system 1).

TABLE 1: Calculated Bond Lengths for $[Mo_6O_{19}]^{2-}$ and $[Mo_6O_{18}R]^{2-}$

atom pair	Calculated Bond Length (Å)[a]	
	$[Mo_6O_{19}]^{2-}$ (system 1)	$[Mo_6O_{18}R]^{2-}$ (system 2)
Mo_1-O_b	1.954 (1.92)	1.972 (1.95)
Mo_1-O_c	2.354 (2.32)	2.270 (2.23)
Mo_2-O_{t2}	1.728 (1.68)	1.728 (1.69)
Mo_1-N_1		1.795 (1.73)

[a] Experimental values are given in parentheses.

tions, the LANL2DZ basis set associated with the pseudo-potential was used to describe the Mo atom, and the 6-31G(d) basis set was used to describe the C, N, O, and H atoms. The bonding in the arylimido molybdate derivatives was examined by NBO.

3. Results and Discussion

3.1. Bonding Character between Arylimido and $[Mo_6O_{19}]^{2-}$. *3.1.1. Geometry and Charge.* The bonding characters of organoimido-substituted POMs have attracted much attention from both experimental and theoretical chemistry fields. With monosubstituted $[Mo_6O_{18}R]^{2-}$ as an example, the nature of the bonding was analyzed. It is well-known that the O atoms in the Lindqvist isopolyanions and their derivatives can be divided into three categories: terminal oxygen (O_t), bridging oxygen (O_b), and central oxygen (O_c) atoms. POMs that contain metal–oxygen octahedra with only one unshared O atom have been classified as Type I by Pope.[56,57] The inherent property of these POMs is that their bonding nature would be affected by adding one or several electrons with only little changes in structure. The optimized partial geometrical parameters are listed in Table 1, which also includes experimental data taken from the compilations of Tytko et al.[58] and Peng et al.[12] Clearly, the important structural parameters are well-reproduced in the theoretical calculations.

The symmetry of $[Mo_6O_{18}R]^{2-}$ is reduced from O_h to C_{2v} when the organoimido is introduced into $[Mo_6O_{19}]^{2-}$. The bond lengths of $Mo-O_t$ do not change significantly, but those of Mo_1-O_b and Mo_1-O_c do: Mo_1-O_b was lengthened and Mo_1-O_c was shortened. The central oxygen atom (O_c) is closer to the imido-bearing Mo atom. These remarkable structural characters reflect the charge density. Using the charge analysis of Poblet,[33] we calculated the charge transfer of Mo atoms. Mulliken population analysis shows that the net charge on Mo_1 is +2.2585, which means that the Mo atom has transferred 37.6% of its valence electrons to the N atom and its adjacent O atoms. This result confirms the significant covalent character of molybdenum–nitrogen interactions.[31] The bonding character will be discussed more specifically below.

3.1.2. Electronic Properties of Monosubstituted Arylimido Derivatives. The bonding character of arylimido–POMs is

interpreted by the orbital distribution of system 2. The isopolyanion $[Mo_6O_{19}]^{2-}$ has the typical molecular orbital arrangement,[33] where the occupied orbitals formally delocalizes over the oxo ligands, and the unoccupied orbitals are symmetry-adapted d-metal orbitals with some antibonding participation of O p orbitals. Mo–O interaction has Mo_d-O_p character. HOMO, HOMO-1, and HOMO-2 orbitals are triply degenerate orbitals with their t_{1g} symmetry. The orbital diagrams and energies for frontier molecular orbital of $[Mo_6O_{19}]^{2-}$ are given in Figure 2. Under the constraint of O_h point group, six Mo atoms are all equivalent. The probabilities of six Mo atoms accepting electrons are equal in the redox reaction.

In system 2, the arylimido R effectively changes the orbital property of molybdate (Figure 3). There are two significant contributions to the HOMO: the first is the delocalized π-bond coming from the C atoms of arylimido, and the second is the d–p π-bond from the d_{xz} orbital on the Mo atom, which links the N atom and p_x orbital on nitrogen. The HOMO shows significant delocalized character. The π-bonding interaction between the organic delocalized π-electrons and the polyanion cluster d electron results in excellent synergistic effect, which leads to stable inorganic–organic hybrid compounds.

