

Fuzzy symmetries of two classes of linear polyacene molecules

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Abstract The fuzzy symmetries of two kinds of linear polyacene molecules are probed into in the paper. In these molecules, any one of the benzene rings abreast connects at most other two rings in two ways: either its two opposite C–C bonds combine with two other rings, respectively, or its two meta-position C–C bonds connect two rings in *cis*- and *trans*-form, respectively. The former is called *p*-polyacenes (or straight polyacenes), and the latter is *m*-polyacenes (or kinked ones). It can be thought as the planar molecule with approximate one-dimensional space periodic transformation (parallel translation) symmetry, namely, group G_1^2 symmetry, when the number of its benzene ring is very large; on the other hand, it can be considered as the fuzzy group G_1^2 symmetry, if the benzene ring number is not large enough. The *p*-polyacene and *m*-polyacene with 20 benzene rings are analyzed as typical examples, and the energies of the π -molecular orbital (MO) and the fuzzy symmetry characters related to the space symmetry transformations are carefully examined. Moreover, the π -MOs of the *p*-polyacenes and *m*-polyacenes with different numbers of benzene ring are investigated to obtain the related rules.

Keywords Polyacenes · One-dimensional fuzzy space periodic transformation · The membership function

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1 Introduction

In the area of theoretical chemistry, the fuzzy symmetry is an interesting topic and a few important results [1–11] have been obtained. In our previous work, some methods [12,13] to study the fuzzy symmetry feature of molecule and molecular orbital (MO) have been introduced. Through these methods, we analyzed the fuzzy symmetry characterization of the static and dynamic states of molecules [14–22]. However, most of them dealt with the characterization of fuzzy point symmetry transformation, and only polyynes and straight chain conjugated polyenes etc have been taken as the examples to investigate the fuzzy space symmetry, i.e. the fuzzy one-dimensional periodic behavior of the linear molecules [17,21]. In the three-dimensional space, the cylindrical group G_1^3 [23,24] is usually introduced to investigate the symmetry of objects with the periodicity in only one particular direction. So, generally speaking, in n -dimensional space, the group G_1^n can be used to discuss the symmetry of periodic objects with periodicity in only one particular direction. Moreover, the periodic linear molecules with periodicity in one particular direction, such as polyynes and its cyanide, can be studied by the fuzzy group G_1^1 symmetry, while the planar molecules with periodicity in one particular direction can be considered to have the fuzzy group G_1^2 symmetry. In the G_1^1 symmetry system, the parallel translation is the only space symmetry transformation. While in the G_1^2 symmetry system, there may be two other kinds of space symmetry transformations, the screw rotation and the glide plane reflection. The conjugated polyene with fuzzy group $ta/2$ (a sort of group G_1^2) has been taken as an example analyzed using the Gaussian program [25], at AM1 level [21]. In this work, the more complex molecules (two classes of linear polyacene molecules) with fuzzy group G_1^2 symmetry are taken as typical examples discussed. In the two kinds of molecules, any benzene ring connects at most other two rings side by side. Hereon, in one class of molecules, the two opposite C–C bonds of the ring combine with other two rings, respectively. However, in the other one, the two *meta*-position C–C bonds of the ring connect other two rings, respectively. The former is called *p*-polyacenes, and the latter is *m*-polyacenes. In *m*-polyacenes, the middle ring connects the two neighboring benzene rings in *cis*- and *trans*-form, respectively. Moreover, they are denoted as *p*-[*n*]acenes and *m*-[*n*]acenes, respectively, if *n* benzene rings are involved. The geometries of *p*-[8]acene (i.e. octacene) and *m*-[8]acene are shown in Fig. 1 (the number of rings may be different for some of the polyacenes discussed in the paper). In Fig. 1, the center line (dashed line) on the molecular plane denotes the periodic orientation. The plane that goes through the dashed line and is perpendicular to the molecular plane is taken as the mirror related to the *p*-polyacenes and as the glide plane to the *m*-polyacenes. For these two polyacenes, the fuzzy space periodic symmetry occurs in only one direction (as the arrowhead shows). The unit cell sizes of the two molecules are different as treated according to one-dimensional crystals, approximately. From the view of point group symmetry, the *p*-polyacenes possess the D_{2h} symmetry and the inverse center is the center of one benzene ring when *n* is odd, while it is located in the center of C–C bond of two connected benzene rings when *n* is even. In addition, *m*-polyacenes have only the C_{2h} or C_{2v} symmetry, which varies with the oddity of *n*.

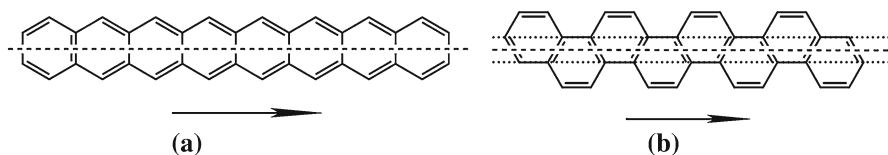


Fig. 1 The geometries of *p*-[8]acene (a) and *m*-[8]acene (b)

The two polyacenes are chosen for the further studies on the fuzzy symmetry of the single-wall carbon nanotubes (SWCNTs). There are mainly two kinds of SWCNTs without optical activity [26–28]: One is the zigzag SWCNTs (ZSWCNT) with the wall circumference arranged as the *p*-polyacenes while the arrangement is changed as the *m*-polyacenes in the tube axis direction. The other is the armchair SWCNTs (ASWCNT) with the *m*-polyacenes arrangement around the wall circumference and the *p*-polyacenes arrangement along the tube axis. In addition, the two types of polyacene are typical low dimensional organic conductors [23]. Therefore, the fuzzy symmetry of more complex systems, such as carbon nanotubes and organic conductors, will be examined in our future papers.

2 Fuzzy symmetry of *p*-polyacenes

The space geometry of the *p*-polyacenes is depicted in Fig. 1a, where the six-membered ring denotes benzene ring (the bonds and H atoms are omitted), and each benzene ring is roughly considered as a unit cell. The molecule is treated as the one-dimensional crystal, in which two C–C bonds of the ring are shared by the neighboring unit cells respectively. Thus, there are merely four C atoms and two H atoms in each unit cell, while two additional C atoms with two H atoms are added to each terminal unit cell. Accordingly, $4n+2$ C atoms and $2n+4$ H atoms are involved in *p*-[*n*]acenes. In addition, these molecules can be considered having the fuzzy group $tm/2$ [24] symmetry if the difference between the conjugated C–C bonds of the benzenes is de-emphasis. Thereby, the parameters, such as the membership functions related to the fuzzy symmetry of the *p*-polyacenes and the MOs can be calculated using the general fuzzy symmetry methods [12–22]. Here the MOs are calculated by using the Gaussian program [25] at the level of STO-3G.

