

Molecular torus group

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Abstract Generally speaking, the highest symmetry of Möbius cyclacene molecule possesses the C_2 symmetry based on the theory of point group according to the previous works. However, based on the topology principle, the fundamental group of Möbius strip is an infinite continuous cyclic group and its border is made up of twice of the generator. Of course, the Möbius strip-like molecule is associated with a finite discrete cyclic symmetry group. For the cyclacene isomers constructed by several (n) benzene rings, these isomers include: the common cylinder Hückel cyclacene (HC- $[n]$) molecules, the Möbius cyclacene (MC- $[n]$) molecules by twisting the linear precursor one time (180°), and the multi-twisted Möbius strip-like cyclacene (M^m C- $[n]$) molecules by twisting the linear precursor m times ($m \times 180^\circ$). The relevant results suggest that in addition to the point symmetry, there is a new kind of symmetry called the torus screw rotation (denoted as TSR). In this article, we take the M^m C- $[n]$ molecules as examples to discuss their TSR group and point group symmetry, and the relative symmetry adaptive atom sets as well as their atomic orbital (AO) sets. Here, the Cartesian coordinates is not quite fit for the investigation of these AOs, so it is replaced by either the torus orthogonal curvilinear coordinates (for M^m C- $[n]$ molecule) or the cylinder orthogonal curvilinear coordinates (for HC- $[n]$ molecule). According to the features of cyclic group, the character table of the irreducible representation of the TSR group could be constructed easily. Some other relevant point-group symmetries maybe also belong to the molecule, so its symmetry maybe called as the torus group symmetry. For multi-twisted Möbius strip-like molecule, there are some correlations in topology characteristics.

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1 Introduction

In last century, for the research of the conjugated molecular system and its aromaticity, chemists began to investigate the characteristics of Möbius strip-like molecules. Theoretical studies mainly focused on the electron wave functions, topological structure [1,2], aromaticity, and the selection rule of pericyclic reaction of Möbius strip-like molecules [3,4]. However, reports on the synthesis of Möbius strip-like molecules are relative tardiness. In 1982, Walba and co-workers synthesized the first molecular Möbius strip via high-dilution cyclization of the tris-tetrahydroxy-methylethulene (THYME) diol ditosylate [5–7]. After entering the new millennium, Herges synthesized the stable Möbius strip-like molecules [8,9]. Because of the topology character of Möbius strip-like molecules and their possible applications in biomedical field, Möbius strip-like molecules attracted more and more attention, and great progresses have been made especially in the synthesis of Möbius strip-like molecules [6,8,9]. Recent years, many theoretical and experimental articles and reviews about Möbius strip-like molecules have been published [10–15].

Usually, the C_2 axis is considered to be the highest symmetry element of Möbius molecule with one knot. Based on the topology principle, the fundamental group of Möbius strip is an infinite continuous cyclic group and its border is made up of twice of the generator [16]. Of course, the Möbius strip-like molecule is described by a finite discrete cyclic symmetry group. This description indicates that further development of the molecular symmetry theory for these Möbius strip-like molecules is very necessary. When discussing molecular symmetry, we often look for help from the point group, while the space group (especially the cylinder group) is needed for the study of macromolecule [17]. However, when we study the symmetry of Möbius strip-like molecule, a kind of new symmetry was found by us, recently. The related results have been announced in the format of communication briefly [18]. But, there still some questions need to expatiate, such as the distribution of atomic orbital (AO) sets and the character table of irreducible representation in Möbius strip-like molecule. These aspects will be discussed in this paper detailedly.

Here, we take the linear [n]-polyacene molecule formed by [18]-benzene rings as an example to pursue the investigation. Its structure is shown in Fig. 1 (omitted the hydrogen atoms for clarity), and the carbon atoms at the same horizontal line are labeled by either $C_{a'}$, $C_{a'}$, $C_{b'}$, or C_b from the top to bottom, respectively. When the C atoms of the left and right ends overlap to form a spacial structure of [18]-polya-

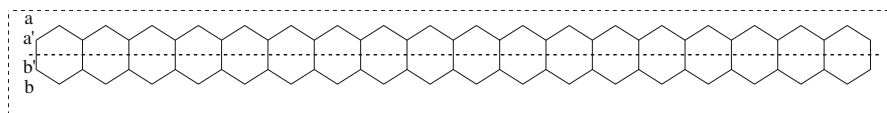


Fig. 1 Structure of linear [18]-polyacene molecule. ($C_{74}H_{40}$; The C-atoms at the same *horizontal line* are labeled by either a, a', b', or b from *top to bottom*, respectively. Hydrogen atoms are omitted for clarity)

cene ring, it can either be a Hückel [18]-cycloacene (denoted as HC-[18]) or a Möbius [18]-cycloacene (MC-[18]), after gluing the ends of the molecular plane together without or with twisting 180° of the molecular plane as shown in Fig. 1. We can also obtain Möbius cycloacene molecules with m knots ($m \geq 2$), denoted as $M^m\text{C}$ -[18], with twisting m times of 180° . Note that they have the same molecular formula $\text{C}_{72}\text{H}_{36}$.

Analyzed by the theory of point group, HC-[n] molecule possesses $4n$ -order D_{nh} symmetry, but the corresponding MC-[n] only has 2-order C_2 symmetry. HC-[n] has a finite n -order cyclic symmetry (C_n point group). By topology principle just mentioned, it can be expected that MC-[n] may have a finite $2n$ -order cyclic symmetry group and maybe not only limited to the C_2 point group. In this paper, we indeed find out a proper kind of $2n$ -order cyclic symmetry group, which does not belong to the point group and may be called the torus screw rotation (TSR) group.

2 Torus screw rotation and torus orthogonal curvilinear coordinates

2.1 The torus screw rotation

In this section, we introduce a new symmetry transformation, namely the TSR. As well-known, rotation of point group is operated by circling the object around a rotation axis which is through a fixed centre point. For a certain point in the 3-dimensional space, its image point after any transformation of point group will be fallen in a spherical surface. While the screw rotation of space group is operated by rotating the object around a fixed line (called screw axis) and accompanied with the translation movement along the screw axis [17]. The image of a certain point obtained by any a screw rotation transformation will then be fallen in a cylindrical surface around the screw axis. So, screw rotation is also known as cylinder screw rotation. However, the TSR transformation is operated by rotating the object around a fixed circle (called base circle, which is formed by the horizontal middle line dotted in Fig. 1 and represented by the biggest circle in Fig. 2a) 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 the same torus, it is then called torus screw rotation and denoted as TSR. Note that the cylindrical surface is an open surface, but the torus and spherical surface are closed with different homeomorphism. The topological characteristics of these surfaces are different. For Möbius strip-like molecules, they can keep invariant under a certain TSR, namely the **TSR** symmetry (Here, we use TSR denoting the torus screw rotation and **TSR** denoting the torus screw rotation symmetry group). When the base circle is reduced to a point (i.e. zero dimension), the TSR will turn into rotation of the point group and the related torus turn into a spherical surface. When the radius of the base circle is expanded to infinite (i.e. a one-dimensional line), the TSR will become the cylindrical screw rotation of space group and the related torus will turn into a cylinder. So, in general, the base circle of TSR is a finite-size circle. Of course, it should be noted that the torus herein is not in homeomorphous with neither the sphere of point group nor 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 [19]. If the movement of planet around star is

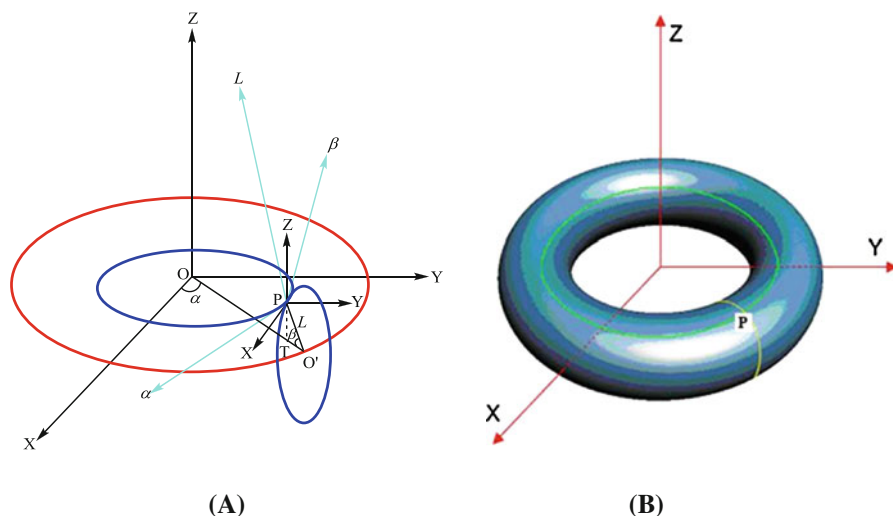


Fig. 2 Torus orthogonal curvilinear coordinate system

regarded as the ordinary rotation, the motion of satellite of the planet is corresponding to the TSR.