The N_1-C_1 distance is 1.362 Å in system 2; however, in the free 2,6-dimethylaniline group, the N_1-C_1 distance is 1.290 Å. The stable derivative is obtained when the Mo atom bonds to the N atom, and the N–C bond in the organoimido is simultaneously weakened. The highest occupied orbital of the Mo atom is the d_{xz} orbital, and the N p_x orbital of the HOMO is on the Mo–N plane. The large overlap results in strong bonding between them. This point will be discussed more specifically in the next section. The HOMO and HOMO-1 of system 2 have the same symmetry, but the energy and electronic distribution of both orbitals are different, with energies of −0.642 and −0.919 eV, respectively. The HOMO-1 energy of system 2 is more similar to the HOMO energy of $[Mo_6O_{19}]^{2-}$ (−0.935 eV). The p_y and p_z orbitals centering on the bridging O atoms are the major contributors to both orbitals. It indicates that the arylimido moiety of system 2 appears first in the HOMO and determines the energy level of the derivative. The HOMO in the $[Mo_6O_{19}]^{2-}$ corresponds to the HOMO-1 in the $[Mo_6O_{18}R]^{2-}$. The difference between the energy of the LUMO and LUMO+1 in system 2 is subtle. Both orbitals are very similar to that of $[Mo_6O_{19}]^{2-}$, of which the main compositions are Mo d-orbitals with the participation of O p-orbitals.

3.1.3. Natural Bond Orbital (NBO) Analysis. The Mo≡N triple bond in the arylimido hexamolybdate derivative has been demonstrated as its short bond length, and an almost-linear Mo–N–C bond angle was observed in the experiment.[11,21] To interpret the arylimido–$[Mo_6O_{19}]^{2-}$ interaction, NBO analysis is summarized in Table 2, using system 2 as an example. There are a Mo–N σ bond (comprised of a $s^1p^{0.01}d^{4.64}$ Mo orbital and
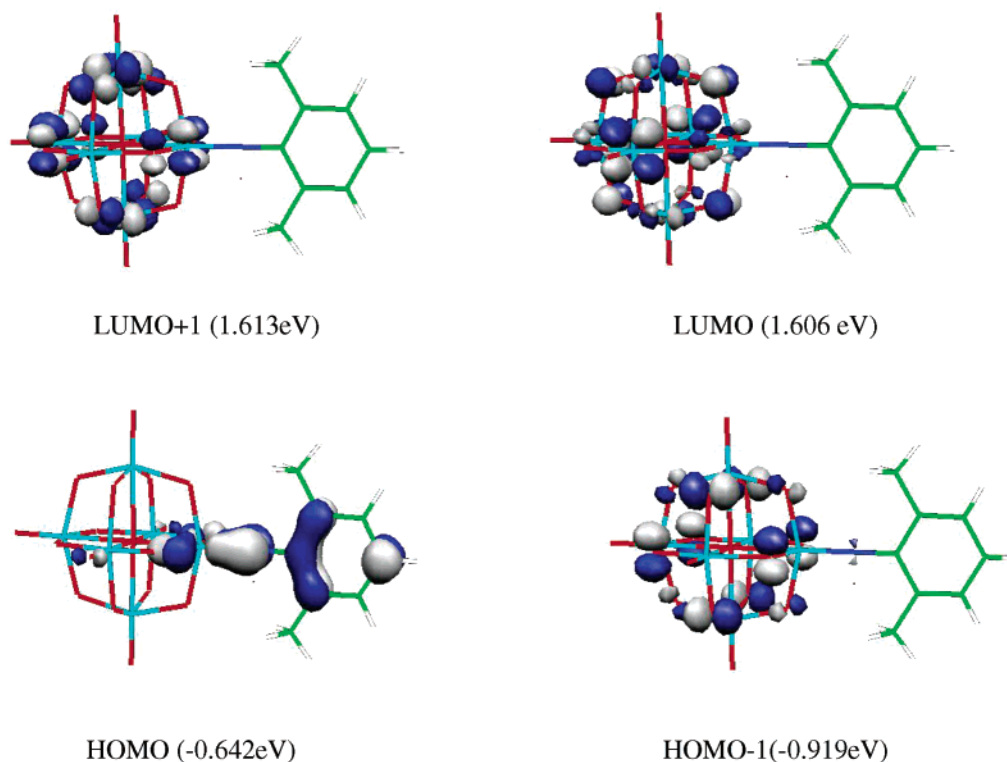
LUMO+1 (1.613eV)   LUMO (1.606 eV)

