The fuzzy D_{6h}-symmetries of azines molecules and their molecular orbitals

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Based on our previous study on the elementary characterization of fuzzy symmetry, we inquire into the fuzzy symmetries of some simple linear and plane molecules. These systems belong to point groups that include the identity and twofold symmetry elements, but not include higher multi-fold symmetry ones, and their molecular orbitals (MOs) only belong to one-dimension irreducible representations. In this paper, we take the azines as a typical model to examine the fuzzy symmetry in relation to the D_{6h} point group. As this group includes multi-fold symmetry elements such as a six-fold rotation axis, some of the MOs may belong to two-dimensional irreducible representations. We inquire into the fuzzy symmetry of these molecules and their MOs in terms of membership functions, representation components and correlation diagrams. In addition to these neutral closed shell molecules, pyridine hydride radical, anion, and cation are also analyzed.

KEY WORDS: fuzzy symmetry, D_{6h} point group, azines

1. Introduction

In the theoretical chemistry, the research on fuzzy symmetry is an interesting field. Important results have been obtained [1–4]. In our previous work [5–8], based on the study of the fuzzy symmetry characterization of molecules and their orbitals (usually in real space), we have analyzed the fuzzy symmetry of some molecules in connection with the primary point group. Now we will start to study the fuzzy symmetry related to more complex point groups that include and only include one multi-fold symmetry element. The Molecular Orbitals (MOs) of a molecule with such a symmetry element may also belong

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to two-dimensional but not higher dimensional irreducible representations, along with the one-dimensional ones. The benzene molecule is a typical model that possesses the D$_{6h}$ point group symmetry. Its MOs belong to certain irreducible representations of this group, which may be analyzed according to the usual quantum chemistry methods. As a MO belongs to a two-dimensional irreducible representation, such a MO cannot be the eigenstates of the all symmetry transformation in D$_{6h}$ point group, simultaneously [9, 10]. However, the two MOs complete set of the corresponding two-dimensional irreducible representation will be the eigenstate of the all transformations in D$_{6h}$ point group, simultaneously. Such a single MO is the eigenstate of some but not all transformations in D$_{6h}$ point group, and then the membership functions of such a MO will be equal to one only for some of but not for all of the symmetry transformations in the D$_{6h}$ point group. The relative membership functions in relation to some transformations may be less one.

The molecules similar to benzene (i.e., benzene-like molecules) ought to belong to the fuzzy D$_{6h}$ symmetry, and their symmetry characterization is more complicated than simpler cases such as ethylene tetra-halide molecules with D$_{2h}$ fuzzy symmetry which only involves the one-dimensional irreducible representations. A single MO may be assigned to either the one-dimensional or two-dimensional irreducible representations. There are two-MO fuzzy sets in the benzene-like molecules that corresponding to two-MO complete sets of a certain two-dimensional irreducible representation of D$_{6h}$ point group in benzene. For the fuzzy set, the membership function in general should be less than one, although the functions related to the symmetry transformations of D$_{6h}$ point group may be larger than those of the single MO. This is different from the benzene molecule with the complete D$_{6h}$ point group symmetry. The difference between these molecules and those in our previous work [5–8] is the multi-fold (fuzzy) symmetry element. How to analyze the molecular fuzzy symmetry when a multi-fold symmetry element exists? We will discuss this problem in detail in this paper. To stress the main point, we may only analyze one fuzzy symmetry element sometimes, i.e., the relative fuzzy symmetry by means of the C$_6$ point group. In this paper, we will use azines, pyridine, diazines, and the pyridine hydride (the radical, cation or anion) as our examples. The derivatives of these molecules have wide-ranging applications in solar, dyes, and other industries [11, 12]. To study the symmetry and other structure characterization of these molecules, it may be useful for the research on these derivatives.

2.   Computational details

In this paper, the atomic numbering and the coordinate axes of the molecule are shown in figure 1. Using the quantum chemical calculation at various levels within Gaussian 98 program [13], we can obtain the relevant MOs which are combined by the atomic orbitals (AOs) in the atomic valance shell. The
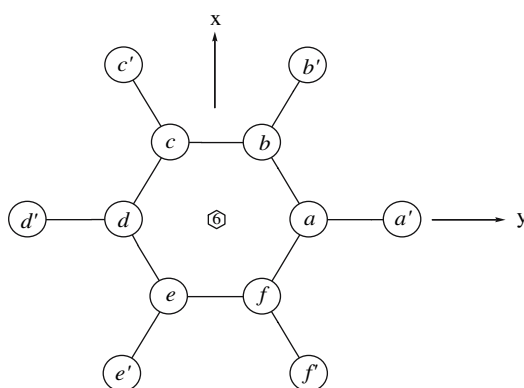
Figure 1. The coordinate axes and the atomic numbering of the benzene-like molecule. Where *a, b, c, d, e*, and *f* denote six atoms of the hexatomic ring, they may be the carbon atoms or hetero-atoms. *a', b', c', d', e'*, and *f'* denote the atoms that link to the hexatomic ring, and may be a hydrogen atom or an empty position. The molecular plane lies on the *xy* coordinate plane, and the (fuzzy) sixfold axis is taken as the *z*-axis.

π-MOs are combined by the *p*-AOs which are perpendicular to the molecular plane, whereas the σ-MOs by the sp^2-AOs in the molecular plane.

The membership functions of symmetry transformations $\hat{G}$ in a point group may be obtained by the method as described in the previous papers [5–8]. If any atom *J* of a molecule *M* moves to the position of the atom *GJ* after the operation $\hat{G}$ of the point group *G* is carried out, then the membership function of this molecule is defined as,

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

where Y_J and Y_{GJ} are denoted the criteria of atom *J* and *GJ*, respectively. For the whole molecule skeleton, *Y* may be the atomic number, *Z*. As for the MO, according to the LCAO-MO theory, the ρth MO Ψ_ρ may be denoted as:

$$\Psi_\rho = \sum_J \sum_i a_\rho(J, i)\phi(J, i), \tag{2}$$

where $\phi(J, i)$ is the *i*th AO of *J*th atom, and $a_\rho(J, i)$ is the corresponding LCAO coefficient which is usually real. The criterion of $\phi(J, i)$, Y_{Ji}, is $a_\rho^2(J, i)$, and then equation (1) as follows:

$$\mu_Y(\hat{G}/G; M) = \left[\sum_J \sum_i (Y_{Ji} \wedge Y_{GJi})\right] \Big/ \left[\sum_J \sum_{Ji} (Y_{Ji})\right]. \tag{3}$$

If for every atom only one AO is used in the combination of a MO, equation (3) will be reduced to equation (1).

As for the benzene-like molecule, although the membership function may also be calculated as mentioned above, the overlap case will be more complex owing to the existence of two-dimensional irreducible representations. For the benzene molecule (as shown in figure 1, the cycles in the hexatomic ring represent the carbon atoms, and others the hydrogen atoms), the π-MO will belong to one of the A2u, B2g, E1g or E2u irreducible representations in D_{6h} point group, whereas the σ-MO will belong to one of the A1g, A2g, B1u, B2u, E1u or E2g irreducible representations in this group. However, for the benzene-like molecule, the π-MO will belong to the fuzzy representations combined with a certain component ratio by the overlap of some of the A2u, B2g, E1g, and E1u irreducible representations, but the σ-MO will belong to the fuzzy representation combined with a certain component ratio by the overlap of some of the A1g, A2g, B1u, B2u, E1u, and E2g irreducible representations in D_{6h} point group. After we obtained the MOs using the quantum chemical calculation at various levels within Gaussian 98 program [13], we calculated the irreducible representation components, utilizing the projection operator [14].