2.1 Fuzzy symmetry of the molecular skeleton of *p*-polyacenes

When the J atom of the molecule M is changed to the GJ one through the symmetry transformation \hat{G} , the membership function [13–22] of the M related to the symmetry transformation \hat{G} is:

$$\mu_Y(\hat{G}; M) = \left[\sum_J (Y_J \wedge Y_{GJ}) \right] / \left[\sum_J (Y_J) \right] \quad (1)$$

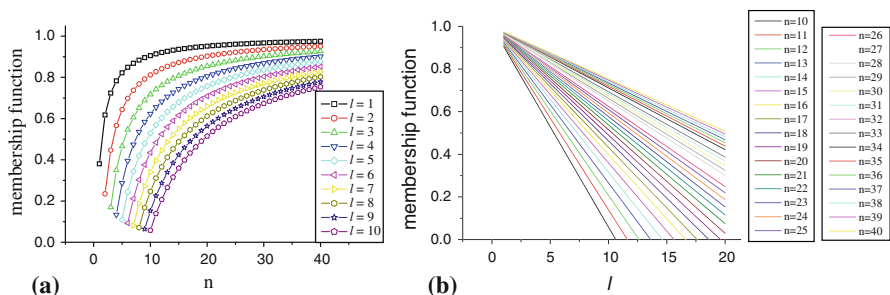


Fig. 2 **a** The membership function of the given parallel translation versus the number of benzene ring (n). **b** The membership function of the given p -polyacenes related to the parallel translation symmetry transformation versus the parallel transformation length (l) (the number of benzene ring translated parallelly)

Here the symmetry transformation \hat{G} may be either the point or the space symmetry transformation. For p -polyacenes, the symmetry transformation \hat{G} can be the parallel translation, translating the skeleton by l unit cell lengths along the one-dimensional fuzzy periodic direction. Y_J and Y_{GJ} are the atomic criterion of J and GJ atom, respectively. In the equation (Eq. (1)), the summation runs over all the atoms in molecule M . Regarding the molecular skeleton, the atomic number of each atom may be taken as its own atomic criterion. Thus, the atomic criterion is 6 or 1, respectively, for C or H atom. Accordingly, for p -polyacenes, the denominator in Eq. (1) is $[\sum_J (Y_J)] = 6(4n + 2) + (2n + 4) = 26n + 16$. If \hat{G} is the transformation $\hat{T}(l)$ that translates the skeleton by l unit cell lengths along one-dimensional fuzzy periodic direction, the numerator in Eq. (1) is $[\sum_J (Y_J \wedge Y_{GJ})] = 26(n - l) + 16$. So, the related membership function can be denoted as Eq. (2):

$$\mu_Y(\hat{G}; M) = [26(n - l) + 16]/[26n + 16] \quad (2)$$

From Eq. (2), we can see that at a given symmetry transformation l , the membership function will increase with the increase of the number of benzene ring (or more properly: the unit cell, i.e. C_4H_2) in the p -polyacenes and will approach one, as shown in Fig. 2a. For the given p -polyacenes, the membership function will decrease with the increase of the length l of parallel transformation, as depicted in Fig. 2b.

The homologous linearity rules have been mentioned when we probed into the fuzzy space groups [29]. We have also pointed out that there are some correlations between the spectral wave number and the membership function of some space symmetry transformations for some homologues [14, 21]. The electron spectrum of p -polyacenes with fewer benzene rings have been examined in the experiments [30, 31]. Their electron spectra mainly include three spectral bands (α -, p -, β -bands), but only the p -band is examined here because of more experimental data available. Figure 3 illustrates the changes of the membership function related to the wave number of p -bands, as translating the skeleton one or two benzene rings ($l = 1$ or 2). The wave number decreases monotonically with the increase of the membership function, resulting in an asymptotical linear relationship, however, as the number of unit cell (n) is small,

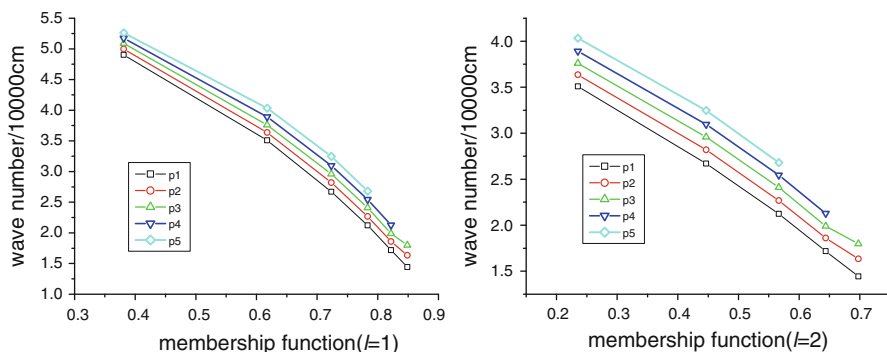


Fig. 3 The spectral wave number of some p -polyacenes versus the membership function of parallel translation symmetry transformation

($n = 1, 2$, for the dots near the vertical axis, namely, benzene and naphthalene), the wave numbers are lower than what the linearity predicted (as shown in Fig. 3).

2.2 Fuzzy symmetry of the π -MO of p -[20]acene

The p -[20]acene (i.e. eicosacene) is taken as an example to discuss the π -MO fuzzy symmetry. The molecular formula is $C_{82}H_{44}$, and its 82 π -MOs form from the 82 conjugated C atoms of the molecule, with 41 bonding and occupied π -OMOs and 41 anti-bonding and vacant π -VMOs. The suffix j denotes the serial number (or rank) of the MO counted from the frontier MO. So, OMO-1 and VMO-1 represent HOMO and LUMO, respectively.

The molecule possesses the D_{2h} point group. So, these π -MOs belong to A_u , B_{1g} , B_{2g} and B_{3u} irreducible representation, respectively, according to the group theory [32]. And there are 20 π -MOs each belonging to A_u and B_{1g} , while 21 π -MOs each to B_{2g} and B_{3u} . The MOs are determined by using Gaussian program at the STO-3G level. Their LCAO-MO coefficients are used to obtain the general and fuzzy symmetry character values, and the energies of the π -MOs are examined, as shown in Fig. 4a where the abscissa is j , negative for the OMO and positive for the VMO. The energy dots corresponding to OMO and VMO are segregated in two sets but close to each other within the set, forming approximately two separated branches. An energy gap appears between the branches of dots of OMO and VMO, which is the similar behavior shown in many large molecules. It is interesting to find that the branches of the collective dots of OMO and VMO are somewhat zigzag rather than smooth. In Fig. 4a, different symbols are used to indicate the π -MO dots corresponding to different irreducible representations. So, we can see that different segments in the branch are mainly contributed by the MOs belonging to certain one or two irreducible representations.