HOMO (-0.642eV)   HOMO-1(-0.919eV)

Figure 3. Schematic orbital diagrams of $[Mo_6O_{18}R]^{2-}$ (system 2).

TABLE 2: Occupancy, Orbital Hybridization (Orbital Coefficients), and Orbital Type of System 2

natural orbital	occupancy	orbital hybridization (orbital coefficients)	orbital type
Mo−N	1.9772	$0.4899\ s^1p^{0.01}d^{4.64}$ (Mo) $+ 0.8718\ s^1p^{0.85}$ (N)	σ
Mo−N	1.8594	$0.5619\ d$ (Mo) $+ 0.8272\ p$ (N)	π
Mo−N	1.8403	$0.5594\ d$(Mo) $+ 0.8289\ p$ (N)	π
N−C	1.9874	$0.7670\ s^1p^{1.18}$ (N) $+ 0.6416\ s^1p^{2.51}$ (C)	σ

a $s^1p^{0.85}$ N orbital) and two Mo−N π-bonds (comprised, respectively, of a pure Mo d-orbital and a pure N p-orbital in system 2. Thus, the interaction of Mo_1 and N_1 shows triple-bond character. The corresponding orbital has significant contributions from both Mo_1 and N_1 atoms. Because the electron occupancies of Mo−N are similar to 2.0, it clearly shows that the arylimido is strongly bonded to the molybdate. This strong interaction can be utilized to construct covalently POM networks. In addition, N_1−C_1 linkage is a σ bond comprised of a $s^1p^{1.18}$ N orbital and a $s^1p^{2.51}$ C orbital, so it indicates dominant N−C single-bond character.

The interaction between the arylimido and the polyanion cluster was similar to that of the Dewar−Chatt−Duncanson model.[59] The dominant bonding interactions of arylimido and molybdate arise from arylimido → molybdenum σ donation and molybdenum → arylimido π back-donation. The most important orbital interactions should be donation from the occupied orbital of arylimido into the empty d_{z2} orbital of molybdenum, and back-donation from the d_{xz} and d_{yz} orbitals of molybdenum to the empty N p-orbital of arylimido (Figure 4).
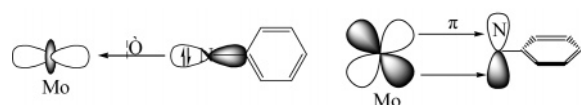

Figure 4. Schematic representation of the synergistic N → Mo σ-donation and N ← Mo π-back-donation.

3.2. Preference of Disubstituted $[Mo_6O_{17}R_2]^{2-}$ to Form an Orthogonal Derivative. *3.2.1. Energy Analysis.* It is very common that the orthogonal structure is available to

TABLE 3: $Mo_6O_{17}R$−R Interaction Energy (ΔE) of Systems 3 and 4

	Value	
parameter	$[Mo_6O_{17}R_2]^{2-}$ (system 3)	$[Mo_6O_{17}R_2]^{2-}$ (system 4)
E_T (eV)	−65726.1697	−65711.9049
$E_{[Mo_6O_{17}R]}$ (eV)	−55791.1741	−55790.9545
E_R (eV)	−9888.4987	−9880.1194
ΔE (eV)	46.4969	40.8310

increase the steric repulsion in organic substituted reactions. Contrary to this expectation, high-purity orthogonal disubstituted $[Mo_6O_{17}R_2]^{2-}$ has been synthesized from the reaction of $[a\text{-}Mo_8O_{26}]^{4-}$ with 2,6- dimethylaniline (RH₂).[13] Why? The total energies of two systems at the BP86 and B3LYP levels favor the orthogonal structure over the diagonal structure by −14.2648 and −14.7034 eV, respectively. The orthogonal structure is more stable than the diagonal structure.