The $a_\rho(J, i)$ in MO may be as follows:

$$a_\rho(J, i) = a_\rho(J, i; \Gamma_1) + a_\rho(J, i; \Gamma_2) + a_\rho(J, i; \Gamma_3) + \cdots + a_\rho(J, i; \Gamma_r)$$
$$= \sum_R a_\rho(J, i; \Gamma_R), \tag{4}$$

where the $\Gamma_R = \Gamma_1, \Gamma_2, \ldots, \Gamma_r$ are the various irreducible representations (they may not all be one-dimensional) in relation to $a_\rho(J, i)$. The $a_\rho(J, i; \Gamma_R)$ should be related to the irreducible representation Γ_R. Therefore, for the ρth MO, Ψ_ρ may be obtained as follows:

$$\Psi_\rho = \sum_J \sum_i \left[\sum_R a_\rho(J, i; \Gamma_R) \right] \phi(J, i)$$
$$= \sum_R \left[\sum_J \sum_i a_\rho(J, i; \Gamma_R) \phi(J, i) \right] \equiv \sum_R \Psi_{\rho R}, \tag{5}$$

where the $\Psi_{\rho R} = \sum_J \sum_i a_\rho(J, i; \Gamma_R) \phi(J, i)$ is only the part in connection with the irreducible representation Γ_R. As the projection operator $\hat{P}(\Gamma_R)$ method [14], such operator may operate to a certain function and retain the part-function only related to the irreducible representation Γ_R. As to above certain MO Ψ_ρ, we can get $\Psi_{\rho R}$, i.e.,

$$\hat{P}(\Gamma_R)\Psi_{\rho R} = \left[\sum_J \sum_i a_\rho(J, i; \Gamma_R) \phi(J, i) \right]. \tag{6}$$

The irreducible representation Γ_R component of Ψ_ρ:

$$X(\Psi_\rho; \Gamma_R) = \left[\sum_J \sum_i a_\rho^2(J, i; \Gamma_R) \right] \Big/ \left[\sum_J \sum_i a_\rho^2(J, i) \right]. \tag{7}$$

It would conform to the normalized condition:

$$\sum_R X(\Psi_\rho; \Gamma_R) = 1. \tag{8}$$

We may use the projection operator method in quantum chemistry to obtain the corresponding irreducible representation components of MOs with the fuzzy symmetry related to various point groups. By means of this method, obviously, we can also obtain the same results with respect to the MOs for ethylene tetra-halide molecules with the D$_{2h}$ fuzzy symmetry as we did in [8]. The projection operator method is more general and convenient for programming, and then we analyze some typical molecular systems further.

We consider the π-MOs in the hexatomic ring of some simple benzene-like molecules. To start with, we utilize some suitable sub-group to replace the complete point group (D$_{6h}$) and the un-normalized projection operator before the further calculate. For the π-MOs in the hexatomic ring of some simple benzene-like molecules, we use the C$_6$ group to replace the D$_{6h}$ point group. For the four irreducible representations that the related π-MOs belong, A2u, B2g, E1g, and E2u of D$_{6h}$ point group are replaced by the four irreducible representations, A, B, E1, and E2 of C$_6$ point group, respectively. We may then transform the irreducible representations of C$_6$ point group to those of D$_{6h}$.

As regards this four irreducible representations Γ_R of C$_6$ point group, the corresponding the un-normalized projection operators $\hat{P}(\Gamma_R^\#)$ may be obtained as follows by means of the character values of C$_6$:

$$\hat{P}(A^\#) = \hat{C}_6{}^0 + \hat{C}_6^1 + \hat{C}_6^2 + \hat{C}_6^3 + \hat{C}_6{}^4 + \hat{C}_6^5, \tag{9a}$$

$$\hat{P}(B^\#) = \hat{C}_6{}^0 - \hat{C}_6^1 + \hat{C}_6^2 - \hat{C}_6^3 + \hat{C}_6^4 - \hat{C}_6^5, \tag{9b}$$

$$\hat{P}(E1^\#) = 2\hat{C}_6^0 + \hat{C}_6^1 - \hat{C}_6^2 - 2\hat{C}_6^3 - \hat{C}_6^4 + \hat{C}_6^5, \tag{9c}$$

$$\hat{P}(E2^\#) = 2\hat{C}_6{}^0 - \hat{C}_6^1 - \hat{C}_6^2 + 2\hat{C}_6^3 - \hat{C}_6^4 - \hat{C}_6^5. \tag{9d}$$

The un-normalized $\Psi_{\rho R}$ can be obtained, as these projection operators $\hat{P}(\Gamma_R^\#)$ denoted in equation (9) operate on Ψ_ρ. The normalizing factors depend on the characterization and dimension of the irreducible representation for the relevant MO. The π MOs in various hexatomic rings with the same dimension of the MO representation should have the same normalizing factor. Therefore through calculation, we may find the normalizing factor of a certain π MO with the irreducible representation Γ_R in the hexatomic ring of benzene molecule, and then

use it as a normalizing factor of the other πMO with the same irreducible representation Γ_R in the hexatomic ring of the benzene-like molecule. In this way, we can obtain the corresponding normalized $\Psi_{\rho R}$. Then we can get the relative irreducible representation (Γ_R) component of Ψ_ρ. Meanwhile, we may assign the A, B, E1, and E2 irreducible representations of C$_6$ point group to the A2u, B2g, E1g, and E2u irreducible representations of D$_{6h}$ point group, respectively, and directly.

The σ-MOs for the hexatomic ring of the benzene-like molecule may also be analyzed similarly. However it must be noticed: (1) owing to the combined components of the σ-MOs that includes the sp^2-AOs in the valance shell of the hexatomic ring, it is more complex than that of the π-MO because the calculation will be more prolix; (2) only four irreducible representations of D$_{6h}$are adopted by the πMOs, but six irreducible representations of D$_{6h}$, including the A1g, A2g, B1u, B2u, E1u, and E2g by the σ-MOs. As we use the C$_6$ point group to analyze the σ-MOs, the related E1 and E2 irreducible representations may be assigned to the E1u and E2g irreducible representations of D$_{6h}$, respectively. However, the A irreducible representation of C$_6$ may be assigned to either A1g or A2g of D$_{6h}$, and the B irreducible representation of C$_6$ may be assigned to either B1u or B2u of D$_{6h}$. Therefore, we must decompose both A and B irreducible representations further, or we may use other sub-group to replace C$_6$ point group and construct the relevant projection operators. Of cause, we may use the D$_{6h}$ point group to construct the projection operators, directly. As for the fuzzy symmetry of the σ-MO, the calculation will be lengthier than that for the π-MO, although the basic calculation rules are the same.

3.   Results and discussion

3.1.   The fuzzy symmetry for the molecular orbitals of benzene

As is well known, benzene molecule has the D$_{6h}$ point group symmetry. Its MOs belong to certain irreducible representations of this group. However, any single MO that belongs to a multi-dimensional irreducible representation should be not the common eigenstate of the all symmetry transformation in D$_{6h}$. Only the MO complete set of this multi-dimensional irreducible representation may be the common eigenstate of all the symmetry transformations in D$_{6h}$ point group. That means for such single MO, the membership functions corresponding to various symmetry transformations in D$_{6h}$ are not all equal to one. Therefore, we may analyze their fuzzy symmetry.

Every carbon atom of benzene molecule has four AOs in the valence shell, and 24 AOs for all ring carbons; these AOs with the six 1s AOs of related hydrogen atoms may combine to form 30 MOs. According to our AM1

Table 1
The LC*pz*-AO coefficients of the π MOs in the valance shell of C_6H_6.