Moreover, the dot distributions seem to hint certain rules, so the MOs with different irreducible representations are studied to clarify the possible rules. As depicted in Fig. 4b, firstly, the serial number j is the mentioned suffix (j) but here always taken as

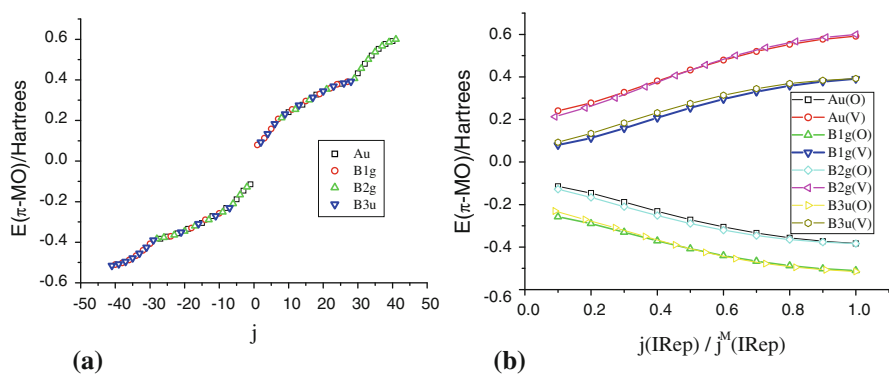


Fig. 4 π -MO energies of p -[20]acene. **a** π -MO energy versus j , **b** π -MO energy versus $j(\text{IRep})/j^M(\text{IRep})$

positive for both OMO and VMO. And it is related to the specific irreducible representation (abbreviation: IRep) by labeling as $j(\text{IRep})$, where the allowed IRep will be A_u , B_{1g} , B_{2g} and B_{3u} , according to the D_{2h} group of the MOs and an O or V in the parentheses will identify the related MO is OMO or VMO respectively. Secondly, the abscissa is labeled as $j(\text{IRep})/j^M(\text{IRep})$ convenient for comparison, where $j^M(\text{IRep})$ is the maximum value of $j(\text{IRep})$. When $\text{IRep} = B_{2g}(\text{V})$ or $B_{3u}(\text{O})$, $j^M(\text{IRep}) = 11$, while $j^M(\text{IRep}) = 10$ for other IRep. For each IRep, the curve is smooth as shown in Fig. 4b. Either for VMOs or OMOs consistently, the curves of $\text{IRep} = B_{1g}$ and B_{3u} , or B_{2g} and A_u are paired, that is to say these eight curves can be divided into four groups, and show approximately a symmetry distribution relative to the nonbonding energy level. It should be noted that the B_{1g} and B_{3u} curves of OMO are in the symmetrical position with those of B_{2g} and A_u of VMO, and vice versa.

The fuzzy space transformation symmetries of p -[20]acene MO are probed into. The membership function for the MOs related to the space symmetry transformation can be calculated using Eq. (1). Here, the atomic criteria Y_j should be the square of LCAO-MO coefficients of J atom in MO, and the symmetry transformation \hat{G} should be the related space symmetry transformation. Figure 5a illustrates the variations of the membership functions of the symmetry transformation $\hat{T}(1)$ with the j , that is, the changes after translating one unit cell (benzene ring) length for each π -MO of p -[20]acene. The MOs belonging to different irreducible representations are denoted using different symbols. For both OMO and VMO, the dots of irreducible representations $\text{IRep} = B_{1g}$ and B_{3u} fall into a pair of branches, in addition, the dots of B_{2g} and A_u fall into other pair of branches. These branches are approximately symmetry distributed relevant to the nonbonding energy level. It should be noted that the B_{1g} and B_{3u} branches of OMO are the counterparts of those of B_{2g} and A_u of VMO, and vice versa. Obviously the rule is similar to the symmetry distribution of the π -MO energies related to the nonbonding energy level. However, there are four up U-shaped branches here, and they can be superposed if the abscissa j is changed to $j(\text{IRep})/j^M(\text{IRep})$. As shown in Fig. 5b, all dots fall approximately into the same up U-shaped curve,

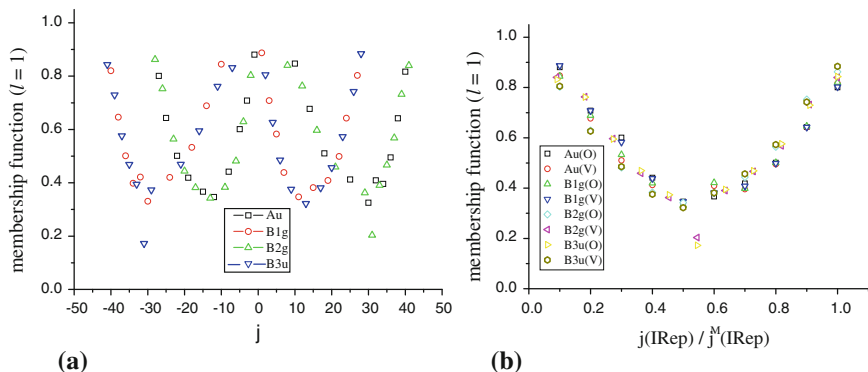


Fig. 5 The plots of membership functions related to translating one unit cell length symmetry transformation of p -[20]acene π -MO. **a** membership function versus j , **b** membership function versus $j(\text{IRep})/j^M(\text{IRep})$

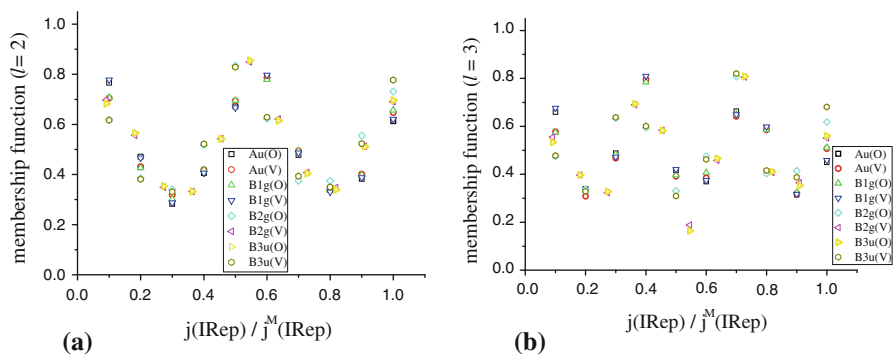


Fig. 6 The plots of membership function related to translating two and three unit cell lengths of p -[20]acene π -MO. **a** the membership function of $\hat{T}(2)$, **b** the membership function of $\hat{T}(3)$

indicating the space transformation shows a similar fuzzy symmetry though the π -MOs belong to different irreducible representations.