There are two kinds of revolving movement in the TSR: (1) rounding the center of basis circle with the longer revolving radius; (2) rounding the edge of basis circle with the shorter radius. The former is in connected with the intrinsic symmetric character of the glued skeleton structure of Fig. 1, and the latter with the Möbius strip-like symmetric character because it is glued after twisting the skeleton of Fig. 1. To construct an $M^m C-[n]$ structure, certain boundary conditions should be satisfied to make the carbon bonds between the overlap of the right and left sides of Fig. 1. So, these two kinds of rotations may be not completely independent with each other. That is, when the movement is circling the center of the basis circle once (360°), it should also accompany by circling the circumference of the basis circle along the twisted edge an integer (including zero) or half-integer times. If it is an integer (including zero) times twisting rotation, the C atoms of right and left sides in Fig. 1 are matched ($C_{a'}$ to $C_{a'}$, and $C_{b'}$ to $C_{b'}$) and to form the loop. Such system possesses an 18-order cyclic group. When the integral is zero, such system is Hückel [18]-cyclacene (HC-[18]). If it is a half-integral times twist rotation, the C atoms of right and left sides in Fig. 1 are overlapped by cross-link ($C_{a'}$ to $C_{b'}$; $C_{b'}$ to $C_{a'}$) and to form the Möbius strip. Such system possesses a 36 order cyclic group (**TSR**). When this half-integral is $1/2$, such system is Möbius [18]-cyclacene (MC-[18]). For these systems, though the order of the associated symmetry group may be bigger, we mainly focus on the latter here. The twisting (either integral or half-integral times) may be clockwise or anticlockwise and could be labeled as positive or negative, respectively. Twisting the same times but along different directions, the pair molecules obtained ought to be the optical enantiomers with each other. The torus groups contain not only the **TSR** cyclic groups but also some other point groups.

2.2 The torus curvilinear coordinates

For Möbius strip-like molecules, using the Cartesian coordinates to deal with the TSR is inconvenient. We need to introduce the torus orthogonal curvilinear coordinates. As shown in Fig. 2a, point O is the origin of the XYZ Cartesian coordinates. The base circle (the biggest circle in Fig. 2a) is drawn in the XY plane and its radius is R (OO'). For an arbitrary point P (e.g. the position of a certain atom) in the 3D Cartesian coordinates with the coordinate values (X, Y, Z), its corresponding torus orthogonal coordinate values (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 extending 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 XO'O' and PO'O, respectively. Because the surface defined by such a constant L-coordinate value in such a coordinate system is a torus, it is called torus orthogonal coordinates. For any point P (the position of a certain atom) in the 3D space, three torus coordinate surfaces will be orthogonal in the P-neighborhood with each other. Similarly, in the P-neighborhood the torus coordinate curves will be orthogonal with each other, too. So the torus coordinates (L, α , β) ought to be an orthogonal coordinate system.

As for a certain point P (denoting an atom), its Cartesian coordinate values (X, Y, Z) are adopted by the Gaussian software. When using the torus orthogonal curvilinear coordinates, it is unchanged for s-AO, but the p-AOs will be changed to p_L -, p_α -, p_β -AOs from p_X -, p_Y -, p_Z -AOs. Where p_L -, p_α -, p_β -AOs are the tangential direction (l, a, b) components of atom orbital in connection with the torus orthogonal curvilinear coordinates (L, α , β) curves, respectively. The LCAO coefficients of p_L -, p_α -, p_β -AOs can be transformed from that of p_x -, p_y -, p_z -(or p_X -, p_Y -, p_Z -)AOs by means of the coordinate system rotational transformation (from x, y, z system to L, α , β system) relationship.

2.3 The torus screw rotation symmetry

The TSR, is a symmetrical operation that rotates the object around both the base circle centre (Z axis) and the circumference of base circle simultaneously. Surely, the coordinate values of α and β change, while the value of L is unchanged in such transformation. So after the TSR, the image point must be kept on the torus surface with the fixed value L. For example, point P(L, α , β) after the TSR, its image point is P'(L, α' , β') with the L value unchanged. Such a transformation is denoted as: TSR (L, $\Delta\alpha$, $\Delta\beta$), where:

$$\Delta\alpha = \alpha' - \alpha \quad \text{and} \quad \Delta\beta = \beta' - \beta \quad (1)$$

Usually, point P denotes a certain atom, so its image point P' should be another atom which is the same as P. Generally, after certain times of transformations, we can expect that the image will reach the source P. This is a necessary condition to determine whether there is a symmetrical transformation in a molecule. Therefore,

the variations $\Delta\alpha$ and $\Delta\beta$ caused by TSR are related to each other and governed by the molecular structure. On one hand, a complete α rotation is the sum of steps with $\Delta\alpha = 2\pi/n$ per time. On the other hand, the companion β rotation will be $n\Delta\beta = m\pi$ through n times such TSR, where m must be the integral number. So we can obtain:

$$\Delta\alpha = 2\pi \quad \text{and} \quad \Delta\beta = m\pi/n \quad (2)$$

Then

$$\Delta\alpha/\Delta\beta = 2/m \quad (3)$$

Where, m corresponds also to the times of twist along the horizontal direction in Fig. 1. For the even number m , when α angle rotates with 2π , the atom P will be return to the original position. However, for the odd number m , when α angle rotates with 2π , the atom P can not be return to its original position, and only when α angle rotates with 4π , the atom P can return to its original position. Of course, n is independent with the times of twist, and it is one of the intrinsic characters of such molecules.

Taking the molecule MC-[18] as an example: where $n = 18$ and $\Delta\alpha = 2\pi/18$ or $\Delta\alpha = 20^\circ$, while $m = 1$ and $\Delta\beta = \pi/18$ or 10° , the corresponding transformation is:

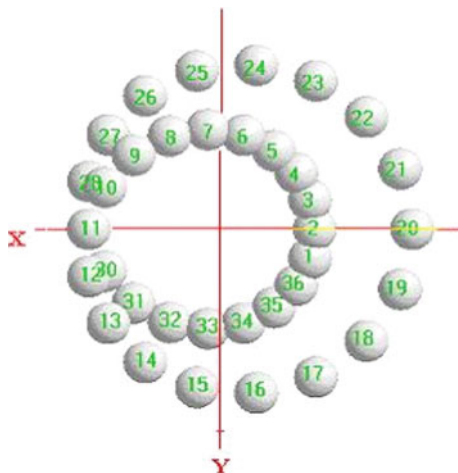
$$\{\text{TSR}(\text{L}, \Delta\alpha, \Delta\beta)\} = \{\text{TSR}(\text{L}, 20^\circ, 10^\circ)\} \quad (4)$$

So the TSR of the MC-[18] can yield a 36-order cyclic group:

$$\mathbf{TSR} = \{[\text{TSR}(\text{L}, \Delta\alpha, \Delta\beta)]^j; j = 0, 1, 2, \dots, 35\} \quad (5)$$

Atoms in a molecule possessing such symmetry may form a set composed of 36 symmetrically equivalent atoms through this transformation, namely a symmetry adaptive (SA) atom set as shown in Fig. 3. The interval of rotation α is $720^\circ (4\pi)$.

Fig. 3 MC-[18] molecule belongs to the 36-order **TSR** group and its possible SA-atomic set. For various SA-atom set, the Z-axis and XY plane are the same, but the directions of the X-, Y-axes and the L-value may be somewhat varying



In addition, when replace $\Delta\beta$ by $-\Delta\beta$, we can get a similar SA atom set, and it constructs the enantiomer of that in Fig. 3. The relative **TSR** group will also be with 36-order.

The s-AOs in the SA atom set can form the SALC-AOs about the $\{\text{TSR}(L, 20^\circ, 10^\circ)\}$ transformation. The p-AOs can not conveniently be analyzed by using the Cartesian coordinates, but can be done by using the torus coordinates. The p-AOs component (p_x -, p_y -, p_z -AOs) should be replaced and analyzed by the tangential components of the torus coordinates (l, a, b), namely the p_L -, p_α -, and p_β -AOs. For the 36 atoms in Fig. 3, by using only one of the p_x -AOs, p_y -AOs or p_z -AOs, we can not construct the SALC-AOs for such **TSR** group. However, by using one of the p_L -AOs, p_α -AOs or p_β -AOs, we can do so. All the SALC-AOs belonging to the same irreducible representation can be combined into one MO. The irreducible representation of such MO may be pure but including different components of SA-AO sets.

3 Symmetry of Hückel and Möbius [18]-cycloacene molecule

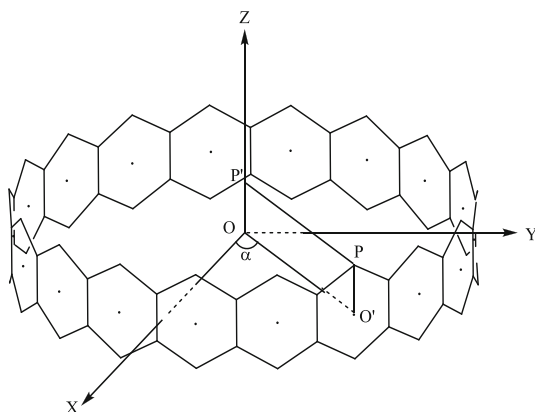
3.1 Symmetry of Hückel-[18]-cycloacene molecule

For comparison, before we investigate the Möbius-molecule, we primarily consider the Hückel-molecule, HC-[18], the cylindrical orthogonal curvilinear coordinates will be applied.

3.1.1 The HC-[18] molecule in the cylindrical orthogonal curvilinear coordinates

For the HC-[18], its geometrical conformation can be seen from Fig. 4, where the Cartesian coordinate system is consistent with the requirement of Gaussian program. In Fig. 4, all the centers of the benzene rings can be connected to form the base circle, and all atoms are almost in the same cylindrical surface. If the torus orthogonal curvilinear coordinates is considered, the β -coordinate ought to keep the constant (90° or $\pi/2$), the L-coordinate is the same as that of the Z-axis, and the α -coordinate may

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



take any value in the whole 360° range. According to the cylindrical orthogonal curvilinear coordinates, the atom P in the HC-[18] can be denoted as (Z, r, α) shown in Fig. 4. The foot O' of the perpendicular line PO' ought to be on the base circle, the Z-coordinate value of P point will be the length of the PO' segment, the value of r is the length of OO' segment which approximately equals to the radius of the base circle, and the value of α is the XOO' angle. In such cylindrical coordinates, the s-AO and p_Z -AO of the LCAO-MO are the same as 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 cylindrical coordinate surface normal and tangential directions (p_N - and p_T -AO), respectively.

