Möbius 环并苯的分子对称性

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摘要: 一般来说, 点群理论认为 Möbius 带环分子最高的对称性只能是 C_2 . 本文讨论了由 18 个苯环组成的环并苯的异构体分子, 包括柱面的 Hückel 型分子(HC-[18])和扭转 180° 的 Möbius 带环分子(MC-[18]). 结果表明除了点对称性外, Möbius 带环分子还存在一种可称为环面螺旋旋转(TSR)变换的对称性, 为此还引用了环面正交曲线坐标系. 此外, 还讨论了这些分子关于 TSR 对称性匹配的原子集和原子轨道(AO)集. 根据 TSR 对称性的循环群特征, 可以建立此类群的不可约表示及有关特征标. 这类分子的分子轨道(MO)关于 TSR 群的不可约表示是纯的, 然而所含的相应的原子轨道对称性匹配的线性组合(SALC-AO)成分可以是多种的.

关键词: Möbius 环并苯; 分子对称性; 环并苯; 环面螺旋旋转变换; 环面正交曲线坐标系; 环面群
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Molecular Symmetry of Möbius Cyclacenes

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Abstract: Generally speaking, the highest symmetry of a Möbius cyclacene molecule is C_2 group based on the point group theory. We here investigated two isomers of cyclacene that were composed of 18 benzene units, i.e., a hoop-like Hückel [18]-cyclacene (HC-[18]) and a Möbius strip-like Möbius [18]-cyclacene (MC-[18]). We found that in addition to being described by C_2 point group transformation, the molecular symmetry of Möbius cyclacene may also be characterized by the so-called torus screw rotation (TSR) symmetrical transformation, which is a symmetry operation of the torus group introduced here. The torus orthogonal curvilinear coordinates were also introduced to express the TSR transformation. Furthermore, both the symmetry adapted atom set and the atomic orbital set that refers to the TSR transformation are discussed. Because the TSR symmetry has cyclic group characteristics, we can establish the irreducible representations and related characteristics for this cyclic group. In addition, for these cyclacenes the irreducible representation of their molecular orbitals (MOs) may be pure while their corresponding symmetry adaptive linear combination of atomic orbital (SALC-AO) components can be numerous.

Key Words: Möbius cyclacene; Molecular symmetry; Cyclacene; Torus screw rotation transformation; Torus orthogonal curvilinear coordinates; Torus group

1 Introduction

Since German mathematician Möbius discovered the famous one-surface Möbius strip in 1858, scientists began to investigate the special structure and curious characteristics of Möbius

strip, then chemists turned to look for molecules with Möbius strip-like structures for new molecular properties such as the molecular symmetry, conjugation effect, and aromaticity.¹ Early theoretical studies mainly focused on the electron wave func-

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tions of the topological structure of Möbius strip and on the characteristics of the atomic orbital basis functions after being turned 180° from the orientation in the molecule of Hückel molecule.^{2,3} Later, about the aromaticity of Möbius strip and the selection rule of pericyclic reaction, theoretical studies have made exciting progress.^{4,5} However, reports on the synthesis of Möbius strip-like molecules are relative tardiness. Since 1982, Walba and co-workers^{6–8} synthesized the first molecular Möbius strip *via* high-dilution cyclization of the tris-tetrahydroxymethylethulene (THYME) diol ditosylate. After entering the new millennium, Herges *et al.*^{9,10} synthesized the stable Möbius strip-like molecules. Because of the topology character of the structure of Möbius strip-like molecules and the possible applications in biomedical field, Möbius strip-like molecules attracted more and more attention, especially in the synthesis field.^{7,9,10} In recent years, many theoretical and experimental articles and reviews about Möbius strip-like molecules have been published.^{10–18}

C_2 axis is generally considered to be the highest symmetry element of Möbius strip-like molecule with one knot.¹⁰ Based on the topology principle,¹⁹ the fundamental group of Möbius strip is a continuous (infinite) cyclic group and its border is made up of twice of the generator. Of course, the Möbius strip-like molecule is a finite discrete cyclic symmetry group. This description may have some contrast with that from the “molecular symmetry”, because the “molecular symmetry” is usually based on the theory of point group. Here, we take the linear [18]-polyacene molecule (Fig.1) formed by [18]-benzene rings as an example to investigate.

The structure of linear [18]-polyacene molecule is shown in Fig.1 (omitted the hydrogen atoms for clarity). As shown in Fig.1, in each structural unit, the carbon atoms are labeled as C_a , $C_{a'}$, $C_{b'}$, and C_b from top to bottom, respectively. When the C-atoms at the left and right ends overlap to each other to form a three-dimensional (3D) structure of [18]-polyacene ring, it can either be a Hückel [18]-cyclacene (denoted as HC-[18]) or a Möbius [18]-cyclacene (MC-[18]), after gluing the two ends of the molecular plane together without or with twisting 180° of one end of the molecular plane. We can also obtain Möbius cyclacene molecules with n knots, denoted as M^nC -[18], with twisting n times of 180° . And they have the same formula $C_{72}H_{36}$. But this paper will chiefly discuss the HC-[18] and MC-[18] molecules.