MO-calculated level	α_1	α_2	α_3	α_4	α_5	α_6
HMO	0.4083	0.5000	0.2887	0.2887	0.5000	0.4083
AM1	0.3311	0.4594	0.2652	0.3316	0.5743	0.5300
HF/STO-3G	0.3333	0.4601	0.2656	0.3299	0.5713	0.5244

(or HF/STO-3G) calculation, we obtained the irreducible representations of D$_{6h}$ as follows (in sequence of energy increase order),

Occupied: (A1g) (E1u) (E1u) (E2g) (E2g) (A1g) (B1u) (B2u) (E1u) (E1u) (πA2u) (E2g) (E2g) (πE1g) (πE1g).

Virtual: (πE2u) (πE2u) (πB2g) (E1u) (E1u) (B1u) (A1g) (E2g) (E2g) (E2g) (E1u) (E1u) (A2g) (B1u),

where the π symbol before the irreducible representation labels denotes the π-MO, and other the σ-MO. Now we analyze the π-MOs in the valance shell of benzene molecule at the HMO, AM1, and HF/STO-3G levels of theory. For all these levels, the six π-MOs may be denoted as follows:

$$\Psi_1(A2u) = \alpha_1[\Phi_a + \Phi_b + \Phi_c + \Phi_d + \Phi_e + \Phi_f], \qquad (10a)$$

$$\Psi_2(E1g) = \alpha_2[\Phi_b + \Phi_c - \Phi_e - \Phi_f], \qquad (10b)$$

$$\Psi_3(E1g) = \alpha_3[2\Phi_a + \Phi_b - \Phi_c - 2\Phi_d - \Phi_e + \Phi_f], \qquad (10c)$$

$$\Psi_4(E2u) = \alpha_4[2\Phi_a - \Phi_b - \Phi_c + 2\Phi_d - \Phi_e - \Phi_f], \qquad (10d)$$

$$\Psi_5(E2u) = \alpha_5[\Phi_b - \Phi_c + \Phi_e - \Phi_f], \qquad (10e)$$

$$\Psi_6(B2g) = \alpha_6[\Phi_a - \Phi_b + \Phi_c - \Phi_d + \Phi_e - \Phi_f], \qquad (10f)$$

where $\Psi_2(E1g)$ and $\Psi_3(E1g)$ are the degenerate HOMOs, whereas $\Psi_4(E2u)$ and $\Psi_5(E2u)$ are the degenerate LVMOs. Here Φ's are corresponding *pz*-AOs. For all these levels of calculations, equation (10) should be true, but the values of α_i ($i = 1$ to 6) may be different at various levels (table 1).

The MOs, $\Psi_1(A2u)$, and $\Psi_6(B2g)$, which belong to the one-dimensional irreducible representation of D$_{6h}$ group, and so all of the membership functions of related various symmetry transformations are equal to one. Here the square of the LCAO coefficient is used as the atomic criterion. Consequently, in such MOs, each atomic criterion would be the same, i.e., $\alpha_a^2 = \alpha_b^2 = \alpha_c^2 = \alpha_d^2 = \alpha_e^2 = \alpha_f^2$,

to ensure any atomic criterion unchanged after any symmetry transformation in relation to D$_{6h}$, and then the corresponding membership function must be one.

However, the degenerate MOs Ψ_2(E1g) and Ψ_3(E1g) belong to a two-dimensional irreducible representation E1g, and form a complete basis set. Similarly, MOs Ψ_4(E2u) and Ψ_5(E2u) also belong to a two-dimensional irreducible representation, E2u, and form a complete basis set. As we select such, the single MO will not be the eigenstate of all transformations in D$_{6h}$, but may be so of all transformations in D$_{2h}$. The membership functions of all corresponding symmetry transformations in D$_{2h}$ are equal to one, but the membership functions of other symmetry transformations in the D$_{6h}$ point group are less to one. For the Ψ_2(E1g) MO, where both atomic criteria of atoms a and d are null, but all other atomic criteria are equal to α_2^2. According to the symmetry transformation of the rotation of 60^0 around the C$_6$ axis, the membership function equals 1/2. The Ψ_3(E1g) MO may be analyzed in the same fashion, and the membership function for the symmetry transformation of the rotation of 60°around the sixfold axis equals 1/2, too. This means that for such degenerate MOs, both their orbital energies and their membership function are equal. However, for the above degenerate MO complete set, all of the membership functions are equal to one, where the atomic criterion is the summation of the square of LCAO coefficients. As for the MO set {Ψ_2(E1g),Ψ_3(E1g)}, the atomic criteria of atom a,b,c,d,e, and f are $4\alpha_2^2$, $\alpha_2^2 + \alpha_3^2$, $\alpha_2^2 + \alpha_3^2$, $4\alpha_3^2$, $\alpha_2^2 + \alpha_3^2$, and $\alpha_2^2 + \alpha_3^2$, respectively. Since membership functions of all these symmetry transformations in D$_{6h}$ point group equal to one, the necessary and sufficient condition should be that all of these criteria must be the same, i.e., $\alpha_2^2 = 3\alpha_3^2$ should be true. As such we known, the coefficients α_2 and α_3 must depend on each other. Such necessary and sufficient condition will be true at various levels, and it may be checked by the data in table 1. We may analyze the MO set {Ψ_4(E2u),Ψ_5(E2u)} in the same way. The results are the same at various MO theoretical levels. It should be noted that when a single MO belongs to a multi-dimensional irreducible representation, its irreducible representation is pure, but some membership functions may be less one. Furthermore, as to other similar π-MOs in the hexatomic ring (including the hetero-atoms and the substituents), we may analyze their fuzzy symmetry based on above results. Their fuzzy representations may overlap by means of some of above four irreducible representations.

The σ-MOs may be discussed similarly, even though the AOs that combine to form them include py-,px-, and s-AOs. The irreducible representations to which the σ-MOs belong are A1g, A2g, B1u, B2u, E1u, and E2g. As for other similar hexatomic ring molecules, the fuzzy symmetry of σ-MOs may be analyzed further, too. The fuzzy representations of their σ-MOs may be the overlap of the six-irreducible representations. According to the chemical view, the π-MOs are more active than σ-MOs, therefore, we will not analyze the σ-MOs in this paper.

3.2.   The fuzzy symmetry of pyridine

Different from benzene molecule, pyridine molecule is composed of the five carbon atoms and one nitrogen atom in its ring, and then the fuzzy D_{6h} symmetry can be used. The geometrical structure of this molecule may be shown as in figure 1, and the d atom in the ring is a nitrogen atom, whereas others are the carbon atoms. The atoms that connect the hexatomic ring are the hydrogen atoms except position d' where there is no atom. In addition to the mirror of molecular plane, this molecule has also a two fold axis and another mirror plane that is perpendicular to the molecular plane, through the nitrogen atom and its *para*-carbon atom. Thus pyridine molecule should belong to C_{2v} point group, with the *y*-axis being its main-axis. According to the fuzzy D_{6h} symmetry, using the equation (1), we may calculate the membership function of pyridine molecular skeleton. Using the atomic number (Z) as the criterion of the atom and zero as the criterion of an empty atom (d'), we can easily find that the membership functions of the all symmetry transformations in C_{2v} point group as above, are equal to one, whereas those of other symmetry transformations in D_{6h} point group, are equal to 0.9524. For this fuzzy D_{6h} point group, according to the idea of Zadeh [15,16], it may be symbolized as:

$$\underset{\sim}{D}_{6h} = \sum_{G \subset C_{2v}} (1/\hat{G}) + \sum_{G \not\subset C_{2v}} (0.9524/\hat{G}), \tag{11}$$