3.1.2 Symmetries of HC-[18] molecule by the point groups D_{18h} and C_{18}

HC-[18] molecule has D_{18h} point group symmetry which is a 72-order group. The irreducible representations and characters of D_{18h} point group can be obtained by the ordinary method of group theory. There are 72 symmetry transformations as the elements of the group:

$$\hat{E}, 2 \hat{C}_{18}^j (j=1, 2, \dots, 8), \hat{C}_2, 9 \hat{C}'_2, 9 \hat{C}''_2, \hat{P}, 2 \hat{S}_{18}^j (j=1, 2, \dots, 8), \hat{M}_h, 9 \hat{M}_d, 9 \hat{M}_v$$

The relative irreducible representations are provided with 8 one-dimensional (1D) and 16 two-dimensional (2D) representations as follows:

$$\begin{aligned} \text{1D: } & A_{1g}, A_{2g}, B_{1g}, B_{2g}, A_{1u}, A_{2u}, B_{1u}, B_{2u} \\ \text{2D: } & E_{\rho g}, E_{\rho u} (\rho = 1, 2, \dots, 8) \end{aligned}$$

Now let's analyze the HC-[18] molecule ($C_{72}H_{36}$) by D_{18h} point group. The atoms included in HC-[18] can be classified as follows (see Fig. 1): the C-set (contains the C_a and C_b atoms), the C'-set (contains $C_{a'}$ and $C_{b'}$ atoms) and the H-set (contains the all hydrogen atoms). All these three sets are the symmetry adapted (SA) atom sets for the D_{18h} point group, and each contains 36 atoms. Where, each SA-atom set constructs two circles each formed by 18 atoms distributed around the same 18-fold rotation axis of a cylinder. For the above three sets, the associated cylinders maybe very close to each other, however, they are not completely identical.

On the other hand, one atom may contain several AOs, so there are more SA-AO sets. Each SA-AO set may construct 36 SALC-AOs, which may be obtained by means of the common group theory method, and the relative irreducible representations may also be obtained. For the s-, p_Z - and p_N -AO of C atoms (C_a and C_b in Fig. 1) and the s-AO of H atoms, there are 36 SALC-AOs included in each kind of AO, the relative representation is as follows:

$$\begin{aligned} \Gamma(1) = & A_{1g} \oplus B_{2g} \oplus A_{2u} \oplus B_{1u} \oplus E_{1g} \oplus E_{2g} \oplus E_{3g} \oplus E_{4g} \oplus E_{5g} \oplus E_{6g} \oplus E_{7g} \oplus E_{8g} \\ & \oplus E_{1u} \oplus E_{2u} \oplus E_{3u} \oplus E_{4u} \oplus E_{5u} \oplus E_{6u} \oplus E_{7u} \oplus E_{8u} \end{aligned} \quad (6-1)$$

For p_T -AO of C-carbon atoms (C_a and C_b in Fig. 1), which include 36 SALC-AOs, the relative representation is as follows:

$$\Gamma(2) = A_{2g} \oplus B_{1g} \oplus A_{1u} \oplus B_{2u} \oplus E_{1g} \oplus E_{2g} \oplus E_{3g} \oplus E_{4g} \oplus E_{5g} \oplus E_{6g} \oplus E_{7g} \oplus E_{8g} \\ \oplus E_{1u} \oplus E_{2u} \oplus E_{3u} \oplus E_{4u} \oplus E_{5u} \oplus E_{6u} \oplus E_{7u} \oplus E_{8u} \quad (6-2)$$

For s -, p_Z -, p_N -AO of C' -carbon atoms ($C_{a'}$ and $C_{b'}$ in Fig. 1), there are 36 SALC-AOs in each kind of AO, the relative representation is as follows:

$$\Gamma(3) = A_{1g} \oplus B_{1g} \oplus A_{2u} \oplus B_{2u} \oplus E_{1g} \oplus E_{2g} \oplus E_{3g} \oplus E_{4g} \oplus E_{5g} \oplus E_{6g} \oplus E_{7g} \oplus E_{8g} \\ \oplus E_{1u} \oplus E_{2u} \oplus E_{3u} \oplus E_{4u} \oplus E_{5u} \oplus E_{6u} \oplus E_{7u} \oplus E_{8u} \quad (6-3)$$

For p_T -AO of C' -carbon atoms ($C_{a'}$ and $C_{b'}$ in Fig. 1), which include 36 SALC-AOs, the relative representation is as follows:

$$\Gamma(4) = A_{2g} \oplus B_{2g} \oplus A_{1u} \oplus B_{1u} \oplus E_{1g} \oplus E_{2g} \oplus E_{3g} \oplus E_{4g} \oplus E_{5g} \oplus E_{6g} \oplus E_{7g} \oplus E_{8g} \\ \oplus E_{1u} \oplus E_{2u} \oplus E_{3u} \oplus E_{4u} \oplus E_{5u} \oplus E_{6u} \oplus E_{7u} \oplus E_{8u} \quad (6-4)$$

Here we use the cylinder orthogonal curvilinear coordinates, so the p_x - and p_y -AO are replaced by p_N - and p_T -AO. Because, the SALC-AO can not be constructed by p_x - or p_y -AO alone. In addition, we can see that the 16 2D irreducible representations are all included in the formulas (6-1)–(6-4), while only 4 of the 8 1D irreducible representations are included in one of these formulas, but each kind of the 1D irreducible representation may be in various SALC-AO sets. Although one MO can belong to a pure irreducible representation, it may include various SA-AO set components. According to the LCAO-MO theory, a MO- Ψ_η can be denoted as:

$$\Psi_\eta = \sum_J \sum_i a_\eta(J, i) \phi(J, i) \quad (7-1)$$

where the $\phi(J, i)$ is the i -th AO of atom J , and the LCAO coefficient related to the AO $\phi(J, i)$ in MO- Ψ_η will be the $a_\eta(J, i)$. Now we replace the sum for atom (J) and the AO (i) in atom by the sum for SA-AO set and the AO in SA-AO set, and the Eq. (7-1) will be:

$$\Psi_\eta = \sum_\vartheta \sum_i a_\eta(\vartheta, i) \phi(\vartheta, i) \quad (7-2)$$

where the $\phi(\vartheta, i)$ is the i -th AO of ϑ -th SA-AO set, and its corresponding LCAO coefficient in MO- Ψ_η is $a_\eta(\vartheta, i)$. In MO- Ψ_η , the composition of ϑ' -th SA-AO set is:

$$X_\eta(\vartheta') = \sum_i a_\eta(\vartheta', i) a_\eta^*(\vartheta', i) \Big/ \sum_\vartheta \sum_i a_\eta(\vartheta, i) a_\eta^*(\vartheta, i) \quad (8)$$

where a and a^* are the complex conjugate numbers with each other. If involving several SA-AO sets (ϑ'), the sum for relevant SA-AO sets would be necessary and we can obtain it by changing the numerator of formula (8).

However, we are more interested in the symmetry of the cyclic group. In HC-[18], the relevant cyclic group is the 18-order rotation point group, C_{18} , which is the sub-group of D_{18h} . By using the real representation, there are two 1D and eight 2D representations. In HC-[18] molecule, there are 36 H atoms and 72 C atoms. According to point group C_{18} , there are six SA-atom sets: four SA C-atom sets (each set including 18 C atoms) and two SA H-atom sets (each set including 18 H atoms). The s -, p_z -, p_N - and p_T -AOs of these atoms will combine to form the SA-AO set composing of 18 AOs, respectively. It should be pointed out that we must use the cylindrical orthogonal curvilinear coordinates instead of the Cartesian coordinates. These SA-AO sets can construct the relevant SALC-AOs, and further combine them into the SALC-AO MOs. For all these SA-AO sets in HC-[18] molecule, the representations of these SALC-AO MOs can be denoted as:

$$\Gamma = A \oplus B \oplus E_1 \oplus E_2 \oplus E_3 \oplus E_4 \oplus E_5 \oplus E_6 \oplus E_7 \oplus E_8 \quad (9)$$

It is the same for all these SA-AO sets no matter that they combine to form σ - or π -MO. For example, the π -MOs are composed mainly by the SALC- p_N -AO, while the σ -MOs are composed mainly by the other SALC-AOs.

3.1.3 The symmetry character of MO in HC-[18]

The molecular formula of HC-[18] is $C_{72}H_{36}$. There are 108 atoms calculated by the Gaussian program at the STO3G/HF level. The MO serial number (J) is defined according to the order of the size of the energy gap between the MO and the frontier MO, and it is negative for OMO and the positive for VMO. Each of these MOs would belong to a certain pure irreducible representation of the D_{18h} point group [20], however the Gaussian calculation program sometime does not provide the direct result for the all MOs in connection to D_{18h} . But by means of projection operator [20] or the fuzzy symmetry theorem [21], we could get the various irreducible representation components of D_{18h} for each MO. The results suggest that each MO approximately belongs to a pure irreducible representation of the D_{18h} point group. However, such MO with pure irreducible representation may include various SA-AO set components, which can obtained by using Eq. (8). As shown in Fig. 5b, it exhibits the MOs near the frontier MO, which are the π -MOs and are composed by SALC $2p_N$ -AO set of C atoms. The other SALC-AO sets will be mainly combined to compose the σ -MOs, but the π -MOs far away the frontier MO may include other SALC-AO components and are not composed by pure SALC $2p_N$ -AO.