To investigate the influence of the arylimido R group on the stability of the disubstituted $[Mo_6O_{17}R_2]^{2-}$, the interaction energies between the arylimido group R and the $[Mo_6O_{17}R]$ fragment of systems 3 and 4 were analyzed using the Gaussian98 program, and the results are shown in Table 3. In the calculation, the arylimido group (R) is considered to be dianionic and the spin multiplicity of R is 1. The $[Mo_6O_{17}R]$ fragment is neutral, in that the spin multiplicity is 1. The $Mo_6O_{17}R$−R interaction energy in system 3 is larger than that of system 4. It indicates that the bonding capability of the $Mo_6O_{17}R$ fragment with the arylimido group R is stronger in system 3 and shows that system 3 should be more stable. The thermodynamic stability of the orthogonal disubstituted structure is an important factor,
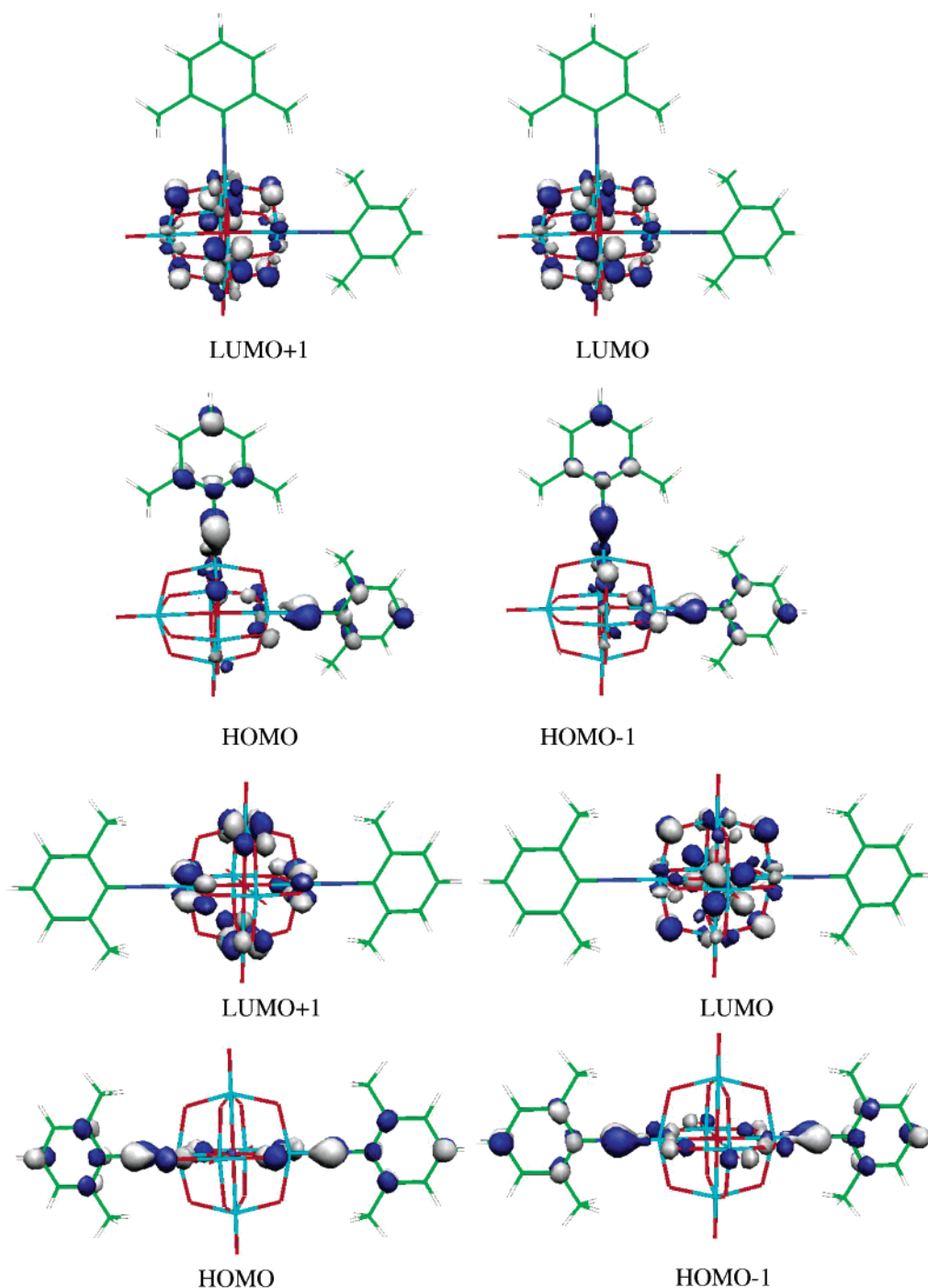
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Figure 5. Schematic orbital diagrams of $[Mo_6O_{17}R_2]^{2-}$.