where $G \subset C_{2v}$ and $G \not\subset C_{2v}$ represent the summation in relation to the symmetry transformation $\hat{G}$ which belong to or not to the symmetry transformation set in the C_{2v} point group above, respectively. It may show that the molecular symmetry of this molecule would be near that of D_{6h} point group because the membership functions of all the symmetry transformations in D_{6h} point group are more than 0.95. There are four symmetry transformations $\hat{G}$ with $G \subset C_{2v}$, and twenty with $G \not\subset C_{2v}$. Some symmetry transformations $\hat{G}$ are equivalent to those in benzene (D_{6h} point group), but not equivalent in benzene-like molecule. For example, three twofold axes through two *para*-atoms of benzene molecule are equivalent elements in D_{6h}. However, in pyridine molecule, the twofold axis through the *para*-CN-atoms and the two twofold axes through the *para*-CC-atoms will not be equivalent in fuzzy D_{6h}. We would like to introduce some different symbols to distinguish these symmetry transformations. The reflection transformations about the mirrors perpendicular to molecular plane can be labeled as $\hat{M}(P;qr)$ and $\hat{M}(N;qr)$, where qr may be *ad, be* or *cf* to denote the two *para*-atoms. $\hat{M}(P;qr)$ means the cross-line between the mirror and molecular plane through the points q and r. $\hat{M}(N;qr)$ means the normal line of the mirror lying on the molecular plane through the points q and r. The rotations 180°

about the twofold axes lain on the molecular plane, can be symbolized as $\hat{C}(P;qr)$ and $\hat{C}(N;qr)$, where $\hat{C}$ (P;qr) and $\hat{C}$ (N;qr) denoted the relative twofold axes through and orthogonal qr, respectively. $\hat{C}(6,l)$ and $\hat{S}(6,l)$ denote the symmetry transformations of $l(l = \pm1, \pm2, \pm3)$ times rotation about the sixfold rotation axis and rotation-reflection about the sixfold roto-reflection axis, respectively. $\hat{E}$ and $\hat{M}(h)$ are the identity transformation and the reflection about the molecular plane as mirror, respectively. As for the center inversion symmetry transformation, $\hat{i}$, it is $\hat{S}(6,3)$. After defining these symmetry transformations, we may start to analyze the fuzzy symmetry of pyridine MOs.

Using the above methods, we have been calculated at AM1 level the various irreducible representation components included in the six π-MOs of the hexatomic ring in pyridine molecule, and results are shown in table 2. The π MO ordinal numbers are derived according to the energy order of the π MO (not including the σ-MO). For benzene molecule, π MO-2 and 3 are the degenerate HOMOs, π MO-4 and 5 are the degenerate LVMOs. Comparison of the π MOs of pyridine and those of benzene molecule it is shown that the main representations (the irreducible representation with maximal components) of pyridine π-MOs are the same as the 'pure' ones of benzene π-MOs. Meanwhile, all the corresponding irreducible representation components are much near one. The fuzzy correlation diagram[8] between the π MOs of pyridine and those of benzene may be matched. It is noteworthy that for benzene the π-MOs belonging to the two-dimensional irreducible representation are degenerate, but they are not for pyridine. That is to say, the pyridine π-MO set that belong to a same two-dimensional irreducible main-representation these two MOs will still not be degenerate. Accordingly, their energy and some membership functions will not be the same. Therefore, the fuzzy irreducible representations will be different from those of the "pure" ones. Such fuzzy representations that both the pyridine π-MO-2 and 3 belong, according to data in table 2, may be expressed as,

$$\underset{\sim}{\Gamma}(\pi\,\mathrm{MO}\text{-}2) = 0.01972\mathrm{A2u} + 0.00005\mathrm{B1g} + 0.97748\mathrm{E1g} + 0.00275\mathrm{E2u}, \quad (11a)$$

$$\underset{\sim}{\Gamma}(\pi\,\mathrm{MO}\text{-}3) = 0.99967\mathrm{E1g} + 0.00033\mathrm{E2u}. \quad (11b)$$

Although the fuzzy representations of π MO-2 and 3 for pyridine are similar, and both are close to the pure E1g irreducible representation, this may be different for some other molecules, and examples may be found in this paper (section 3.4).

The results as above at HF/STO-3G level are similar. In figure 2, the irreducible representation components of pyridine π MOs at various levels are shown. For reference, the irreducible representation components of benzene π MOs are also shown in the same figure, and the results are the similar at

Table 2

The irreducible representation components of the π MOs in the valance shell of C_5H_5N in relation to D_{6h} at AM1 level.

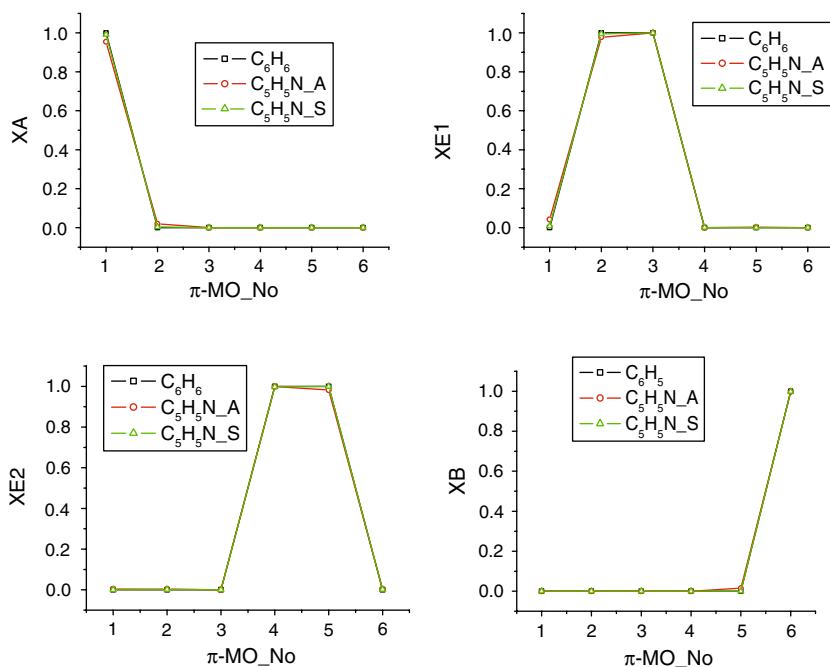| π MO serial order	Irreducible representation components				The main representation and its components
	A2u	B1g	E1g	E2u	
π MO-1	0.95384	0.00047	0.04169	0.00399	A2u—0.95384
π MO-2	0.01972	0.00005	0.97748	0.00275	E1g—0.97748
π MO-3	0	0	0.99967	0.00033	E1g—0.99967
π MO-4	0	0	0.00023	0.99977	E2u—0.99977
π MO-5	0.00025	0.01501	0.00232	0.98242	E2u—0.98242
π MO-6	0.00001	0.99706	0.00010	0.00283	B2g—0.99706

Figure 2. The irreducible representation components for the π MOs of pyridine in relation to the D_{6h} point group at various levels of theory. Where the vertical axes $X\Gamma$ (Γ = A, B, E1 or E2) denote the components of the Γ representations that the MOs belong to; and the horizontal axis, the π-MO_No denotes the serial number of the π MOs. $C_5H_5N\_A$ and $C_5H_5N\_S$ denote at AM1 and HF/STO-3G levels, respectively. Here C_6H_6 denotes the result of benzene for reference.

various levels. It is evident that the irreducible representation components of pyridine π MOs are much close to each other at the AM1 and HF/STO-3G levels, and they are near that of the corresponding π MO in benzene molecule.