For the π -MOs near the nonbonding energy level, they possess almost pure SALC-AO and their irreducible representations are almost pure too. The calculated HOMO of HC-[18] molecule is shown in Fig. 6.

3.2 Symmetry of Möbius-[18]-cyclacene molecule

The Möbius-[18]-cyclacene (MC-[18]) molecule can be obtained by twisting the HC-[18] molecule by 180° . Discussing the Möbius molecule usually involves the TSR symmetry and needs the torus orthogonal curvilinear coordinate system.

Fig. 5 The SALC-AO components of the near frontier MOs in HC-[18] (at the STO3G/HF level)

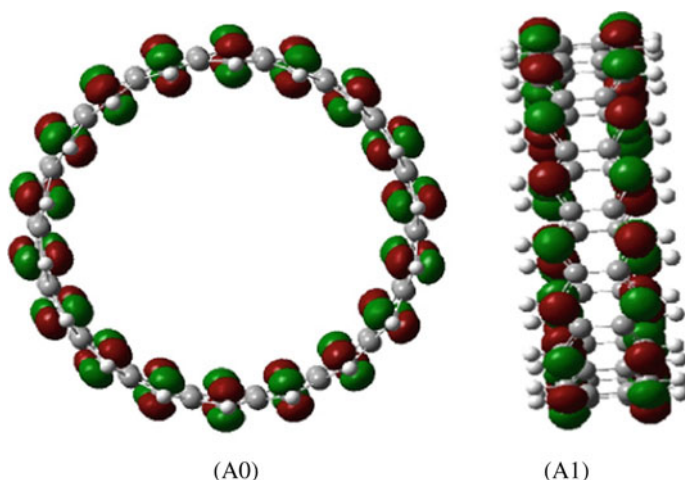
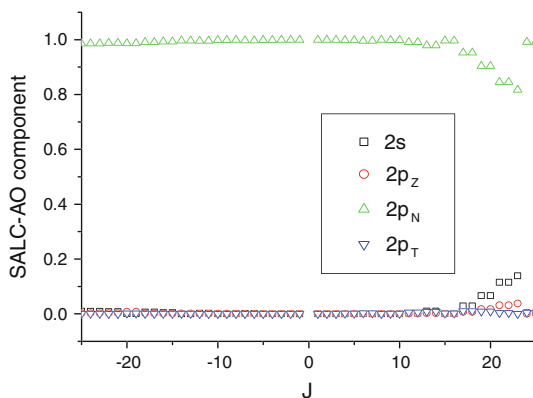


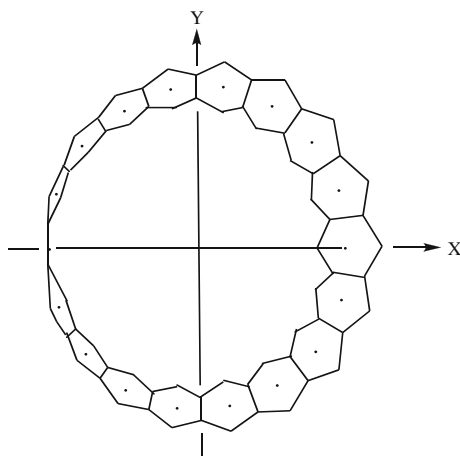
Fig. 6 The view of HOMO of HC-[18] (at STO3G/HF level). **A0** Near top view, **A1** near side view

3.2.1 The MC-[18] molecule and torus orthogonal curvilinear coordinates

The geometric skeleton of MC-[18] molecule is formed by cutting and twisting the [18]-polyanene molecule (see Fig. 1) by 180° and gluing its two ends to form the cycle as shown in Fig. 7. Here the atomic distances are taken the same as that of the optimized HC-[18] molecule.

As shown in Fig. 7, the tiny dot in the centre of benzene rings may be linked to form the base circle. The XY plane is placed on the paper plane and the Z-axis is perpendicular to the XY plane. The X-axis is passing through two C and two H atoms of the MC-[18] molecule's right side, and is perpendicularly passing through the center of the benzene ring at the left side of MC-[18] molecule. The previously research has well accepted that the C_2 axis of MC-[18] is just the X-axis without any other point symmetry.

Fig. 7 Geometrical skeleton of the MC-[18]



The molecular formula of MC-[18] and HC-[18] are the same, $C_{72}H_{36}$, but the symmetry of the two isomers would be very different. According to the point group theory, HC-[18] possesses the symmetry of D_{18h} point group, but MC-[18] only has C_2 point group. On the other hand, as we have pointed out, MC-[18] should possess the symmetry of 36-order cyclic group, **TSR**, as shown in Eq. (5), and the torus orthogonal curvilinear coordinates is prior for the investigation. In this coordinate system, the **TSR** elements in MC-[18] molecules are as follows: $\{\text{TSR}(L, 20^\circ, 10^\circ)\}^j$; $j = 0, 1, 2, \dots, 35$. In this **TSR** group, there are three SA-atom sets in the MC-[18] molecule: 36 C ($C_a + C_b$) atoms, 36 C' ($C_{a'} + C_{b'}$) atoms and 36 H atoms, respectively. Any atom in MC-[18] molecule under the $\{\text{TSR}(L, 20^\circ, 10^\circ)\}^j$ can find another identical atom belonged to the same SA-atom set in the proper location. The L-coordinate values of the atoms in identical SA-atom set are the same. The 36 atoms in various SA-atom sets are all arranged in the way shown in Fig. 3. The XY planes of different SA-atom sets would be parallel with each other, but the L-coordinate values of the atoms in various SA-atom set may be somewhat different.

3.2.2 The MC-[18] molecule with the TSR symmetry

First of all, we analyze the **TSR** symmetry of MC-[18] molecule, which is a 36-order cyclic group, **TSR**(18/1). There are 36 group elements (the symmetry transformations): **TSR**(18/1; j) ($j = 0, 1, 2, \dots, 35$). Here the group element is **TSR**: **TSR**(18/1; j) = **TSR**(L, $20j^\circ$, $10j^\circ$), where the '18' in bracket denotes the inherent order of the rotation without the twisted states, and the '1' following the '/' denotes the twist time (i.e. 180° for each time). As $j = 0$, **TSR**(18/1; 0) is the unit element. The **TSR**(18/1; j) and **TSR**(18/1; $36-j$) are the inverse elements with each other. According to the ordinary group theory [20], the character table of 36-order **TSR** cyclic group in MC-[18] molecule is isomorphism with that of the C_{36} point group. The character table of the related complex representation is shown in Table 1, similarly. Where, the E_ρ stands for two conjugate 1D complex representations, or one 2D real representation

Table 1 The table of character for 36-order **TSR** cyclic group

Irreducible representation	Symmetry transformation			
	TSR(18/1;0)	TSR(18/1; <i>j</i>)	TSR(18/1;18)	TSR(18/1; <i>j</i>)
	<i>j</i> = 0	<i>j</i> = 1, 2, ..., 17	<i>j</i> = 18	<i>j</i> = 19, 20, ..., 35
A	1	1	1	1
B	1	(−1) ^{<i>j</i>}	−1	(−1) ^{<i>j</i>}
E _ρ (ρ = 1–17)	1	e ^{ρ<i>j</i>} = exp(2πρ <i>ji</i> /36)	(−1) ^ρ	e ^{ρ<i>j</i>} = exp(2πρ <i>ji</i> /36)
	1	e ^{−ρ<i>j</i>} = exp(−2πρ <i>ji</i> /36)	(−1) ^ρ	e ^{−ρ<i>j</i>} = exp(−2πρ <i>ji</i> /36)

by combining the two above. As shown in Table 1, there are thirty-six 1D (complex) representations; meanwhile they may be treated as the real representations including two 1D and seventeen 2D representations.

There are three SA-atom sets in the MC-[18] molecule of the **TSR** symmetry group. The s-AOs of these atoms may compose the related SA-AOs set, and each set includes 36 s-AOs. These s-AOs can be linear combined to form 36 independent SALC-AOs, and the representations associated with this **TSR** group are as follows:

$$\Gamma = A \oplus B \oplus E_1 \oplus E_2 \oplus E_3 \oplus E_4 \oplus E_5 \oplus E_6 \oplus E_7 \oplus E_8 \oplus E_9 \\ \oplus E_{10} \oplus E_{11} \oplus E_{12} \oplus E_{13} \oplus E_{14} \oplus E_{15} \oplus E_{16} \oplus E_{17} \quad (10)$$

Because the form of p_X-, p_Y- or p_Z-AOs as adopted in Gaussian software can not conveniently compose the SALC-AO for MC-[18], it is necessary that the p-AOs and sequentially the LCAO-coefficients of p_X-, p_Y-, p_Z-AOs are transformed to p_L-, p_α-, p_β-AOs of the torus orthogonal curvilinear coordinates. Such transformation relationship can be obtained by means of the vector rotation transformation relationship between the (*x*, *y*, *z*)- and the (*l*, *a*, *b*)-coordinates (see Fig. 2a). The p_L-, p_α-, p_β-AOs of each SA-atom set may be grouped to form their own SA-AO set, respectively. And every SA-AO set can be linear combined to form 36 independent SALC-AOs, which belong to the representation of **TSR** group (see Table 1) and can be denoted as Eq. (10). The SALC-AOs belonging to the same irreducible representation (but including various SA-AO sets) can further combine to form the SALC-MO. Calculated by Gaussian program at STO-3G/HF level, for the MC-[18] molecule, the geometrical data in the Cartesian coordinates have been calculated with the single point (SP) method and transferred into the torus orthogonal curvilinear coordinates for further analyzing the symmetry of MO in MC-[18]. Similar as the method in Sect. 3.1.3, the various SALC-AO components of the near front MO in MC-[18] can be obtained, and the related results are shown in Fig. 8.