As for more complex space transformations, for example, the symmetry transformation $\hat{T}(l)$ related to translating the skeleton by l unit cells, $4l$ U-branches will be obtained as plotting the membership function of 82 π -MOs versus j . For each branch, bigger l results in fewer dots and in more intersectant up U-shaped branches, which exhibits a dispersed distribution with “starriness” pattern. Thereby, the inherent fuzzy symmetry related rule will be concealed. However, the rule will appear to some extent if the abscissa j is changed to $j(\text{IRep})/j^M(\text{IRep})$. Figure 6 illustrates the relationships for the symmetry transformations $\hat{T}(2)$ and $\hat{T}(3)$, which translate the skeleton by two and three unit cell lengths, respectively. For $\hat{T}(2)$ and $\hat{T}(3)$, 82 dots of π -MOs depicted belong to different irreducible representations and fall into curves with two and three up U-shaped branches, respectively. Therefore, the related dots for a parallel transformation $\hat{T}(l)$ will fall into a curve with l up U-shaped branches.

2.3 Fuzzy symmetry of the π -MO of various p -[n]acenes

The analogous analyses are made to p -polyacenes with different number of benzene rings, and similar results are obtained. However, the fewer the benzene rings (n) the bigger the departure of the results, the fewer the number of π -MOs in the molecule and the less apparent the rules related to the fuzzy symmetry. The correlation between the fuzzy symmetries of various p -polyacenes with different n is analyzed.

$4n + 2$ π -MOs are involved in p -[n]acenes, and the π -MO energies of molecules with different n are shown in Fig. 7a. Convenient for comparison among the molecules with different n , the abscissa is j/j^M rather than j . Here $j^M = 2n + 1$, is the maximum value of j among the π -MOs of the molecule of p -[n]acene, and j/j^M is positive. The dots with different n are denoted using different symbols, while the symbol of MOs belonging to different irreducible representations is kept the same. Noticeably, all these molecules share one pair of j/j^M versus $E(\pi$ -MO) curves. Furthermore, when the abscissa in Fig. 7a is changed to $j(\text{IRep})/j^M(\text{IRep})$, as depicted in Fig. 7b, the dots can be divided into four groups, and fall mainly into four curves, respectively. From the top down, the IRep is corresponding to the $A_u(\text{V})$ & $B_{2g}(\text{V})$, $B_{3u}(\text{V})$ & $B_{1g}(\text{V})$, $A_u(\text{O})$ & $B_{2g}(\text{O})$, and $B_{3u}(\text{O})$ & $B_{1g}(\text{O})$ in sequence. It is in consistent with that of π -MOs of the p -[20]acene (Fig. 4b). In Fig. 7b, the dots plotted are not distinguished for different IRep as done in Fig. 4b, and the two adjacent curves are in fact merged into one.

The fuzzy space symmetry transformations of the MOs of p -[n]acenes are examined as follows. In Fig. 8a, we plot the membership functions of symmetry transformation $\hat{T}(1)$, i.e. the parallel transformation by one unit cell length, for every π -MO of the p -[n]acenes, but the MOs belonging to different irreducible representations are not identified with different symbols. All the MOs fall into two intersecting and up opening branches. The left branch (near to the frontier MO) is corresponding to $\text{IRep} = B_{2g}(\text{O})$, $A_u(\text{O})$, $B_{-1g}(\text{V})$ and $B_{3u}(\text{V})$, and the right one (away from the frontier MO) relates to $\text{IRep} = B_{2g}(\text{V})$, $A_u(\text{V})$, $B_{-1g}(\text{O})$ and $B_{3u}(\text{O})$. This phenomenon obviously agrees with that of the π -MOs of p -[20]acene in Fig. 5a. The two U-shaped branches will approximately overlap into one but much dispersed curve, if

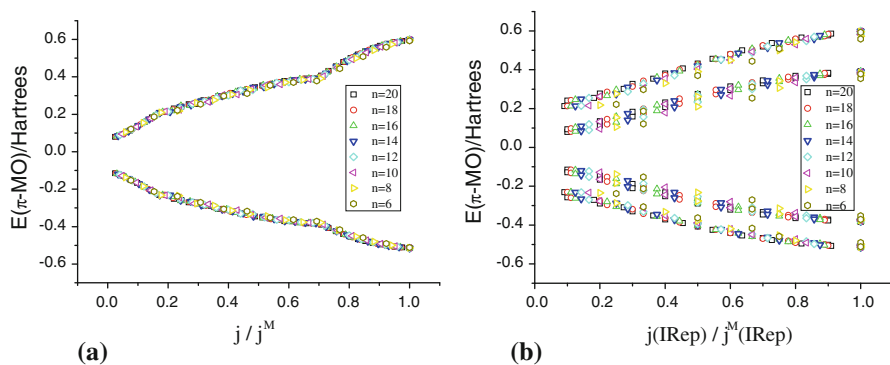


Fig. 7 π -MO energies of different p -[n]acenes. **a** π -MO energies versus j/j^M , **b** π -MO energies versus $j(\text{IRep})/j^M(\text{IRep})$