Now we cut the symmetry transformations in the D_{6h} point group into four subsets:

$$G0 = \{\hat{G}_0\} = \{\hat{E}, \hat{M}(\text{ h}), \hat{M}(P, ad), \hat{C}(P, ad)\}, \tag{12a}$$

$$G1 = \{\hat{G}_1\} = \{\hat{M}(L, ab), \hat{M}(L, cd), \hat{C}(L, ab), \hat{C}(L, cd), \hat{C}(6, \pm 1), \hat{S}(6, \pm 1)\}, \tag{12b}$$

$$G2 = \{\hat{G}_2\} = \{\hat{M}(P, be), \hat{M}(P, cf), \hat{C}(P, be), \hat{C}(P, cf), \hat{C}(6, \pm 2), \hat{S}(6, \pm 2)\}, \tag{12c}$$

$$G3 = \{\hat{G}_3\} = \{\hat{M}(L, bc), \hat{C}(6, 3), \hat{C}(L, bc), \hat{i}\}. \tag{12d}$$

The membership functions of these symmetry transformations for pyridine and benzene π MOs may be obtained using the method mentioned in section 2 of this paper. For equation (12), we may designate a certain transformation as the typical transformation, and for the subset $Gm (m = 0, 1, 2, 3)$, the $\hat{C}(6, m)$ may be taken as the representative and called the typical symmetry transformation. In fact, it corresponds to the analysis of the fuzzy symmetry with C_6 point group. Sometimes, this is convenient, but not necessary.

The membership functions in relation to all symmetry transformations in $G0$ subset are equal to one. As to other subsets, the membership functions in relation to all symmetry transformations of the same subset should have the same values, but those of different subsets may be different as shown in figure 3. It is notable that the difference among the membership functions may be more obvious than that among the irreducible representation components. By the way, for the abscissa coordinate in figure 3, It is apparent that for both pyridine molecular skeleton and their π-MO, the membership functions related to the symmetry transformations in $G0$ subset are equal to one. However, for the symmetry transformations in other subsets for pyridine molecular skeleton, all membership functions equal 0.9524, but those for various π MOs may be different. After we obtain the membership functions of various π MOs, we can denote the corresponding Zadeh formulation [15, 16].

3.3. The fuzzy symmetry of diazine

Now we turn to analyze the fuzzy symmetry for diazine. There are three diazine isomers: o-diazine (pyridazine), m-diazine (pyrimidine), and p-diazine (pyrazine). The molecular geometries are still arranged as in Figure 1, where the four carbon atoms and two nitrogen atoms constitute the hexatomic ring. The nitrogen atoms occupy the (b, c), (b, f), and (a, d) positions of o-, m-, and p-isomers, respectively. For the hexatomic ring, each carbon atom will be adjacent to a hydrogen atom, but every nitrogen atom is adjacent to none. We may now analyze the membership functions of these three isomers in relation to various symmetry transformations. By means of
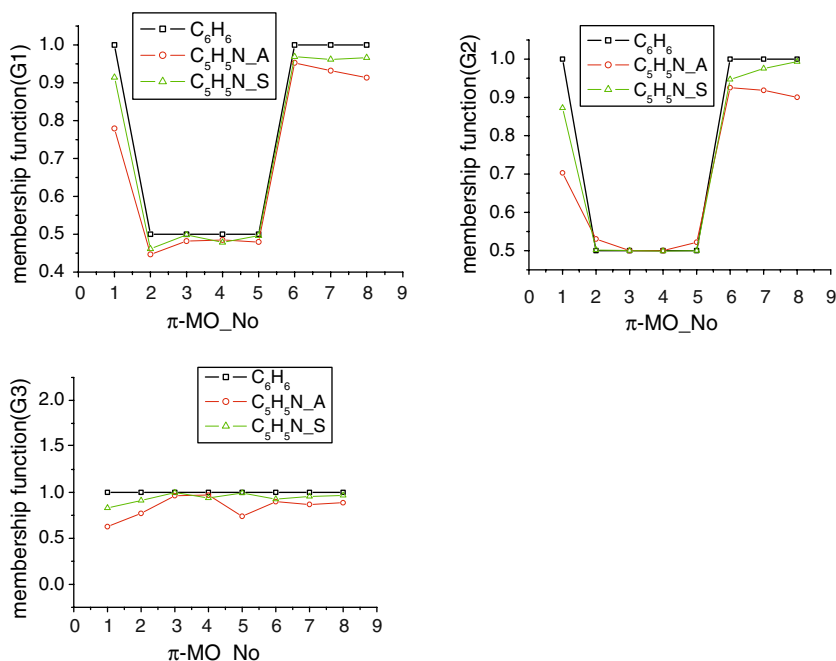
Figure 3. The membership functions of pyridine π MOs in relation to the symmetry transformations in the D$_{6h}$ point group, at various levels of theory. Where the vertical axes denote the membership functions in relation to the symmetry transformations, and the horizontal axis, π-MO_No, denotes the same as in figure 2, whereas 7 and 8 denote the MO (2 and 3) and MO (4 and 5) sets, respectively. C$_6$H$_6$ denotes the result of benzene for reference. The other symbols denote the same as in figure 2.

the C$_6$ point group and using the atomic numbers as the criteria, we can calculate the related membership functions via equation (1). Results are shown in table 3. Observation of the data in this table indicates that the membership functions are still a bit different are even though they may be equal to or close to one. It is important that the membership function for the o-C$_4$H$_4$N$_2$ molecule in relation to the $\hat{C}(6, \pm1)$ is bigger than that to the $\hat{C}(6, \pm2)$ because two nitrogen atoms in this molecule will move from bc-positions to cd-positions (figure 1) under the operation of $\hat{C}(6, \pm1)$ transformation, where c-position is occupied by nitrogen atom both before and after the operation. However, the nitrogen atom will move to de-positions after the operation of $\hat{C}(6, \pm2)$ transformation, whereas both d- and e-positions are not the positions of nitrogen atoms before the operation. The less membership function means the less similarity of the molecular geometries before and after the operation. On the other hand, the membership function μ of any elements x and y in a fuzzy group must satisfy [3, 17],

$$\mu(x) = \mu(x^{-1}),\tag{13a}$$

symmetry		Membership function			
transformation	C$_6$H$_6$	C$_5$H$_5$N	o-C$_4$H$_4$N$_2$	m-C$_4$H$_4$N$_2$	p-C$_4$H$_4$N$_2$
$\hat{C}(6, 0) = \hat{E}$	1	1	1	1	1
$\hat{C}(6, \pm 1)$	1	0.9524	0.9524	0.9048	0.9048
$\hat{C}(6, \pm 2)$	1	0.9524	0.9048	0.9524	0.9048
$\hat{C}(6, 3)$	1	0.9524	0.9048	0.9048	1

$$\mu(xy) \geqslant \mu(x) \wedge \mu(y), \tag{13b}$$

$$\mu(e) = 1, \tag{13c}$$

where x^{-1} is the inverse of x, and e is the identity element. Usually, equation (13a) and (13c) may be true. If both x and y are the $\hat{C}(6, \pm 1)$ transformation, then the xy ought to be the $\hat{C}(6, \pm 2)$ transformation. Thus, the relative membership function μ may not satisfy equation (13b). It means that for the o-C$_4$H$_4$N$_2$, in relation to C$_6$ or D$_{6h}$ point group transformation, the corresponding fuzzy symmetry set is not a fuzzy group. As two carbon atoms (or their adjoined hydrogen atoms) in o-positions of benzene are replaced by some other atoms, the relative fuzzy symmetry set would not form a fuzzy group. By the way, as the tri-atomic ring, this case will not appear owing to $\hat{C}(3, 1) = \hat{C}(3, -1)$.