Note that for any given MO (namely, *J* value is fixed), a pure irreducible representation will be associated, but it may include various SALC-AO components. As shown in Fig. 8, for MOs near the frontier MO in MC-[18], they are mainly composed by the p-AOs of C atoms, and the all components of the SALC-p_L-, p_α-, and p_β-AO, have some contribution, but the SALC-p_L-AO contributes a little more.

Fig. 8 The SALC-AO components of the near front MOs included in MC-[18] (at the STO3G/HF level)

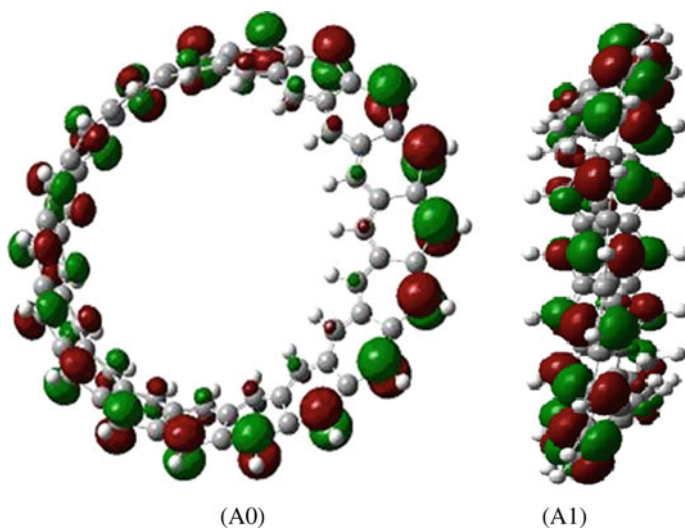
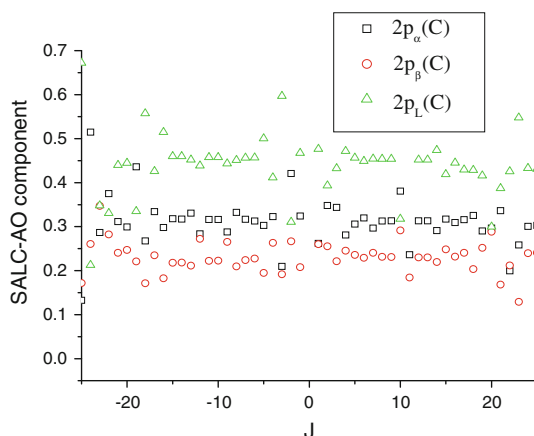


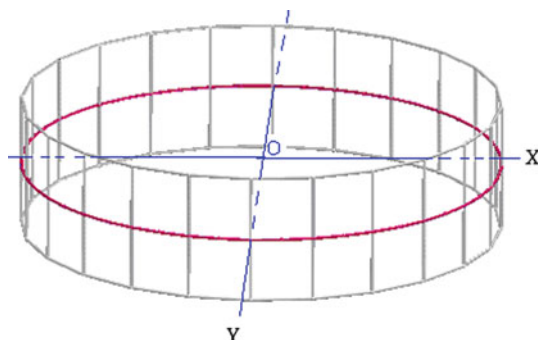
Fig. 9 The view of HOMO of MC-[18] (at STO3G/HF level): **A0** near *top view*, **A1** near *side view*

As mentioned above, based on Gaussian program and the fuzzy symmetry method [21], we can get all the MOs in MC-[18] and their representations ought to be all pure as shown in Table 1. In Fig. 9, it shows the HOMO of MC-[18] molecule as regards the TSR symmetry.

4 Symmetry of multi-twisted Möbius cyclacene molecule

Although the synthesis of Möbius strip-like cyclic compounds was succeeded only for twisted the linear precursor one time (180°) so far, Möbius molecules with twisting many times (especially the Möbius cyclacenes with two or three knots) [14] have attracted more and more attention by molecular structure designers since the new

Fig. 10 The diagram and symmetry of Hückel-cylindrical band



millennium. Previous research on the symmetry of Möbius strip-like molecule is mainly based on the point symmetry, which may have some contrast with the symmetry characteristics from the view of topology. The reason may be mainly due to the ignoring of the TSR symmetry. A symmetry group which contains the **TSR** and the point group symmetries meanwhile, called the torus group.

For the molecules having the symmetry of torus group, the torus orthogonal curvilinear coordinate system should be introduced. For example, MC-[18] has both the **TSR** symmetry and the C_2 point group symmetry; while M^2C -[18] has the relevant **TSR** symmetry and the D_2 point group symmetry. For analyzing such kind of molecules, we need to start with investigating the point symmetry characteristics of the multi-twisted Möbius strip band.

4.1 Symmetry of multi-twisted Möbius strip band

When the polyacene molecule as shown in Fig. 1 is glued between its right and left sides directly, it will form the Hückel-cyclacene molecule HC-[18] as shown in Fig. 10. And if twisted one time before glued, it will form the Möbius-cyclance molecule MC-[18]. It should be noted here that for the cyclacene molecule including $n(0)$ benzene-rings with $n(t)$ times twisted Möbius molecule, we denote it as $M^{n(t)}C$ -[$n(0)$]. Thus, the multi- $n(t)$ -twisted isomers can be denoted as $M^{n(t)}C$ -[18].

Such geometric surface (in Fig. 10) ought to possess the symmetry of point group $D_{\infty h}$, when $\lim n(0) \rightarrow \infty$ (infinite):

$$D_{n(0)h} \rightarrow D_{\infty h} = D_{\infty} \otimes C_s. \quad (11)$$

The key character of geometry of this cylinder surface is its upper and lower boundary circles, which are symmetric distributed about the base circle (the mid circle in Fig. 10), exhibiting the C_s symmetry of the surface. The axis vertical to the base circle and through the centre (O) is the rotation principal axis of the point group C_{∞} . The straight lines containing the diameter of base circle and vertical to the principal axis are all two-fold rotation axes. These two-fold axes and the principal axis form the D_{∞} symmetry of two boundary circles of the side of the cylinder. Where the C_{∞} rotation group is an infinite-order cyclic group, and the order of D_{∞} point group ought to be

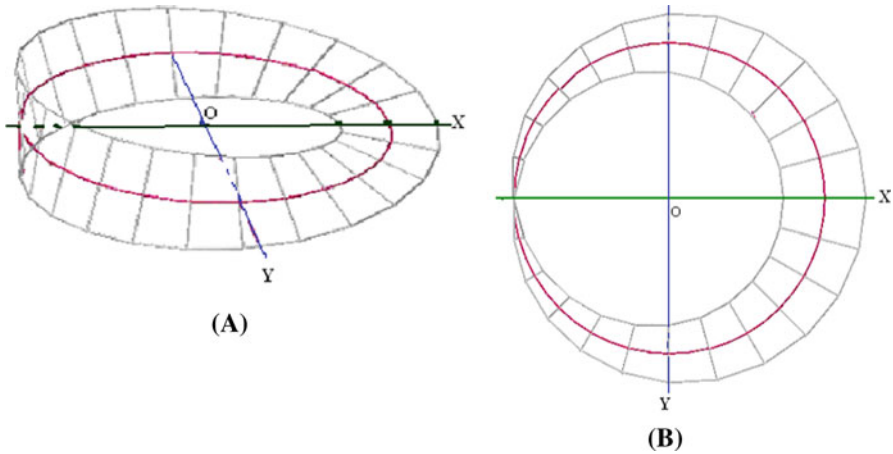


Fig. 11 The diagram and symmetry of Möbius-strip band. **a** *Oblique view to the base circle.* **b** *Top view to the base circle*

twice of C_∞ rotation group, but D_∞ is not a cyclic group. The order of $D_{\infty h}$ point group is quadruple of that of C_∞ rotation group, and $D_{\infty h}$ is also not a cyclic group.

The Möbius strip band can be formed by cutting, twisting and gluing the cylinder side once as shown in Fig. 11, and it only possesses the C_2 symmetry of the point group with the OX axis as the relevant two-fold axis.

It should be pointed out that the base circle of the produced Möbius strip-band is the same as that of the Hückel-cylindrical band. The Hückel-cylindrical band includes two boundary circles which separate the surface into the inner and outer two surfaces. However, the Möbius strip-band includes only one boundary and one surface without being separated, and this surface possesses only the symmetry of the point group C_2 . However, based on the topology principle [16], the fundamental group of Möbius strip is an infinite continuous cyclic group and its border is made up of twice of the generator of the common cyclic group. Such cyclic group may be characterized with the border of Möbius strip-band (see Fig. 11a, b), and such cyclic group is a TSR transformation group:

$$\mathbf{TSR}(n(0)/1; j) = \{\mathbf{TSR}(L, 2\gamma, \gamma)\}^j = \{\mathbf{TSR}(L, 2j\gamma, j\gamma); 2j\gamma \subseteq (0, 2\pi)\} \tag{12}$$

where $\lim \gamma \rightarrow 0$ is equivalent to $\lim n(0) \rightarrow \infty$. When $j = \pi/\gamma$, we have $\mathbf{TSR}(L, 2j\gamma, j\gamma) = \mathbf{TSR}(L, 2\pi, \pi)$, but it is not the identity transformation; only when $j = 2\pi/\gamma$, we have $\mathbf{TSR}(L, 2j\gamma, j\gamma) = \mathbf{TSR}(L, 4\pi, 2\pi) = \mathbf{TSR}(L, 2\pi, 2\pi)$, and it is the identity transformation indeed. Such TSR transformation group is a cyclic group, and its order will be the twice of the $C_{n(0)}$ (or $\lim_{n(0) \rightarrow \infty} C_{n(0)} \rightarrow C_\infty$) rotation group. The symmetry of such surface belongs to the torus group: $C_2(\text{OX}) \otimes \mathbf{TSR}(n(0)/1; j)$. Where OX denotes the two-fold axis C_2 being in OX direction. The order of such torus group is quadruple of the $C_{n(0)}$ rotation group, but is not a cyclic group. The key geometrical character of Möbius strip-band is that it only has one border line.