leading to the synthesis of high-purity orthogonal disubstituted $[Mo_6O_{17}R_2]^{2-}$. The theoretical results agree very well with the experimental result.[13]

3.2.2. Influence of the Central Oxygen (O_c). In $[Mo_6O_{19}]^{2-}$, the distances of all Mo−O_c bonds are all equivalent and the central oxygen atom (O_c) inside the hexamolybdate cage bonds to each Mo atom, keeping the O_h symmetry of $[Mo_6O_{19}]^{2-}$. The polyhedron formed by the Mo atoms and the O_c atom have obvious asymmetry in the organoimido derivative; however, how does the O_c atom affect the structure of $[Mo_6O_{17}R_2]^{2-}$? To answer this question, the properties of monosubstituted $[Mo_6O_{18}R]^{2-}$ are first discussed. The distances between the O_c atom and the Mo atoms are altered by introducing the organoimido group R. In system 2, the distance of Mo_1−O_c is 2.270 Å; the O_c atom is drawn closer to the imido-bearing Mo atom

and Mo_1−O_c becomes shorter, because of the interaction between the Mo_1 and O_c atoms. The Mo_4−O_c distance is 2.365 Å, which is similar to that in $[Mo_6O_{19}]^{2-}$. Among the Mo−O_c bond lengths of $[Mo_6O_{18}R]^{2-}$, the largest one is Mo_3−O_c (2.382 Å). In $[Mo_6O_{18}R]^{2-}$, the distances of Mo−O_c are not equivalent, at the same time, Mo atoms and O atoms formed an ellipsoid. The fact that the second arylimido is introduced into Mo_4 or Mo_2 sites has maximal probability. It undergoes a lower energy process. If the second arylimido was introduced into the Mo_3 atom site, the O_c atom would be closer to the Mo_3 atoms. The bonding stability of Mo_1−O_c, Mo_4−O_c, and Mo_2−O_c would be affected and is unfavorable to the stability of the disubstituted derivative.

The Mo−O_c distances in system 3 are different from those of $[Mo_6O_{18}R]^{2-}$. In system 3, both of the distances (Mo_1−O_c

TABLE 4: Fragment Analysis (ΔE_O, ΔE_E, ΔE_P, and ΔE_B) for [Mo$_6$O$_{17}$R$_2$]$^{2-}$ Derivatives