Analyzed by the theory of point group, HC-[18] molecule exists 72-order D_{18h} symmetry, but the corresponding MC-[18] only has 2-order C_2 symmetry. HC-[18] has a finite 18-order

cyclic symmetry (C_{18} point group). By topology principle just mentioned, it can be expected that MC-[18] may have a finite 36-order cyclic symmetry group, no more limited to the C_2 point group. In this paper, we indeed find out this kind of 36-order cyclic symmetry group, but it is not the point group and may be called torus screw rotation (TSR) group. Similarly, as the case of cylinder group G_1^3 ,²⁰ the torus screw rotation group may be called as a special kind of torus group.

2 TSR transformation and torus orthogonal curvilinear coordinate

In this section, we introduce a new symmetry transformation, namely TSR transformation. As well-known, rotation transformation of point group is operated by circling the object around a rotation axis, which is through a fixed point; while screw rotation transformation of space group is operated by rotating the object around a fixed line (called screw axis) and accompanied with translation along the screw axis,²⁰ which is also known as cylinder screw rotation. But TSR transformation is operated by rotating the object around a fixed circle (called base circle, which is formed by the dotted line in Fig.1 and represented by the red line in Fig.2), and accompanied with rotating around the center of the base circle (i.e., the origin O). Because all the points after this transformation are in a same torus, it is called torus screw rotation. For Möbius cyclacene molecules, they have TSR transformation so can keep invariant under certain TSR transformation. When the base circle is reduced to a point (i.e., an object with zero dimension), TSR will turn into the rotation transformation of point group and the related torus turn into a sphere (spherical surface). When the radius of the base circle is expanded to infinite (i.e., a one-dimensional line), TSR will become the cylindrical screw rotation transformation of space group and the relative torus turn into a cylinder. So, in general circumstances, the base circle of TSR is a finite-size circle. Of course, it should be noted that the torus herein is not homeomorphous with the sphere of point group and the cylinder of one-dimensional space group, so they should have different mathematical characteristics. Perhaps TSR can be used as an effective tool to deal with the symmetry of the fractal system.²¹ If the movement of planet around star is regarded as the ordinary rotation, the motion of satellite of the planet is corresponding to the torus screw rotation. In this paper, we will only discuss the symmetry issues of Möbius cyclacene molecules.

For Möbius cyclacene molecules, using Cartesian coordinates to deal with TSR symmetry transformation is not conve-

Fig.1 Structure of linear [18]-polyacene molecule

In each structural unit, C-atoms labeled as C_a , $C_{a'}$, $C_{b'}$, and C_b from top to bottom, respectively. Hydrogen atoms are omitted for clarity.

Fig.2 Torus orthogonal curvilinear coordinates

nience, so we introduce torus orthogonal curvilinear coordinates. As shown in Fig.2, point O is the origin of the XYZ three-dimensional Cartesian coordinates. Now, a base circle (the red circle) in the XY plane is drawn and its radius is R (OO'). For a point P in the 3D Cartesian coordinates with the coordinate values (X, Y, Z) , its corresponding torus orthogonal coordinate value (L, α, β) may be defined as follows: making a vertical line from the P point to the XY plane intersecting at the T point, and then extend the OT line until intersecting with the base circle at the O' point. Connecting points O' and P, and the length of $O'P$ segment is set the L value in the torus orthogonal coordinates. The other two values α and β are determined by the angles XOO' and $PO'O$, respectively. Because the surface defined by such a constant L coordinate value is a torus, it is called torus orthogonal coordinates. The torus screw rotation transformation, TSR, is a symmetrical operation that circles the object around both the Z axis and the base circle simultaneously in the torus orthogonal coordinate. Surely, the coordinate values of α and β change, but the value of L remains unchanged in such transformation. Such a transformation is denoted as: $\text{TSR}(L, \Delta\alpha, \Delta\beta)$, where $\Delta\alpha$ and $\Delta\beta$ are the variations of values α and β , respectively. Usually, point P is a particular atom, so its image point P' should be another atom which is the same as P point, and so on. After several such transformations, we can expect that the image P' will reach the source P. This is a necessary condition to determine whether there is a symmetrical transformation in a molecule. In addition, the variations $\Delta\alpha$ and $\Delta\beta$ caused by TSR transformation are related to each other governed by the molecular structure. Taking the MC-[18] as an example, after one TSR transformation, the corresponding transformation is $\text{TSR}(L, 20^\circ, 10^\circ)$ or $\text{TSR}(L, 2\pi/18, \pi/18)$. So the TSR transformation of the MC-[18] can obtain a 36-order cyclic group:

$$\text{TSR}(\text{MC-[18]}) = \{\text{TSR}(L, 20^\circ, 10^\circ); j=0, 1, 2, \dots, 35\} \quad (1)$$