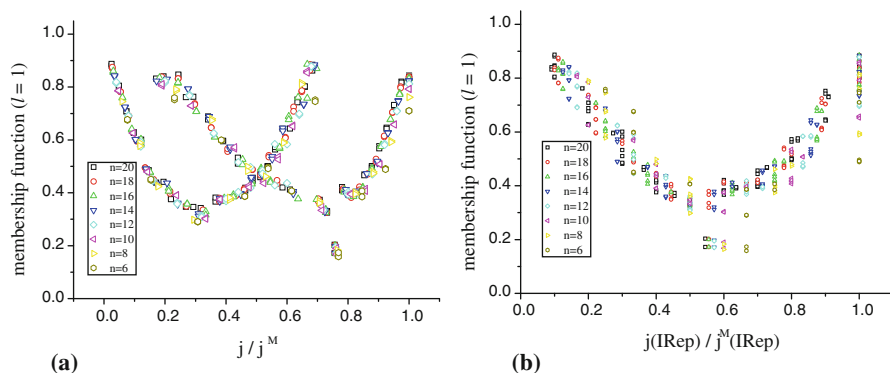


Fig. 8 Membership function translating one or two unit cells of various p -[n]acenes π -MOs. **a** Membership function for $\hat{T}(1)$ versus j/j^M , **b** Membership function for $\hat{T}(1)$ versus $j(\text{IRep})/j^M(\text{IRep})$

the abscissa j in Fig. 8a is changed to $j(\text{IRep})/j^M(\text{IRep})$ as shown in Fig. 8b. This indicates that the space transformations of these π -MOs have similar fuzzy symmetry though the π -MOs belong to different irreducible representations. In addition, for the π -MOs satisfying $j(\text{IRep}) = j^M(\text{IRep})$, the corresponding dots fall into a vertical line, which means the plot of membership function versus $j(\text{IRep})/j^M(\text{IRep})$ is multivalued. Moreover, the membership function increases with the increasing of the size of molecule, and approaches to 1. The membership function of $\hat{T}(l)$ ($l > 1$), i.e. translating the skeleton by l unit cell lengths, can also be analyzed similarly, here the detail of analysis is omitted.

3 Fuzzy symmetry of the m -polyacenes

The space geometry of the m -polyacenes is shown in Fig. 1b. Two benzene rings (more properly speaking, one naphthalene or di-acene ring with two of its conjugated C–C bonds shared by two neighboring unit cells respectively) form a unit cell, $[(\text{C}_4\text{H}_2)_2]$, and the whole molecule can be approximately dealt with as the one-dimensional crystal [24]. Because two C–C bonds are shared by the adjacent unit cells, there are eight C atoms and four H atoms in each unit cell except the terminal unit cells. So, similar to the p -[n]acene, the m -[n]acene molecule contains $4n + 2$ C atoms and $2n + 4$ H atoms. If we do not emphasize the differences about the conjugated C–C bonds in the benzene rings, these molecules can be approximately considered having the fuzzy group $ta/2$ symmetry [24]. And the related membership function can thus be calculated using the general method of molecular fuzzy symmetry [12–22].

The MO calculations are generally achieved using the Gaussian program at the STO-3G level [25]. The main difference between the m - and p -polyacenes lies in their different symmetry. Examined from the view of the translation space group along the one-dimensional periodic direction, the minimum periodic unit cell of m -[n]acene molecule contains two benzene rings (di-acene ring), while each benzene ring can be regarded as a minimum structure unit [24] and the translating distance of the parallel transformation is by a even number of benzene rings. Moreover, the

symmetry operations also include a combined space transformation: translating odd number of benzene rings and a twofold point symmetry transformation (i.e. mirror reflection or twofold rotation transformation), which actually is the glide reflection or the screw rotation transformation. The fuzzy symmetry of the molecular skeleton of *m*-polyacenes can similarly be treated as the *p*-polyacenes have been done. The membership function related to the space symmetry transformation (\hat{G}) can still be calculated using the Eq. (1). While here the space transformation is translating the skeleton either by even *l* or by odd *l* benzene ring lengths accompanied by some kind of second-order point symmetry transformation, such as the glide reflection or the screw rotation transformation as mentioned. For the molecular skeleton, the atomic criteria in the Eq. (1) is taken as the atomic number. The dependency relationships of the membership function related to the benzene ring number (*n*) of the skeleton of the *m*-polyacenes and related to the benzene ring number (*l*) of the length of the space transformation are consistent with those of the *p*-polyacene. Namely, Fig. 2 is applicable for both *p*- and *m*-polyacenes. Of course, the space transformations (\hat{G}) related to these two molecules are different. Examined from the view of point group symmetry, the *p*-polyacenes have the D_{2h} point group symmetry, while the *m*-polyacenes have lower symmetry and only possess the symmetry of the subgroup of D_{2h} , i.e. C_{2h} or C_{2v} symmetry, determined by the oddity of the benzene ring number (*n*) of the molecule. Although the particular formation of the two subgroups is different, both are the true subgroups of D_{2h} point group, so can be dealt with similarly. In this paper, we only concentrate on the molecules possessing even number (*n*) of benzene rings, which have C_{2h} subgroup symmetry.

When the polyacenes are analyzed according to the D_{2h} symmetry point group, the possible irreducible representations of their π -MOs are: B_{2g} , A_u , B_{1g} and B_{3u} . If the molecules are analyzed using the C_{2h} point group, the irreducible representations belonging to D_{2h} but not belonging to C_{2h} should be not taken into account, and they should belong possibly to A_u and B_g . However, the MOs belonging to A_u and B_{3u} in D_{2h} point group will belong to A_u in C_{2h} point group. And the MOs belonging to B_{1g} and B_{2g} in D_{2h} point group will change to B_g in C_{2h} point group. So, for the *p*-polyacenes and their MOs, the faultless symmetry analysis can be achieved based on the D_{2h} point group symmetry using the conventional group theory method, while for the *m*-polyacenes, only their fuzzy symmetry can be analyzed.

The irreducible representations of the π -MOs in *m*-polyacenes are analyzed in terms of the C_{2h} point group symmetry after the MOs were calculated using the Gaussian program. In addition, we should, according to the fuzzy symmetry analysis, further obtain the related components of the irreducible representation of the D_{2h} point group. For these MOs belonging to the irreducible representations of the C_{2h} point group, only two kinds of irreducible representations of the D_{2h} point group are relevant. As long as we properly choose a twofold symmetry transformation that can produce different characteristics for these two kinds of irreducible representations of the D_{2h} point group, the irreducible representation components about the D_{2h} point group can be obtained by calculating the symmetric and antisymmetric components relevant to the symmetry transformation, based on the fuzzy symmetry theoretical method [12–22]. The plane that is perpendicular to the molecular plane and in the one-dimensional periodic direction can be taken as a mirror, and the reflection transformation related

to the mirror can be chosen as the required twofold symmetry transformation. For the p -polyacenes, there is indeed such a mirror (through the dashed line and perpendicular to the molecular plane as shown in Fig. 1a). The membership function of their π -MO related to the reflection transformation is 1. The corresponding irreducible representation is pure, and its irreducible representation components are either one or zero.