Similarly, the irreducible representation components of these three isomers were obtained and shown in table 4 at the AM1 level, and similar figure as figure 2 can readily be obtained easily, but omitted here. These results are near close to those of benzene. Usually, we may neglect their symmetry defect for these MOs. Thus, their main irreducible representations would be the same as the "pure" ones of benzene π MOs. Their fuzzy correlation diagram may be matched.

According to the above analysis, we may inquire into the membership functions in relation to various symmetry transformations for the π MOs of these three isomers. Although the representations which these π MOs belong to are more "pure," but the relative membership functions may be somewhat different, each other. According to equation (12), we may classify the symmetry transformations into four subsets, by grouping the equal membership functions into the same subset. This methods may be used to all these three isomers, m-, o-, and p-C$_4$H$_4$N$_2$, however for the $G1$ and $G2$ subsets the contents in relation to the m- and o-C$_4$H$_4$N$_2$ isomers are different. As to the p-C$_4$H$_4$N$_2$, their membership function values of these two subsets are the same. Obviously, the reason is that both the common point groups for both m-C$_4$H$_4$N$_2$ and o-C$_4$H$_4$N$_2$

Table 4
The irreducible representation components for the π MOs in the valance shell of azines in relation to the D$_{6h}$ point group.

π MO_No	Irreducible representation components			
	XA	XB	XE1	XE2
C$_6$H$_6$				
1	1	0	0	0
2	0	0	1	0
3	0	0	1	0
4	0	0	0	1
5	0	0	0	1
6	0	1	0	0
C$_5$H$_5$N				
1	0.95384	0.00047	0.04169	0.00399
2	0.01972	0.00005	0.97748	0.00275
3	0	0	0.99967	0.00033
4	0	0	0.00023	0.99977
5	0.00026	0.01501	0.00232	0.98242
6	0.00001	0.99706	0.00009	0.00283
o-C$_4$H$_4$N$_2$				
1	0.90142	0	0.09475	0.00384
2	0.04921	0	0.95009	0.00070
3	0	0.00001	0.99765	0.00233
4	0.00044	0	0.00161	0.99795
5	0	0.02599	0.00093	0.97308
6	0	0.99492	0.00009	0.00499
m-C$_4$H$_4$N$_2$				
1	0.97146	0.00167	0.02357	0.00331
2	0	0	0.98998	0.01002
3	0.0105	0.00012	0.98679	0.00258
4	0.00025	0.01124	0.0022	0.98631
5	0	0	0.00663	0.99337
6	0.00003	0.99800	0.00009	0.00188
p-C$_4$H$_4$N$_2$				
1	0.98882	0	0	0.01118
2	0	$<10^{-5}$	1	0
3	0	0	1	0
4	0	0	0	1
5	0.00131	0	0	0.99869
6	0	0.99980	0.00020	0

are the proper subgroups for that of p-C$_4$H$_4$N$_2$. Although both o-C$_4$H$_4$N$_2$ and m-C$_4$H$_4$N$_2$ belong to the C$_{2v}$ point group, their main-axis directions are different, and the symmetry transformations in $G1$ and $G2$ are classified differently. On the other hand, the union subsets, $G1 \cup G2$, are the same for all of these isomers.

Besides the typical symmetry transformations, $\hat{C}(6, m)$, for the subsets Gm ($m = 0, 1, 2, 3$), others included in these subsets may differ for various isomers, depending on the common molecular symmetry point group of these isomers. The symmetry transformations for pyridine and m-diazine are the same, but they are different for o-diazine. As for the p-diazine, the symmetry transformations may be classified to the subsets, according to both the ways as for m-and o-diazine. However for these two methods, the union subsets G0∪G3 of p-diazine are the same, and so are its union subsets G1∪G2.

For comparing, the membership functions of the symmetry transformations in the subset $Gm(m = 0, 1, 2, 3)$ which include the $\hat{C}(6, m)$ are shown in Figure 4. It is evident that the membership functions of single πMO2 or πMO3 are less than those of the $\{\pi$MO2, πMO3$\}$ set, (π-MO_No:7). As for the $\{\pi$MO4, πMO5$\}$ set, (π-MO_No:8), the results are similar to those of (π-MO_No:7).

According to the D_{6h} point group, the main-irreducible representations which the πMOs of the azine hexatomic ring belong to are as follows: (A2u), (E1g), (E1g), (E2u), (E2u), and (B2g). They are the same as the irreducible rep-
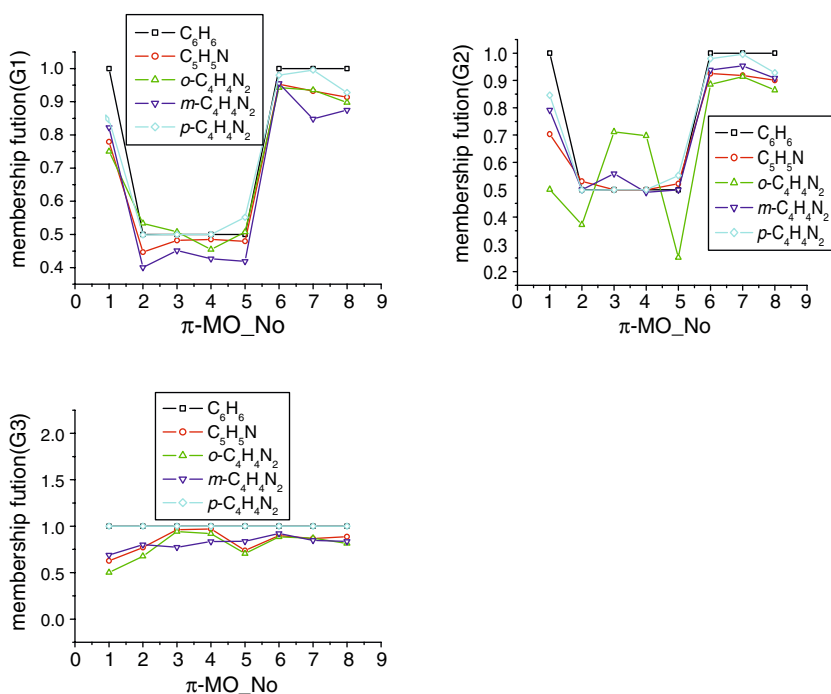

Figure 4. The membership functions of the AM1 πMOs of azines in relation to the symmetry transformations in the D_{6h} point group. Where the vertical axes denote the membership functions in relation to the symmetry transformations, the horizontal axis, π-MO_No, denotes the same as in figure 3. C_6H_6 denotes the result of benzene for reference.

resentations of the πMOs in benzene hexatomic ring. Therefore, the correlation diagram may be drawn and ought to be mapped by the D$_{6h}$ irreducible representation of one-to-one correspondence. It is noticed that the MO set of benzene, which belongs to D$_{6h}$ two-dimensional irreducible representation in real number field, is combined by two degenerate and orthogonal MOs. However, the corresponding MO set of azine in relation to a fuzzy two-dimensional irreducible representation are two non-degenerate MOs. Now we need to analyze how such two π-MOs of azine hexatomic ring correlate with and match each other. In general, we may analyze this using certain symmetry transformations, i.e., some subgroups. As the example shown in figure 5, the π-MOs of benzene which belong to E1g and E2u irreducible representation are degenerate, but the π-MOs of azine are not. By means of the symmetry transformations about the mirrors of xz- and yz-coordinate planes as shown in figure 1, we may analyze the representations of related π-MOs, these representations are either symmetrical or asymmetrical. Furthermore, we may attain the MO fuzzy correlation relationship. In general cases, the energies of the MOs belong to a same two-dimensional fuzzy irreducible representation will only differ a little, whereas their energetic order may differ at various theoretical levels. In figure 5, the result at the AM1 level is shown.