Atoms in a molecule possessing such symmetry may form a set composed of 36 symmetrical equivalent atoms through this

Fig.3 The 36-order symmetrical transformation group in the MC-[18] molecule and its possible atomic set

transformation, namely a symmetry adaptive (SA) atom set as shown in Fig.3. The rotation scope of α is 720° (4π). When changing $\Delta\beta$ into $-\Delta\beta$, we can get the similar symmetry adaptive atom set, and its structure is the enantiomer of that in Fig.3.

The s -AOs in the SA atom set can form the SALC-AOs for the $\{\text{TSR}(L, 20^\circ, 10^\circ)\}$ transformation. And the p -AOs component should be analyzed by adopting the tangential components of the torus coordinates (L, α, β) , namely p_L -, p_α -, and p_β -AOs. The character of the irreducible representation associated with the cyclic group can be obtained by using the general group theory.²² Moreover, all the SALC-AOs belonging to the same irreducible representation can be combined into the MOs, resulting in that they may belong to different SA-AO sets.²³⁻²⁵

3 Symmetry of Hückel [18]-cyclacene molecule

Before we compare the Hückel cyclacene with the Möbius cyclacene, they will be investigated separately. For the Hückel [18]-cyclacene (HC-[18]), its geometrical conformation can be seen from Fig.4, all the centers of the benzene rings can con-

Fig.4 Geometrical skeleton of the HC-[18] molecule and the cylindrical coordinate system

Hydrogen atoms are omitted for clarity.

nect to form a base circle without knot so that they are in the same cylindrical surface. This molecule is more suitable to adopt the cylindrical orthogonal curvilinear coordinate during symmetry analysis.²³ As for one atom P in the HC-[18], its cylindrical coordinates can be denoted as (Z, r, α) where $r=OO'$. In this cylindrical coordinates, the s -AO and p_z -AO of the LCAO-MO are the same as those in the Cartesian ones, but the p_x - and p_y -AO should be replaced by p_r - and p_α -AO which are the components of p -AO along the two orthogonal directions. That is to say, p_r - and p_α -AO are the components of p -AO along the surface normal and tangential directions (p_N - and p_T -AO) as shown in Fig.4.

HC-[18] molecule has D_{18h} point group symmetry and it is a 72-order group. The irreducible representations and characters of D_{18h} point group can be obtained following the ordinary method of group theory. The relevant SALC-AO of HC-[18] molecule can be dealt with by using general method of the group theory to identify their respective irreducible representations.²²

The various SALC-AOs may belong to the same irreducible representation of D_{18h} point group, so they can be further assembled into MOs. That is to say, this kind of irreducible representation of one MO belonging to D_{18h} point group is pure. Of course, we can also find out all the SALC-AO components of each MO by the method being used to analyze the full carbon ring molecule.²³ Some MOs contain a simple SALC-AO composition. For example, the frontier MOs in HC-[18] are the π -MOs mainly composed by the SALC- p_N -AO of valence shell of carbon atoms. The contribution of other SALC-AO will increase when the MOs are gradually away from the frontier MO. Sometimes, we are more interested in the symmetry of the HC-[18] molecule viewed through the cyclic group. The cyclic symmetry group for HC-[18] is the 18-order rotation point group C_{18} . It is the subgroup of D_{18h} point group, so that we can use the C_{18} to do a similar investigation.

4 Symmetry of Möbius [18]-cyclacene molecule

The molecule of Möbius [18]-cyclacene (MC-[18]) is formed by twisting the HC-[18] by 180° and its geometrical conformation can be seen from Fig.5. From Fig.5, the XY plane is placed on paper plane and the Z axis is perpendicular to the XY plane. The previously well accepted C_2 axis of MC-[18] is just the X -axis, and there is no existence for any other point symmetry in the MC-[18] molecule.