But for the m -polyacenes, this mirror does not possess strictly the same meaning as that for the p -polyacenes. If we choose the slide plane, which is through the molecular middle line, as the reflection plane (through the dashed line and perpendicular to the molecular plane in Fig. 1b), the atom J in the molecule will hardly find its corresponding atom GJ. Thus, the parallel planes at both sides of the slide plane have to be selected as the mirror planes. These two planes should pass through as much as possible atoms and reflect as much as possible between J and GJ pairs. Each of these two planes can be easily found (the plane is placed through any one of the two dotted lines and perpendicular to the molecular plane as shown in Fig. 1b), and their corresponding fuzzy symmetry characteristics are equal. Based on this reflection mirror, the irreducible representation components of π -MO about the D_{2h} point group can be obtained by the aforementioned method [12–22].

3.1 Fuzzy symmetry of the π -MO of m -[20]acene

The m -[20]acene is taken as an example to explore the fuzzy symmetry of π -MO. It is the isomer of p -[20]acene, and its 82 π -MOs are also formed by 82 conjugated C atoms, with half bonding occupied π -MOs (π -OMOs) and other half anti-bonding vacant π -MOs (π -VMOs). This molecule only has the C_{2h} symmetry, i.e. the subgroup of D_{2h} . So, these π -MOs can be equally divided and belong to two kinds of irreducible representations, A_u and B_g , which can be determined with the group theory method [32]. The energies of these π -MOs are investigated as follows:

In Fig. 9, the different irreducible representations of the π -MO of the C_{2h} point group are expressed by different symbols, and the pattern of distribution of the membership functions is a little more complex than that of p -[20]acene in Fig. 4a. That is, the major energy gap exists between the OMO and the VMO, while there are other narrower energy gaps. The A_u irreducible representation of subgroup C_{2h} corresponds to the A_u and B_{3u} irreducible representations of group D_{2h} , and the B_g irreducible representation of subgroup C_{2h} relates to the B_{1g} and B_{2g} irreducible representations of group D_{2h} .

$$\{A_u(D_{2h}), B_{3u}(D_{2h})\} \approx A_u(C_{2h}) \quad (3-1)$$

$$\{B_{1g}(D_{2h}), B_{2g}(D_{2h})\} \approx B_g(C_{2h}) \quad (3-2)$$

In other words, in terms of D_{2h} point group, MO belonging to $A_u(C_{2h})$ is, to some extent, the fuzzy representation of the superposition of $A_u(D_{2h})$ and $B_{3u}(D_{2h})$. Indeed, $A_u(D_{2h})$ and $B_{3u}(D_{2h})$ are all anti-symmetric related to the center inverse transformations, as $A_u(C_{2h})$ is. However, with regard to the aforementioned reflection symmetry transformation, the $A_u(D_{2h})$ is anti-symmetric, while $B_{3u}(D_{2h})$ is

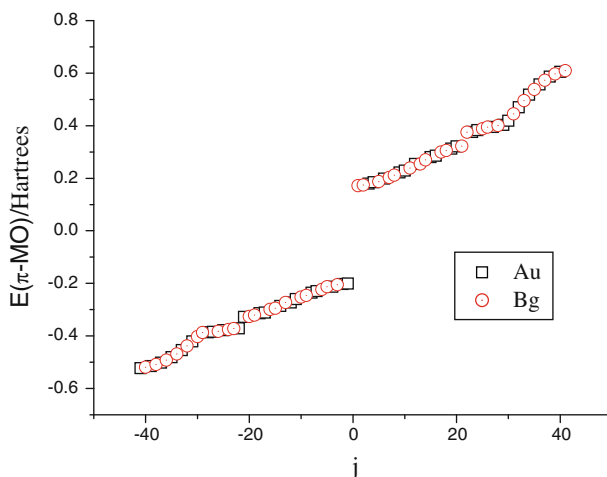


Fig. 9 The energy of π -MO of m -[20]acene molecule

symmetric. The summation of the fraction of their corresponding irreducible representation components, $X[A_u(D_{2h})] \equiv X_A$ and $X[B_{3u}(D_{2h})] \equiv X_S$, will satisfy $X_A + X_S = 1$. Similarly, the MO belonging to $B_g(C_{2h})$ is the fuzzy representation of the superposition of $B_{1g}(D_{2h})$ and $B_{2g}(D_{2h})$. Both $B_{1g}(D_{2h})$ and $B_{2g}(D_{2h})$ are symmetric related to the center inverse symmetry transformation, which is consistent with that of $B_g(C_{2h})$. However, $B_{1g}(D_{2h})$ is symmetric and $B_{2g}(D_{2h})$ is anti-symmetric related to the reflection transformation. The summation of the fraction of their corresponding irreducible representation components, $X[B_{2g}(D_{2h})] \equiv X_A$ and $X[B_{1g}(D_{2h})] \equiv X_S$, will satisfy $X_A + X_S = 1$. The contribution of all the irreducible representation components of these MOs about the D_{2h} point group can be calculated with the fuzzy symmetry theory method, as shown in Fig. 10. It can be seen from Fig. 10 that, for the MOs far away from the frontier orbital, one of the two irreducible representation components of D_{2h} is the dominant one, whose fraction is close to 1. So the energies of these π -MOs of m -[20]acene and those of the corresponding orbitals of p -[20]acene are close to each other. However, for some other MOs, both of these two irreducible representations of the D_{2h} will contribute more evenly. In such cases, the π -MO energy distributions of m -[20]acene and p -[20]acene will have some differences (the detail analyses are not shown).

For some of the π -MOs in m -[20]acene, their space symmetry transformation can also be explored with the fuzzy symmetry theory method. It should be noted that the fuzzy one-dimensional periodic unit cell contains two benzene rings (two C–C bonds are shared with the adjoining unit cells). For the space transformation contained l benzene rings, when l is an even, the corresponding symmetry transformation is parallel translation. While for an odd l , the related symmetry transformation is slide reflection or screw rotation. Here each unit cell contains two benzene rings (each benzene ring is a structure unit). Now turn to Fig. 11, the membership function of the π -MO of m -[20]acene is related to the slide reflection or screw rotation, and is calculated using Eq. (1). In Fig. 11, the MOs related to the irreducible representation A_u and B_g of the