	Value	
parameter	[Mo$_6$O$_{17}$R$_2$]$^{2-}$ (system 3)	[Mo$_6$O$_{17}$R$_2$]$^{2-}$ (system 4)
ΔE_O (eV)	−13.3671	−13.2306
ΔE_E (eV)	−31.7860	−31.5219
ΔE_P (eV)	24.9867	24.6643
ΔE_B (eV)	−20.1664	−20.0882

and Mo$_4$−O$_c$) are 2.237 Å, and the Mo$_5$−O$_c$ distance is 2.377 Å. The largest bond distance, for Mo$_3$−O$_c$, is 2.449 Å, which is longer than that in system 2. It can be seen that the O$_c$ atom is closer to the imido-bearing Mo atoms in the organoimido derivatives. The O$_c$ atom has an important function that stabilizes the organoimido derivative cluster. The reasonable conclusion is that the third organoimido group is bonded to Mo$_5$; thus, the trisubstituted derivative may be obtained.

3.2.3. Fragment Analysis. In the ADF program, the bonding energy (E_B) analysis can effectively described as the fragment relative effect on bonding stability. According to the transition-state method of Ziegler and Rauk,[60] the molecular bonding energy (E_B) can be decomposed as

$$E_B = E_E + E_P + E_O \quad (1)$$

where E_E, E_P, and E_O are the electrostatic interaction, Pauli repulsion, and orbital mixing term, respectively. Descriptions of the physical meaning of these properties have been given by Landrum, Goldberg, and Hoffmann,[61] and by Bickelhaupt and Baerends.[62] E_E is an electrostatic term whose contribution is primarily dominated by the nucleus−electron attractions. The Pauli repulsion[63] acts as the destabilizing effect, which is caused by the larger energy shift of antibonding orbitals to bonding orbitals. E_O results from the mixing of occupied and unoccupied orbitals. Therefore, E_E and E_O show stabilizing effects. E_B is a total molecular bonding energy, relative to the sum of the single atoms. A fragment approach to the molecular structures of the polyanions can provide further insight into the bonding stability.[39] For comparison with the influence of the central O$_c$ atom in disubstituted [Mo$_6$O$_{17}$R$_2$]$^{2-}$, the following decomposition scheme was used:

$$[Mo_6O_{16}R_2]^0 + [O_c]^{2-} \rightarrow [Mo_6O_{17}R_2]^{2-} \quad (2)$$
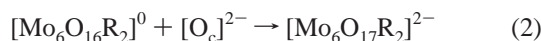
The bonding energy relative to the fragments described by eq 2 is given by

$$\Delta E_B = \Delta E_E + \Delta E_P + \Delta E_O \quad (3)$$

The results are shown in Table 4. It can be observed that the interaction between [Mo$_6$O$_{16}$R$_2$] and the O$_c$ atom in system 3 generates a stronger contribution than that of system 4. ΔE_O and ΔE_E have an important contribution. Comparison with system 4 shows that the stronger interaction of [Mo$_6$O$_{16}$R$_2$] and the O$_c$ atom in system 3 leads to stronger overall bonding, and the bonding between the O$_c$ atom and the Mo atoms makes a significant contribution to the stability of the orthogonal [Mo$_6$O$_{17}$R$_2$]$^{2-}$ cluster.

3.2.4. Electronic Properties of Disubstituted Arylimido Derivative. When the organoimido group locates at the different sites of [Mo$_6$O$_{19}$]$^{2-}$, the stability of the compound is affected and the electronic property of the derivative may be altered as well. The frontier molecular orbital (FMO) schemes of systems 3 and 4 are depicted in Figure 5, and their energy levels of FMOs are shown in Figure 6. The following conclusions can be given:
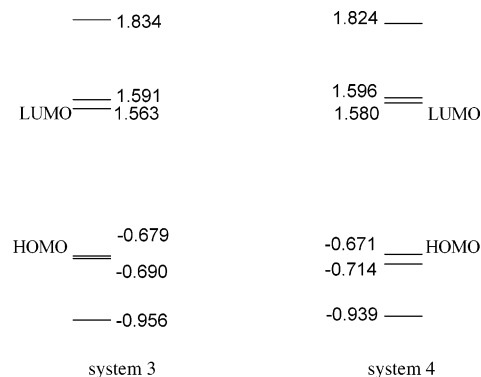
Figure 6. Energy levels (given in eV) of the frontier molecular orbitals (FMOs) of [Mo$_6$O$_{17}$R$_2$]$^{2-}$.