3.4.   *The fuzzy symmetry of pyridine hydride*

In our previous work, we only analyzed the fuzzy symmetry of the neutral closed shell molecule. Now we start to investigate the fuzzy symmetry for the radical and ion, which will be the preliminary preparation for the fuzzy symmetry probe of the chemical dynamic system. For example, the pyridine hydride (C_5NH_6), compared with the benzene molecule, replaces a carbon atom by a nitrogen atom in the ring. If the atomic numbers is set as the atomic criteria, according to equation (1), the membership function of the symmetry transformation in relation to the rotation of 60° around the sixfold axis is $42/43 = 0.97674$ which is more closer to unity than that of the molecules analyzed above. On the other hand, although the membership function of the skeleton of the radical, anion or cation of pyridine hydride is the same, the chemical characterizations will be different considerably. This difference should appear in the MO fuzzy symmetry. In table 5, the irreducible representation components in relation to D$_{6h}$ point group for the πMOs of the pyridine hydride radical, cation and anion are listed. Some of these main-representation components are between 0.75 and 0.9, which are less than those in table 4, although the main-representation and the "pure" irreducible representation of the corresponding π-MOs in benzene are the same. We also calculated the α- and β-spin MOs of pyridine hydride radical at the HF/STO-3G level, and the results are somewhat different from those at the AM1 level in table 5, but will not affect the following analysis essentially.
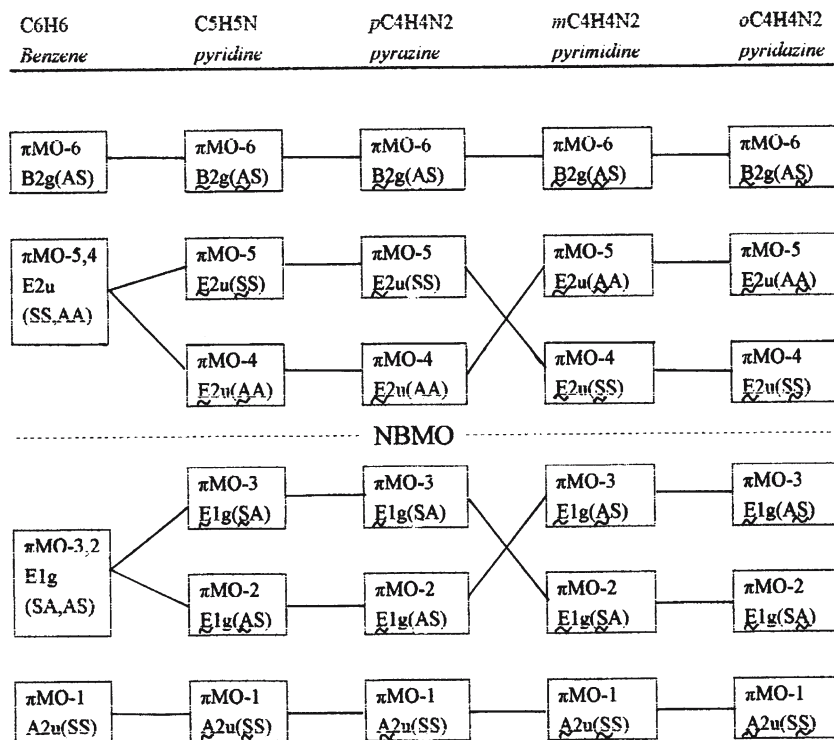
C6H6	C5H5N	pC4H4N2	mC4H4N2	oC4H4N2
Benzene	*pyridine*	*pyrazine*	*pyrimidine*	*pyridazine*

Figure 5. The AM1 π MO fuzzy correlation diagram for azines. The first row in every quad denotes the π MO serial number in the same order as the orbital energy, following with the irreducible representation in relation to the D$_{6h}$ point group. The symbols in brackets denote the irreducible representations (*S*, symmetrical, *A*, asymmetrical) about the mirrors with *xz* and *yz* coordinate planes (figure 1), respectively. The "∼" below the Irreducible representation symbol denotes related fuzzy irreducible representation.

Using the above method, we may obtain the correlation diagram (figure 6) for the π MOs of the radical, cation, and anion of pyridine hydride. From left to right in this figure, the order of columns is according to the order of the increase of electronic number, and the last column on pyridine is shown for comparison. The α-spin π MO-4 of the radical is the HOMO, but the π MO-4 of the anion is the LUMO. There is a σ-MO near π MO-4, and its energy level is higher than that of the α-spin π MO-4 in the radical, but lower than that in anion. The main-representations of the π MO-4 and π MO-5 belong to the two-dimensional irreducible representation E2u of D$_{6h}$ point group, and are linked by crossed lines in the correlation diagram.

As mentioned above, the effects of radical and ion on the symmetry with defect or fuzzy characterization are much evident for the hexatomic ring π MO. Maybe, it is introduced owing to the Jahn–Teller effect [18, 19]. In addition, the membership functions may be varied considerably with a small change of

Table 5
The irreducible representation components for the π-MOs of C_5NH_6 at AM1.

		Irreducible representation components			
		XA	XB	XE1	XE2
C_5NH_6−(anion)	π−MO-1(O)	0.98675	0.00084	0.01122	0.00119
	π−MO-2(O)	0.01437	$< 10^{-5}$	0.98510	0.00053
	π−MO-3(O)	0	0	0.97714	0.02286
	π−MO-4(V)	$< 10^{-5}$	0.08524	0.00015	0.91461
	π−MO-5(V)	0	0	0.00990	0.99010
	π−MO-6(V)	0.00004	0.96705	0.00006	0.03285
C_5NH_6+(cation)	π−MO-1(O)	0.77062	0.00852	0.18825	0.03262
	π−MO-2(O)	0.06142	0.00891	0.67802	0.25166
	π−MO-3(O)	0	0	0.99590	0.00410
	π−MO-4(V)	0.00147	0.04630	0.03912	0.91312
	π−MO-5(V)	0	0	0.00160	0.99840
	π−MO-6(V)	0.00015	0.94944	0.00100	0.04941
C_5NH_6·(radical) (α-spin)	π−MO-1(O)	0.78170	0.00073	0.17967	0.03790
	π−MO-2(O)	0.11072	0.0744	0.80909	0.00579
	π−MO-3(O)	0	0	0.90476	0.09524
	π−MO-4(O)	0.00270	0.11392	0.02677	0.85661
	π−MO-5(V)	0	0	0.04151	0.95849
	π−MO-6(V)	0.00366	0.87742	0.01228	0.10664
C_5NH_6·(radical) (β-spin)	π−MO-1(O)	0.91141	0.02999	0.05240	0.00620
	π−MO-2(O)	0.02512	0.00289	0.87490	0.09709
	π−MO-3(O)	0	0	0.92792	0.07208
	π−MO-4(V)	0	0	0.03157	0.96843
	π−MO-5(V)	0	$<10^{-5}$	0.05390	0.94609
	π−MO-6(V)	0.00546	0.99205	0	0.00248

the irreducible representation component. The membership functions of these π MOs in relation to the various symmetry transformations of D_{6h} point group are shown in figure 7 where the meaning of the transformation (GJ; $J = $ 1, 2, 3) subsets are the same to equation (12). The membership functions of all the transformations in $G0$ subset are equal to one, but are omitted in Figure 7. Comparison with figures 3 and 4 indicates clear difference. To sum up, the smaller main-representation components, the smaller membership functions of symmetry transformations. The effects are somewhat different for the symmetry transformations of different molecules. There is a new research field.