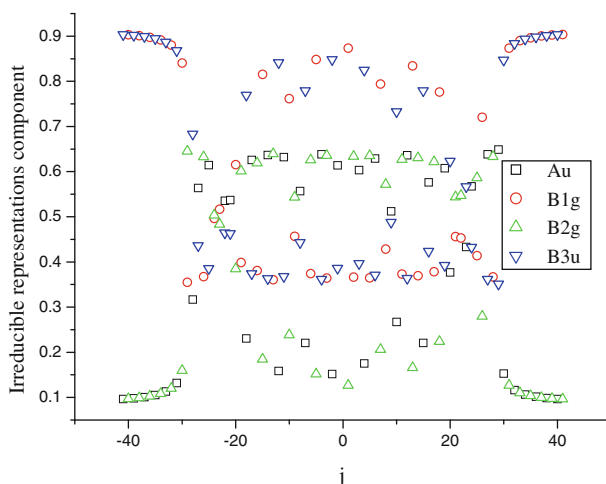


Fig. 10 The distribution pattern of the fraction of any of the specified irreducible representation component of π -MO related to D_{2h} point group in the m -[20]acene

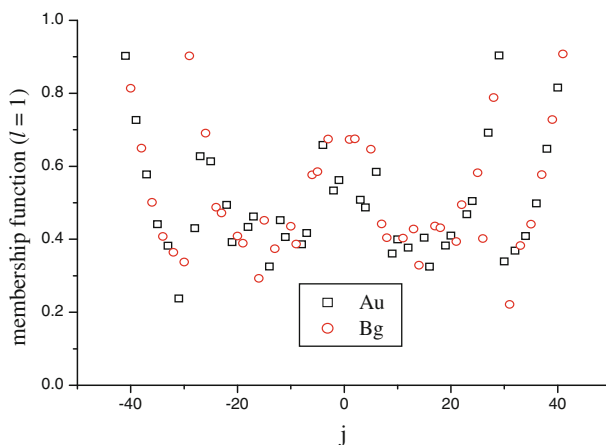


Fig. 11 The membership function of the MO involves translating one space length ($l = 1$) of the m -[20]acene

C_{2h} are expressed with different symbols. Compared with the π -MO of p -[20]acene (Fig. 5a), the MOs far away from the frontier orbital have similar distribute pattern for both molecules. However, for the MOs near the frontier orbital, their distribution patterns are different, due to the superposition from the irreducible representation components of the D_{2h} point group for the m -[20]acene. For the π -MO of m -[20]acene, the space translation symmetry transformation with various translating numbers (l) can also be studied by using fuzzy symmetry analysis, which is omitted here.

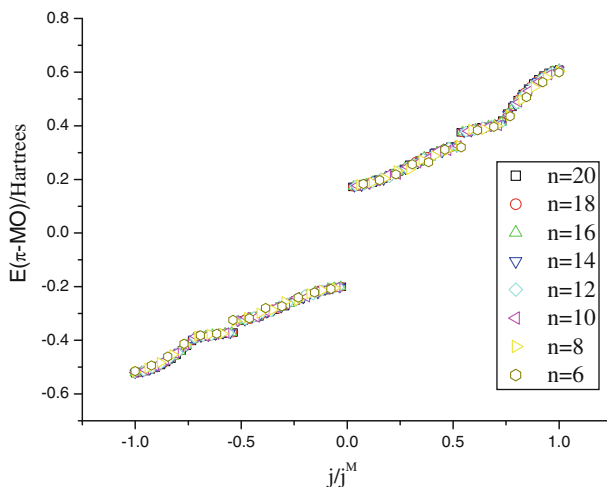


Fig. 12 π -MO energy distribution pattern of m -polyacenes

3.2 Fuzzy symmetries of the π -MO in various m -polyacenes

The following analysis is about the relative characters between the fuzzy symmetries related to m -[n]acenes with different n values. The energy of the $(4n + 2)$ π -MOs of the m -[n]acenes with different n values are shown in Fig. 12. Convenient for the comparison of the pattern of the energy distributions among different n values, the abscissa is set as j/j^M and the corresponding dots are labeled with different symbols for different n values sole, without distinguishing the different irreducible representations further. Noticeably, all these molecules share one pair of j/j^M versus $E(\pi\text{-MO})$ curves. Besides the energy gap between OMO and VMO, there are other two narrower gaps that can be clearly seen, but they are missing in p -polyacenes as mentioned early.

The fuzzy point symmetry of m -[n]acenes is analyzed according to their symmetry of the D_{2h} point group. The irreducible representation components of their π -MOs are shown in Fig. 13. Noticeably, all these molecules share one pair of j/j^M versus X curves, where X stands for the fraction of any of the specified irreducible representation component.

It should be noted that in Fig. 13, for the π -MOs belonging to $A_u(C_{2h})$, only the fraction of the component of $A_u(D_{2h})$, i.e. $X[A_u(D_{2h})]$, is listed, while the fraction of the component of $B_{3u}(C_{2h})$, i.e. $X[B_{3u}(D_{2h})] = 1 - X[A_u(D_{2h})]$, is not shown. Similarly, for the π -MO belonging to $B_g(C_{2h})$, only the fraction of the component of $B_{1g}(D_{2h})$, i.e. $X[B_{1g}(D_{2h})]$, is shown, while the fraction of the component of $B_{2g}(D_{2h})$, i.e. $X[B_{2g}(D_{2h})] = 1 - X[B_{1g}(D_{2h})]$, is omitted. Therefore, there are some apparent differences between Figs. 10 and 13, for example, the symmetry of the distribution pattern related to the non-bonding energy level ($j/j^M = 0$) in Fig. 13 are not so perfect as that in Fig. 10. However, in fact, if the omitted irreducible represent components about the D_{2h} point group are also included in Fig. 13, this difference will

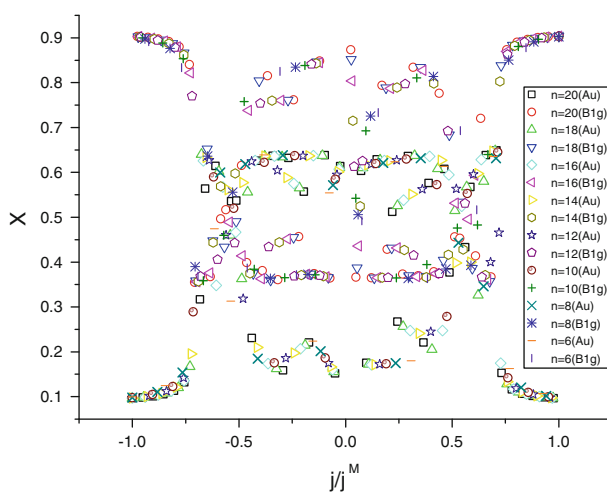


Fig. 13 The distribution pattern of the fraction of the irreducible representation component(X) of π -MO of m -[n]acenes about the D_{2h} point group