Though MC-[18] and HC-[18] molecules have the same molecular formula ($C_{72}H_{36}$), the symmetries of the two isomers are very different. MC-[18] has a 36-order cyclic group, i.e., TSR group (see the formula (1)). Obviously, the centers of all the benzene rings can be connected to form the base circle of the torus orthogonal curvilinear coordinates (seen in Fig.2). And according to this TSR group, there are three SA atom sets: 36 carbon atoms (C_a+C_b), 36 carbon atoms (C_b+C_c), and 36 hydro-

Fig.5 Geometrical skeleton of the MC-[18] molecule

Hydrogen atoms are omitted for clarity.

gen atoms. In each SA atom set, the atomic arrangement of the 36 atoms can be seen in Fig.3. The L coordinate values of different SA atom sets are different. Again, this cyclic group includes 36 group elements, i.e., 36 symmetrical transformation: $TSR(L, 20^\circ, 10^\circ)$; $j=0, 1, 2, \dots, 35$. When $j=0$, the symmetrical transformation is unit element (identity transformation). $TSR(L, 20^\circ, 10^\circ)$ is the inverse element of $TSR(L, 20^\circ, 10^\circ)^{36-j}$. Based on the general group theory about the cyclic group,²¹ we can obtain the characters of MC-[18] which is belonged to the 36-order cyclic group and the latter is isomorphic with the C_{36} point group. So, we can discuss their irreducible representations, and they will be similar to the double value representations of the group C_{18}^* .²⁶

As mentioned above, there are three SA atom sets in MC-[18] about the TSR group, for example the s -AO can compose symmetry adaptive atomic orbital (SA-AO) set. In each SA-AO set, there are 36 AOs and they can be linearly composed into 36 independent SALC-AOs. As for the p -AOs of carbon atom, any set of the 36 p_x -, p_y - or p_z -AOs can not produce SALC-AO just within itself. It needs to transform the p_x -, p_y -, and p_z -AOs into the p_L -, p_α -, and p_β -AOs, and transform their LCAO coefficients accordingly. This conversion relationship can be obtained from the vector transformation, that is from transforming the Cartesian coordinates (X, Y, Z) into the torus orthogonal curvilinear coordinates (L, α, β) as shown in Fig.2. Thus, each SA atom set, p_L -, p_α -, or p_β -AOs, can form its own SA-AO set, respectively. Then, from these SA-AO sets, SALC-AOs belonging to the same irreducible representation can be further combined into MOs. We can use the similar method as that in dealing with the HC-[18] to find out the SALC-AO components of the MO in MC-[18], but it should do in the torus orthogonal coordinates instead of the cylindrical orthogonal coordinates. For the MOs near the frontier MOs in MC-[18], they are composed by the SALC-AO belonging to the same irreducible representation from different SA-AO sets. These MOs are mostly formed from the p -AOs of carbon atom. However, the SALC of p_L -, p_α -, p_β -AO will all have a certain contribution, in which the contribution from p_L -AO is the somewhat more among them.

5 Symmetry of multi-twisted Möbius [18]-cycloacene molecule

Although the synthesis of Möbius strip-like cyclic compounds was succeeded just for the one by twisting the linear precursor one time (180°) so far, Möbius molecules with being twisted many times (especially the Möbius cycloacenes with two or three knots) have attracted more and more attention by molecular structure designers since the new millennium.¹⁴ From the view of topology, Möbius cycloacene with odd and even knots have different characteristics. Previous research on the symmetry of Möbius strip-like molecule is mainly based on the point symmetry, which may have some contrasts with the symmetry characteristic from the view of topology. The reason may be mainly due to the lack of the torus screw rotation (TSR) symmetry in the theory of point group. And, a symmetry group which contains the TSR and the point group symmetries at the same time can be called the torus group. For example, MC-[18] has both the TSR group symmetry and the C_2 point group symmetry; while M^cC-[18] has the relevant TSR group symmetry and the D_2 point group symmetry. A lot of works in this area need our further exploration.

6 Conclusions

In this paper, the symmetry characteristics of the Hückel [18]-cycloacene (HC-[18]) and Möbius [18]-cycloacene (MC-[18]) molecules are investigated and a new type of molecular symmetry group (torus group) is found in the Möbius molecule. For HC-[18] molecule, it has the D_{18h} point group symmetry, which contains a cyclic subgroup C_{18} . Usually, it can be discussed by the cylindrical coordinates and its MOs near the frontier MO are mainly consisted of the involved SALC-(p_N)-AO component.

In Möbius molecule, there exists the torus screw rotation (TSR) transformation, which is the combination of the rotation transformations around the center and the base circle, simultaneously. The TSR transformation group is Abel cyclic group and belongs to the torus group. For convenient, the torus orthogonal curvilinear coordinates are introduced and its characteristics and the correlation with the Cartesian coordinates are also briefly investigated. For MC-[18], it has the 36-order TSR symmetry, while it only has the C_2 symmetry based on the theory of point group. In addition, the MOs near the frontier MO mainly consist of the involved SALC-(p)-AO components. Note that the three components (p_σ , p_π , and p_τ -AO) may all be contained in these MOs, but the p_τ -AO component is somewhat more and the s -AO component is very tiny. For M^cC-[18] molecule, it has the 18-order TSR symmetry, while it has D_2 point group symmetry analyzed by the ordinary point symmetry.

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