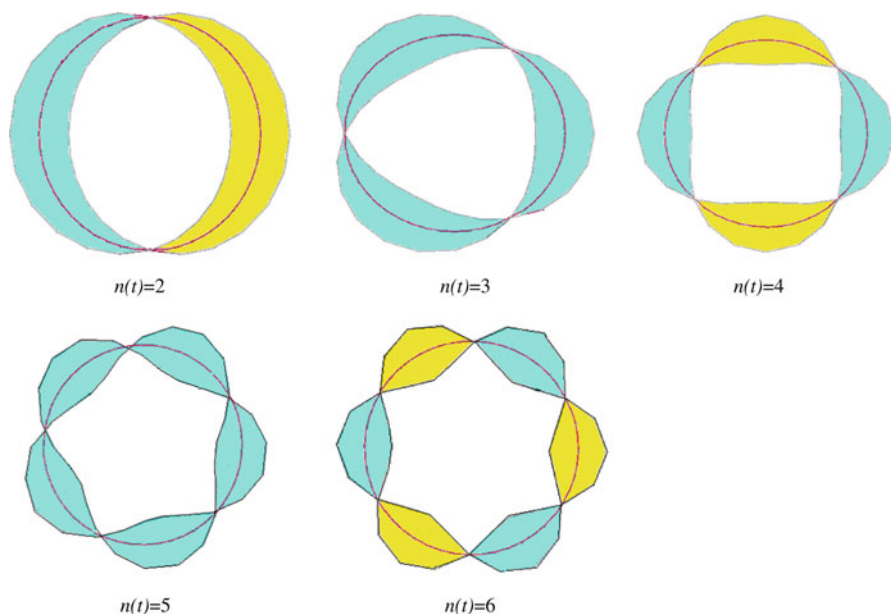


Fig. 12 The multi($n(t) = 2$ –6)-twisted Möbius-strip band, top view to base circle

As shown in Figs. 10 and 11, the base circles of Hückel- and Möbius-bands are the same. For Hückel-band, all the straight lines which contain the diameter of base circle are the 2-fold axes and the plane contain the whole base circle is a symmetry mirror. For the Möbius-band, there is only one 2-fold axis, i.e. the OX axis. As for the OZ axis which is vertical to the base circle, it is the C_1 rotation axis for Hückel-band and the C_1 (no symmetry) axis for Möbius-band. Although the base circle still exists in the Möbius-band, it is no longer a mirror and there is only one 2-fold axis through a particular diameter of the base circle.

Similarly, we may analyze other multi-twisted Möbius-strip band. As shown in Fig. 12, it shows the top view of the base circles with the twisted $n(t) = 2$ –6. When $n(t)$ is odd integer, there are only one continuous surface and one curve (including knots) border in the Möbius strip band. When $n(t)$ is even integer, there are two discrete surfaces separated by two boundary curves (including catenanes).

As for $n(t) = 1$, the Möbius strip band has been shown in Fig. 11 already, and is not plotted in Fig. 12. All these Möbius strip bands with different $n(t)$ have the same base circles. The axis vertical to the base circle and through the centre (i.e. the OZ axis, C_Z) ought to be the $n(t)$ -fold rotation axis, $C_{n(t)}$. Based on the point group theory, if there exists 2-fold rotation axis which is perpendicular to the $C_{n(t)}$, there is the point group $D_{n(t)}$ in the system. Therefore, the Möbius strip bands with $n(t) = 2$ –6 would have the symmetry of the point groups D_2 , D_3 , D_4 , D_5 and D_6 , respectively. As for $n(t) = 1$, it can be considered that it has the symmetry of point group D_1 . However, in this system the C_Z is C_1 , and in fact there is only one 2-fold axis vertical to C_Z . So, it may be often called such system possessing the symmetry of point group C_2 , where the C_2 axis is not the C_Z axis. It is obvious that in the Hückel band, the C_Z axis would

be a infinite cyclic rotation axis $C_{n(0)} = C_\infty$. If the related $n(0)$ is finite, the $C_{n(t)}$ axis may not exist in the Möbius strip band, and it should be replaced by the $C_{(n(0),n(t))}$ axis, resulting that the relevant point group $D_{n(t)}$ would also be changed into the point group $D_{(n(0),n(t))}$, where the subscript $(n(0), n(t))$ means the greatest common divisor of $n(0)$ and $n(t)$, moreover if $n(0)$ is infinite, then $(n(0), n(t)) = n(t)$.

In addition to the point group, Möbius strip still possesses an infinite cyclic group, namely the TSR group:

$$\begin{aligned} \mathbf{TSR}(n(0)/n(t); j) &= \{\mathbf{TSR}(L, 2j\gamma, n(t)\gamma)^j\} \\ &= \{\mathbf{TSR}(L, 2j\gamma, jn(t)\gamma); 2j\gamma \subseteq (0, 2\pi)\} \end{aligned} \quad (13)$$

where $\lim \gamma \rightarrow 0$ results $\lim n(0) \rightarrow \infty$. As $j = \pi/\gamma$, $\mathbf{TSR}(L, 2j\gamma, jn(t)\gamma) = \mathbf{TSR}(L, 2\pi, n(t)\pi)$ may be not an identity transformation. In fact, as $n(t)$ is even, the $\mathbf{TSR}(L, 2\pi, n(t)\pi)$ will be the identity one, while as $n(t)$ is odd, the $\mathbf{TSR}(L, 2\pi, n(t)\pi)$ will not be. So, only when $j = 2\pi/\gamma$, $\mathbf{TSR}(L, 2j\gamma, jn(t)\gamma) = \mathbf{TSR}(L, 2\pi, 2n(t)\pi)$ is so. For $n(t)$ is even or odd, the symmetry character of Möbius strip-band will be somewhat different. When Möbius strip-band with odd $n(t)$, it will only have one border (closed and knotted) curve which is invariable under the TSR. And this infinite cyclic group will be made up of twice of the generator as that of the base circle. When Möbius strip-band with even $n(t)$, it will have two boundary (catenate) curves and the relative infinite cyclic group will be made up of the same order of the generator as that of the base circle.

There are two kinds of the group elements included in the point group $D_{n(t)}$. The first one is the $C_{n(t)}$ rotation about the C_Z axis, and it can commonly be denoted as some TSR. The $C_{n(t)}$ usually may interchange with the relevant TSR, $C_{n(t)}\mathbf{TSR} = \mathbf{TSR}C_{n(t)}$. The other one is the 2-fold rotation C_2 about the axis vertical to the $C_{n(t)}$ axis. Such C_2 transformations often can not interchange with the relevant TSR.

4.2 Symmetry of multi-twisted Möbius strip cyclacene molecule

For the cyclacene including $n(0)$ benzene-rings with $n(t)$ times twisted Möbius molecule, as shown in Sect. 4.1, we denote it as $M^{n(t)}C-[n(0)]$. It is noteworthy that the configuration of the SA atom set in MC-[18] molecule about the TSR in Fig. 3 is similar to the border shape of the Möbius strip band with $n(t) = 1$ in Fig. 11b. It is conceivable that if the 36 H atoms in Fig. 1 lay in both the up- and down- borders of the corresponding rectangle, then they will be in the border of Möbius strip band when the rectangle forms the Möbius strip band. As for the 72 C atoms, they can be distinguished into two sets (C_a, C_b) and ($C_{a'}, C_{b'}$), respectively. If the 36 C atoms of the either set mentioned above lay in the border, the similar configuration should also be obtained. Such relationship between the SA atom set and the boundary curve associated with the TSR is also existed in both of the Hückel- and multi-twisted Möbius-molecules. Figure 13 shows the TSR SA atom sets of $M^{n(t)}C$ -[24] molecule with $n(t) = 1-6$, and that of HC-[24] molecule. Comparing with the relevant curved surface in Figs. 11 and 12, the TSR SA atom sets in Fig. 13 obviously are in consistency with that curved surface border.