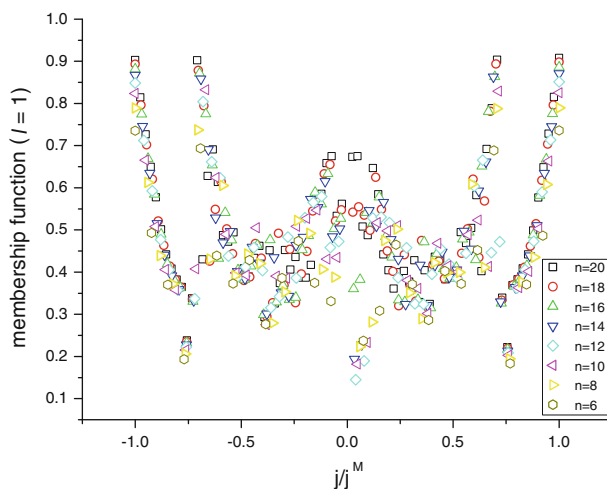


Fig. 14 The membership function of the π -MO involves translating one structure unit length of the m -[20]acene

disappear. Therefore, the study on the fuzzy point symmetry of m -[20]acene can surely be extended to other m -polyacenes.

Of course, for the π -MO of m -[20]acene, the investigation of the fuzzy symmetry related to some space symmetry transformation (Fig. 11) can also be extended to other m -[n]acenes with different n values: The membership function of the π -MO of m -[n]acene is related either to a translation slide reflection or to a screw rotation, and is calculated using Eq. (1) and shown in Fig. 14. The MOs related to the irreducible representations A_u and B_g of C_{2h} are calculated by Gaussian program, and the same

MO involved in different irreducible representations is labeled by the same symbol, just as what adopted in Fig. 11.

The similar analysis can be done to the π -MOs of m -[20]acene and m -[n]acenes related to the space parallel symmetry transformation, which is omitted here.

By the way, the molecules of p -polyacenes possess the D_{2h} point group, and their MOs belong to some pure irreducible representations of D_{2h} point group, such as A_u , B_{1g} , B_{2g} and B_{3u} . While the molecules of m -polyacenes only possess the C_{2h} symmetry, a subgroup of D_{2h} , and their MOs belong possibly to A_u and B_g irreducible representations of C_{2h} point group. Therefore, only the fuzzy symmetry of the molecule of m -[20]acene can be analyzed basing on the D_{2h} point group symmetry, while its MOs belong to a fuzzy representation which will be a superposition of different irreducible representations of D_{2h} point group. In fact, the π -MOs of m -[20]acene belonging to $A_u(C_{2h})$ will also pertain to the fuzzy representation of the superposition of $A_u(D_{2h})$ and $B_{3u}(D_{2h})$, and the π -MOs belonging to $B_g(C_{2h})$ pertain to the fuzzy representation of the superposition of $B_{1g}(D_{2h})$ and $B_{2g}(D_{2h})$. When more than one irreducible representation is included, the major one is denoted as the main representation. And finally, based on the D_{2h} point group, the MO correlation diagram of p -polyacenes can be drawn by using these irreducible representations, while for m -polyacenes, only the main or the next main representation can be used to build the MO (fuzzy) correlation diagram [15].

4 Conclusion

In the paper, we examine both p -polyacenes and m -polyacenes, which are the one-dimensional planar molecules with different point group symmetries and space group symmetries. In deed, these two kinds of planar molecules with fuzzy one-dimensional periodicity can be thought as the systems with the fuzzy group G_1^2 symmetry. The related fuzzy symmetry characters are analyzed, and the main conclusions are summarized as follows:

- (1) The p -polyacenes can approximately be considered as having the fuzzy one-dimensional periodic $tm/2$ group symmetry when the differences of the conjugated C–C bonds in benzene rings are ignored. They have D_{2h} symmetry according to the view of the point group. Thus, they can be dealt with in terms of one-dimensional crystal, each unit cell includes one benzene ring with two conjugated C–C bonds shared by the neighboring unit cells.
- (2) The membership function of p -polyacenes skeletons related to the parallel transformation is examined. With the increasing of the number of the benzene ring, the membership function increases and approaches to one. In addition, the membership function reduces to zero with the increasing of the translation length. Moreover, certain dependency relationship may exist between the molecular electronic spectrum and the membership function.
- (3) As an example, the p -[20]acene is analyzed. The π -MO energies distribute into two branches with an energy gap and at the two sides of the nonbonding energy level, when the serial number of the π -MO determined according to the irreducible representation of D_{2h} point group which the π -MO is belonged

to. However, when the serial number is specified as $j(\text{IRep}(O/V))$, the plot of the energy of the π -MO, $E(\pi\text{-MO})$, versus the relative serial numbers, $j(\text{IRep})/j^M(\text{IRep})$, shows one pair of distribution curves symmetrically and smoothly extending at both sides of the nonbonding energy level for each irreducible representation.

- (4) For the p -[n]acenes with different n , the related curves mentioned in the above conclusion (3) almost overlap into one curve when using the relative serial numbers (namely, the serial number/the maximum serial number) as the abscissa.
- (5) The m -polyacenes can be thought approximately as possessing the fuzzy one-dimensional periodic group $ta/2$ symmetry when the differences of the conjugated C–C bonds in benzene rings are not stressed. The m -polyacenes have C_{2h} symmetry when the number of the benzene ring is even, in terms of the point group. They can be dealt with according to one-dimensional crystal, each unit cell includes two benzene rings in which two C–C bonds shared with the neighboring unit cells, and as an altered view, each benzene ring may be considered as one structure unit, and in each structure unit two conjugated C–C bonds are shared with the neighboring structure unit.
- (6) The m -[20]acene is taken as an example to be analyzed. The π -MO energies are distributed forming a curve pattern, symmetrically but non-smoothly, at the two sides of the nonbonding energy level. Different from that of p -[20]acene, there are two narrower energy gaps, besides the major one between OMO and VMO. The molecule possesses C_{2h} point group which is a subgroup of D_{2h} , thereby, these π -MOs will belong to the superposition of more than one irreducible representation if analyzed according to D_{2h} point group. So, some of the π -MOs belong mainly to one irreducible representation of D_{2h} , while there are other π -MOs which are belonging to various irreducible representations of D_{2h} with large fraction. And the energies and fuzzy symmetry characters of the former class of π -MOs are similar to that of the π -MOs of the p -[20]acene, for the latter ones the differences are apparent.
- (7) The m -[n]acenes with different specified number n of the benzene ring are analyzed. The results are similar to that of m -[20]acene. The related curves mentioned in the above conclusion (6) will almost overlap together for the m -[n]acenes with different n , when plotted using the relative serial numbers (namely, the serial number/the maximum serial number).

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