(1) The energy level of the highest occupied molecular orbital (HOMO) and HOMO-1 in system 3 are almost degenerate. At the same time, the major contributors to HOMO and HOMO-1 are the p-orbitals centered at the C atoms and N atoms, d$_{yz}$-orbitals centered at the Mo atoms, and p-orbitals centered at the O atoms which are close to two organoimido groups. Furthermore, for the FMO, the d−p π-bonding is formed by the symmetry-adapted d$_{yz}$-orbitals on the Mo atoms and p-orbitals on the N atoms.

(2) The lowest unoccupied molecular orbital (LUMO) and LUMO+1 in system 3 concentrate on the POM cluster coming from both Mo atoms and O atoms.

(3) In FMO, the arylimido can modify the occupied molecular orbital and extend its organic π-electron to the POM skeleton.

(4) The same electron distribution behavior occurs in system 4.

The important function of the central oxygen atom (O$_c$) bonds with six Mo atoms is to stabilize [Mo$_6$O$_{19}$]$^{2-}$ and its derivatives. In systems 3 and 4, the O$_c$ atom occupies the deep orbitals; thus, it helps to stabilize both systems. The O$_c$ atom in system 3 has sp^2 hybridization and orients the bridging O atoms, which leads to strong interaction between the O$_c$ atom and the neighboring bridge O atoms. At the same time, the favorable electrommunication occurs in system 3. The O$_c$ atom in system 4 has no hybridization and points outward along the axial orientation. It is disadvantageous to produce strong interaction between the O$_c$ atom and the neighboring bridge O atoms, because of the steric distance. This is also a factor to make system 3 more stable.

4. Summary and Conclusions

Herein, we have reported, for the first time, to use density functional theory (DFT) calculations to interpret the bonding character, favorable orthogonal [Mo$_6$O$_{17}$R$_2$]$^{2-}$, and electronic properties of arylimido derivatives. The computational results are in good agreement with the experimental results and provide rational interpretation to several problems that could not be resolved by the experiments. Several important conclusions are given as follows:

(1) The close interaction of the organoimido delocalized π-electron with the d-electrons of the molybdate polyanion leads to stronger synergistic effects. Consequently, the stable organic−inorganic hybrid compounds are obtained with determining structures. Natural bond orbital (NBO) analysis was performed to investigate further the bonding character of an arylimido derivative. The strong Mo≡N triple bond can be formed through the N → Mo σ-donation and N ← Mo π-back-donation in the formation of the arylimido derivative.

(2) The energy analysis showed that system 3 is more stable than system 4. The bonding capability of the Mo$_6$O$_{17}$R fragment

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with the arylimido group R in orthogonal $[Mo_6O_{17}R_2]^{2-}$ is stronger than that of diagonal $[Mo_6O_{17}R_2]^{2-}$. According to the distance between the central oxygen atom (O_c) and the Mo atoms, it is confirmed that the favorable orthogonal $[Mo_6O_{17}R_2]^{2-}$ is formed when a second organoimido group R is introduced into $[Mo_6O_{18}R]^{2-}$.

(3) Compared to $[Mo_6O_{19}]^{2-}$, the arylimido effectively changed the properties of the occupied molecular orbital of the $[Mo_6O_{18}R]^{2-}$ and $[Mo_6O_{17}R_2]^{2-}$ derivatives. In the highest occupied molecular orbital (HOMO), the d–p π-bond is formed between the symmetry-adapted d_{yz}-like orbital of the Mo atom with the p_x-orbital of the N atom of the derivative. The organic π-electrons extend their conjugation to the polyanion cluster. The lowest unoccupied molecular orbital (LUMO) of arylimido derivatives is similar to that of $[Mo_6O_{19}]^{2-}$.

(4) The central oxygen atom (O_c) is closer to the imido-bearing Mo atom in the organoimido derivatives. The O_c atom is responsible for stabilizing the cluster.

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