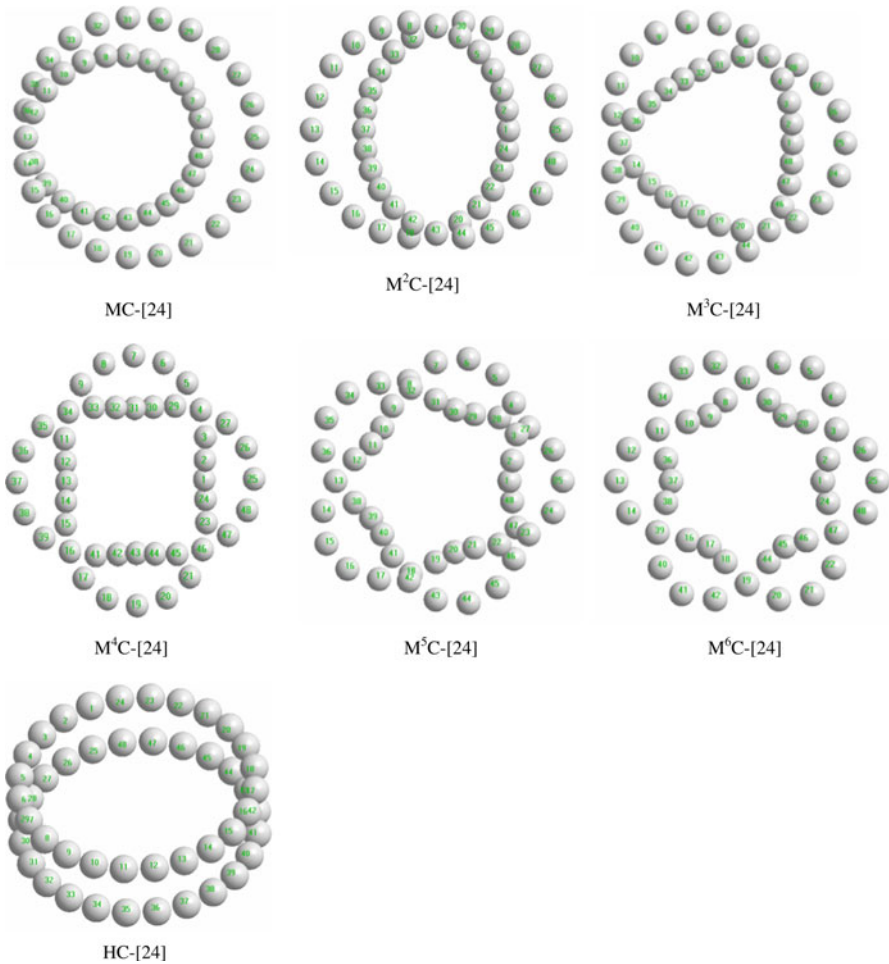


Fig. 13 The TSR SA atom set of $M^{n(t)}C-[24]$ (*top view to base circle*) and HC-[24] molecules (somewhat deviate *top view to base circle*)

In order to show the atom position of these SA atom sets in these molecules clearly, the space filling graph of such molecules are shown in Fig. 14. In the graph, the shallow and deep atoms denote the H and C atoms, respectively. Comparing the Figs. 13 and 14 (especially, the H atoms), the relativity should be very obvious.

For the ordinary Möbius strip band and Möbius strip-like molecule, the main difference between their TSR symmetry characters is that the TSR symmetry of the former is an infinite cyclic group, while it is a finite one for the latter. The torus group includes the point group and TSR group, the TSR group is finite or infinite will effect the point group, too. On the other hand, for Hückel-band, the C_Z axis is the infinite, $n(0) = \infty$ -fold rotation axis, and it possesses the symmetry of point group $D_{\infty h}$.

The $n(t)$ -time twisted Möbius band will belong to the point group $D_{(n(0),n(t))}$. Because $n(0) = \infty$, we can obtain $D_{(n(0),n(t))} = D_{n(t)}$. Even if the Hückel mole-

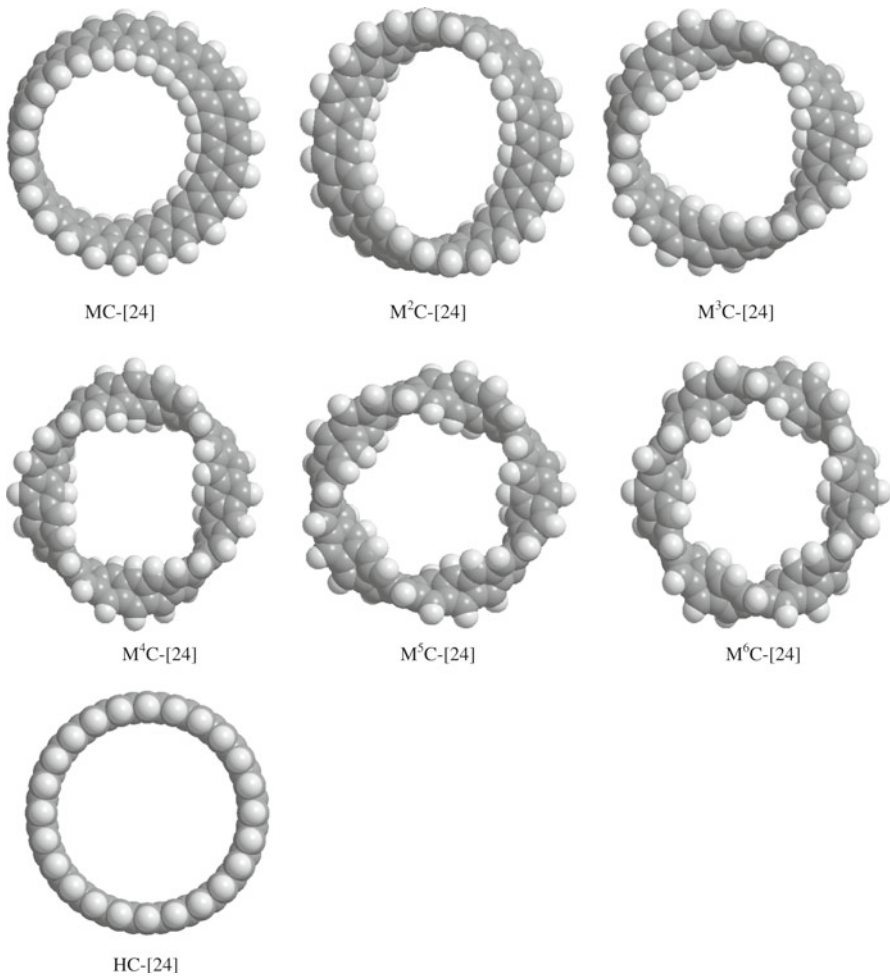
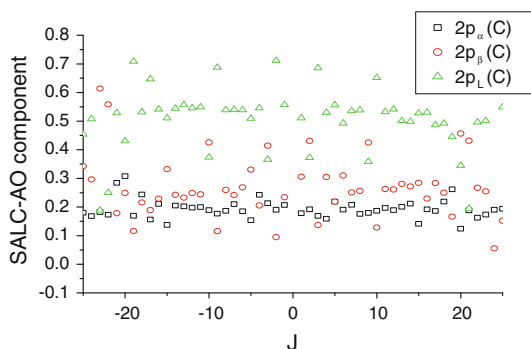


Fig. 14 The space filling graph of $M^{n(t)}C$ -[24] and HC-[24] molecules (*top view to base circle*)

cule possesses the finite point group $D_{n(0)h}$ symmetry, the point group of the relevant $n(t)$ -time twisted Möbius strip-like molecule, $D_{(n(0),n(t))}$, may not equal to $D_{n(t)}$. Only if $n(t)$ is the reducible factor of $n(0)$, the relationship, $D_{(n(0),n(t))} = D_{n(t)}$, will come into existence. For example, for the M^5C -[24] molecule, $n(t) = 5$ and $n(0) = 24$, there is no common divisor between them (except 1), so it only has the D_1 symmetry. Though it seems that there is the symmetry of point group D_5 seen from Figs. 14 and 15, in fact it is only an incomplete or fuzzy symmetry of D_5 point group. However, the MC-[24], M^2C -[24], M^3C -[24], M^4C -[24] and M^6C -[24] molecules have the symmetry of point groups $D_1(C_2)$, D_2 , D_3 , D_4 and D_6 , respectively. As for the M^4C -[18] molecule, the greatest common divisor between the $n(t) = 4$ and $n(0)=18$ is 2, we can know that it has the symmetry of point group D_2 .

Fig. 15 The various SALC-AO components in the near front MOs of M^2C -[18] (at STO3G/HF)



On the other hand, in relation to **TSR** group, the Eq. (13) is still true for Möbius strip-like molecule, but both the $n(0)$ and $\gamma = \pi/n(0)$ are finite. This group includes j_m elements, where $j = 0, 1, 2, \dots, j_m - 1$:

$$\mathbf{TSR}(n(0)/n(t); j) = \{\mathbf{TSR}(L, 2\pi/n(0), \pi n(t)/n(0))\}^j [j = 0, 1, 2, \dots, j_m - 1] \quad (14)$$

When $j = n(0)$, the group element will be $\mathbf{TSR}(L, 2\pi, n(t)\pi)$. If $n(t)$ is even, when $j = n(0) = j_m$, the group element $\mathbf{TSR}(L, 2\pi, n(t)\pi)$ is an identical transformation, namely $j_m = n(0)$. As $n(t)$ is odd, when $j = n(0) = j_m/2$, the group element $\mathbf{TSR}(L, 2\pi, n(t)\pi)$ will not be an identical transformation, except when $j = 2n(0)$, the group element $\mathbf{TSR}(L, 2\pi, 2n(t)\pi)$ can be an identical one, namely $j_m = 2n(0)$. The behaviors are different for the Möbius strip-like molecule whether $n(t)$ is even or odd.

4.3 Symmetry of the MOs of multi-twisted Möbius strip cyclacene

For multi-twisted Möbius strip-like molecule, the relevant symmetry group is the torus group, which includes two kinds of subgroups: the point group and the **TSR** group. Such symmetry character will also appear in their MOs. Furthermore, the **TSR** group is a cyclic group, and the irreducible representation and character of both point group and **TSR** group can be analyzed and obtained by using the group theorem. For the torus group, we can also analyze them by the group representation theorem. We may analyze the MO of multi-twisted Möbius strip-like molecule from the representation theorem of torus group. The method is similar to that we used for the MO of MC-[18] in Sect. 3.2.2. For example, for $M^{n(t)}C-n(0)$, we can obtain the various SA-AO and SALC-AO sets based on the SA-atom set in relation to the molecular torus group. The SALC-AOs which belong to the same irreducible representation can be combined to form MOs further. Such constructed MOs belong to the pure representation, but their SALC-AO included may be composed by various SA-AO sets, i.e. each MO may include components of several SA-AO sets. The related method and results of such investigation are similar to that of MC-[18] molecule. For example,

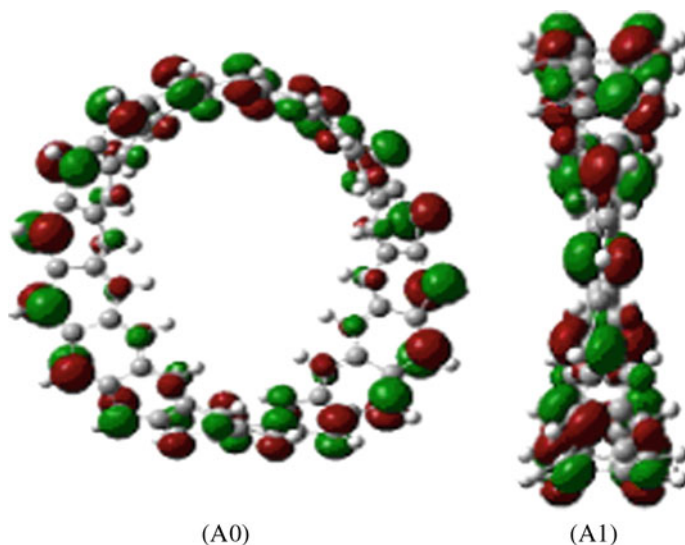


Fig. 16 The view of HOMO of M^2C -[18] (at STO3G/HF level). **A0** Near *top view*, **A1** near *side view*

for M^2C -[18], its SALC-AO components are shown in Fig. 15. Such figure seems somewhat similar to Fig. 8 for MC-[18] molecule.

The related HOMO is shown in Fig. 16. The similar analysis for other related molecules is omitted.

5 Conclusion

In this paper, the cyclacene and its isomer are taken as examples to interpret how to analyze the symmetry of the Möbius strip-like molecule, and we find out that there is a new molecular symmetry group which is different from the usual point group. The main conclusions are summarized as follows:

1. Similar to the screw rotation, there exists the TSR. TSR is the combination of the rotation around of both the center and the circumference of the base circle. The image of any source point after conducting the TSR will certainly be on a torus, and the trajectory is a helix on the torus. All of such points their trajectories will gather to form a whole torus and the corresponding symmetry transformations will compose a group called the torus group. In the 3D space, a TSR is applied to the object that has rotational symmetry in the direction along the base circle. The torus screw rotation group **TSR** is a kind of torus group.
2. Torus orthogonal curvilinear coordinate is introduced to discuss the symmetry of Möbius strip-like molecule. Its character, selection method and the relationship with the Cartesian coordinates are introduced, briefly. For a point $P(L, \alpha, \beta)$, under the operation of the TSR, the L coordinate value is invariable, while the α and β values can be changed by applying certain rules. Such transformation does not belong to the general point group.

- For Hückel molecule, HC- $[n(0)]$, it has the $D_{n(0)h}$ symmetry, which includes a subgroup, $n(0)$ -fold rotation cyclic group. Ordinarily, the cylinder orthogonal curvilinear coordinate system can be introduced to study the Hückel molecule. The symmetry adapted linear combinations atomic orbital (SALC-AO), in the cylinder orthogonal curvilinear coordinates, may be composed by only one kind of their components (either one of s -, p_z -, p_N -, and p_T -AO), and they can further combine to form the MO. These MOs may belong to a pure irreducible representation of the point group $D_{n(0)h}$, but the contained SALC-AOs can be various. In the HC- $[n(0)]$ molecule, the MOs near the frontier MO mainly include the SALC- (p_N) AO component.
- For Möbius strip-like molecule with twisting one time, MC- $[n(0)]$, it has the symmetry of $2n(0)$ -fold torus screw rotation group $\mathbf{TSR}(n(0)/1)$. From the view of common point group symmetry, such molecule only possesses the symmetry of point group C_2 , however, both the TSR group and the C_2 point group would be the subgroups of such molecular torus group:

$$\text{Molecular torus group} = \{\mathbf{TSR}(n(0)/1); C_2\}$$

The \mathbf{TSR} is an Abelian cyclic group. The symmetry adapted linear combination (SALC)-AO set about the molecular torus group may only include the s -AOs of the same kind of atoms. However, for the p -AO, the torus orthogonal curvilinear coordinates system would be introduced. The SALC-AO sets composed by various AOs (s -, p_α -, p_β - or p_L -AO) may belong to the same irreducible representation. And these SALC-AO sets with the same irreducible representation may further combine to form MOs. Vice versa, those MOs may include AOs from different SALC-AO sets. In MC- $[n(0)]$, the MOs near the frontier MO mainly include the SALC- (p) -AO component. Here all the three components of p -AO (p_α -, p_β -, and p_L -AO) ought to be included, while the p_L -AO component will be the somewhat larger and the s -AO component will be very tiny.

- At last, the special symmetry of multi-twisted Möbius-molecule is analyzed and some important results are obtained. For the multi- $n(t)$ -twisted Möbius molecule, if the corresponding Hückel-molecule has the symmetry of point group $D_{n(0)h}$, then such $n(t)$ -twisted Möbius-molecule will possess the symmetry of torus group which is composed by the subgroups of the point group $D_{(n(0),n(t))h}$ and the TSR group $\mathbf{TSR}(n(0)/n(t))$. Thus,

$$\text{Molecular torus group} = \{\mathbf{TSR}(n(0)/n(t)); D_{(n(0),n(t))h}\}$$

where the subscript symbol of the point group, $(n(0), n(t))$, is denoted the maximal common divisor of $n(0)$ and $n(t)$. When $n(t)$ is odd, the TSR group, $\mathbf{TSR}(n(0)/n(t))$, is a $2n(0)$ -fold cyclic group. When $n(t)$ is even, the TSR group, $\mathbf{TSR}(n(0)/n(t))$, is an $n(0)$ -fold cyclic group. The symmetry adapted (SA) atom set about the torus group will be distribute along the curves similar as the borderline (including the knot or catenane) of the relative Möbius strip. The SALC-AO set about the molecular torus group may only include the s -AOs of the same kind of atoms. However, for the p -AO, the torus orthogonal curvilinear coor-

dinates must be introduced. The SALC-AOs may composed by various AOs (s -, p_{α} -, p_{β} - or p_L -AO) belonging to the same irreducible representation, These various SALC-AOs with the same irreducible representation may further combine to form MOs. These MOs may belong to the various pure irreducible representations, respectively, but they may include AOs from different kind of SALC-AO sets.

It should be pointed out that what reported here is the result from the preliminary probe into the symmetry of Möbius-molecule by using the torus group. Lots of problems need to be investigated further, the other-Möbius molecules and non-Möbius ones (such as some DNA molecules) with torus group symmetry, the every possible forms of the molecular torus group and the relevant general representation theorems, the relationship between the molecular torus group and other torus defined in the mathematical field, and the fuzzy or irregular torus group when the base circle replaced by other closed curve, etc.

References

1. D.P. Craig, N.L. Paddock, *Nature* **181**, 1052–1053 (1958)
2. D.P. Craig, *J. Chem. Soc.* 997–1001 (1959). doi:[10.1039/JR9590000997](https://doi.org/10.1039/JR9590000997)
3. E. Heilbronner, *Tetrahedron Lett.* **5**(29), 1923–1928 (1964)
4. H.E. Zimmerman, *Acc. Chem. Res.* **4**, 272–280 (1971)
5. D.M. Walba, M. Richards, R.C. Haltiwanger, *J. Am. Chem. Soc.* **104**, 3219 (1982)
6. D.M. Walba, T.C. Homan, R.M. Richards, R.C. Haltiwanger, *New J. Chem.* **17**, 661 (1993)
7. W.Y. Qiu, F.L. Zhang, *Chemistry* **11**, 59 (1988) (in chinese)
8. D. Ajami, O. Oeckler, A. Simon, R. Herges, *Nature* **426**, 819 (2003)
9. D. Ajami, K. Hess, F. Köhler, C. Näther, O. Oeckler, A. Simon, C. Yamamoto, Y. Okamoto, R. Herges, *Chem.-Eur. J.* **12**, 5434 (2006)
10. R. Herges, *Chem. Rev.* **106**, 4820–4842 (2006)
11. H.S. Rzepa, *Chem. Rev.* **105**, 3697–3715 (2005)
12. D. Geuenich, K. Hess, F. Koehler, R. Herges, *Chem. Rev.* **105**, 3758 (2005)
13. J.-M. Andre, B. Champagne, E.A. Perpete, M. Guillaume, *Int. J. Quantum Chem.* **84**, 608 (2001)
14. S. Martin-Santamaria, H.S. Rzepa, *J. Chem. Soc. Perkin Trans.* **2**, 2378–2381 (2000)
15. H.-L. Xu, Z.-R. Li, Z.-M. Su, S. Muhammad, F.L. Gu, K. Harigaya, *J. Phy. Chem. C* **113**, 15380–15383 (2009)
16. M.A. Armstrong, *Basic Topology* (Springer Science+Business Media, Inc., NY 10013, USA, 2000), pp. 139–140
17. R.H. Wang, K.X. Gao, *Symmetry Group of Crystallography (in Chinese)* (Science Press, Beijing, 1990)
18. S.K. Xing, Y. Li, X.Z. Zhao, Z.S. Cai, Z.F. Shang, G.C. Wang, *Acta Phys. Chim. Sin.* **27**(5), 1000–1004 (2011)
19. Z.R. Yang, *Fractal Physics (in Chinese)*. (Shanghai Scientific and Technological Education Publishing House, Shanghai, 1996)
20. F.A. Cotton, *Chemical Application of Group Theory*, chap. 4. (Wiley, New York, 1999)
21. S.K. Xing, Y. Li, X.Z. Zhao, Z.F. Shang, X.F. Xu, Z.S. Cai, G.C. Wang, R.F. Li, *Acta Phys. Chim. Sin.* **26**(7), 1947–1958 (2010)