4.   Conclusions

In our previous papers in connection with the molecular fuzzy symmetry, we have discussed the characterization of some simple linear and plane molecules. These molecules connect with the point group which includes only
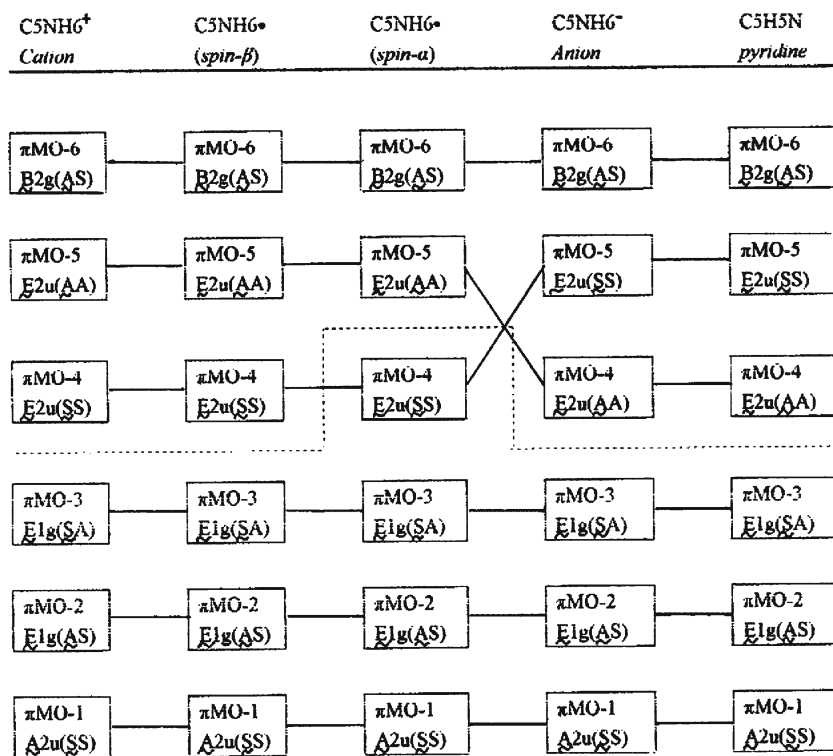
C5NH6⁺	C5NH6•	C5NH6•	C5NH6⁻	C5H5N
Cation	*(spin-β)*	*(spin-α)*	*Anion*	*pyridine*

Figure 6. The AM1 πMO fuzzy correlation diagram for pyridine hydride. The first row in every quad denotes the πMO serial number in the same order as the orbital energy, following with the irreducible representation in relation to the D$_{6h}$ point group. The symbols in brackets denote the irreducible representation (*S*, symmetrical, *A*, asymmetrical) about the mirrors with *xz* and *yz* coordinate planes (figure 1), respectively. The "∼" below the irreducible representation symbol denotes related fuzzy irreducible representation. Above the dotted line, there are the virtual MOs, and below this dotted line are the occupied MOs.

the identity and twofold symmetry elements. Moreover, the related MO belongs only to a one-dimensional irreducible representation. In this paper, using the azines as our model, we have analyzed the fuzzy symmetry in terms of the D$_{6h}$ point group. Some of the related MOs may belong to the fuzzy two-dimensional irreducible representation. Here, for these molecules and their MOs, we have examined their fuzzy symmetry, the membership functions, the representation components, and the correlation diagrams. Besides the fuzzy symmetry of neutral closed shell molecule, we also investigated the radical, cation, and anion. The main conclusions are as follows:

(1) According to the basic characterization of the fuzzy symmetry for the molecules and their MOs together with the modified method of the projection operator, we have established methods that involve the membership
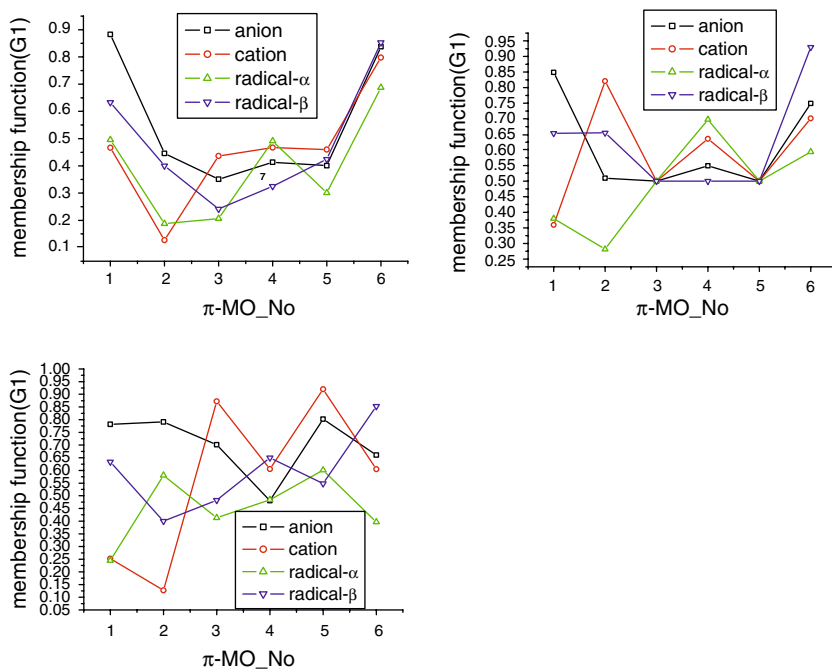
Figure 7. The membership functions of the AM1 π MOs of pyridine hydride in relation to the symmetry transformations in the D$_{6h}$ point group. Where the vertical axes denote the membership functions in relation to the symmetry transformations, the horizontal axis, π-MO_No, denotes the same π MO serial number as in figure 2. The radial-α and radical-β denote the α and β-spin π MOs, respectively.

functions, the representation components, and the correlation diagrams in terms of the D$_{6h}$ point group to calculate the fuzzy symmetry of azines and their MOs. These methods may be used to the systems that belong to the point groups that include more than twofold rotation symmetry transformation. The MOs of the systems may belong to the multi-dimensional irreducible representation. These methods ought to be programmed and implemented, as our present analysis of the fuzzy symmetry for the molecules has demonstrated.

(2) In order to stress how to analyze the fuzzy symmetry of the MOs, which belong to the two-dimensional fuzzy representation as a result of the multi-fold symmetry transformation, and avoid the lengthy and tedious calculation, we have only analyzed the related π MOs in this work. The σ-MOs may be analyzed in the similar way, but related calculation is lengthier and should be programmed.

(3) As to the planar molecules studied here, the reflection symmetry transformation about the molecular plane as a mirror is a common symmetry transformation. Subsequently, for both the molecular skeleton and MOs,

the membership function of the reflection symmetry transformation would be equal to 1. However, the membership functions of other symmetry transformations may be between 0 and 1, and the irreducible representation components of MOs may also be between 0 and 1.

(4) As for the point group includes only one two/threefold symmetry element, the relative fuzzy point symmetry transformation set must be a fuzzy point group. However, the point set includes one multi-fold symmetry element, the related fuzzy point symmetry transformation set may be either a fuzzy point group or a fuzzy set.

(5) For benzene or other molecules which have D$_{6h}$ point group symmetry, their two MOs may be combined to construct a complete basis set of a two-dimensional irreducible representation. Corresponding to such MOs, the two-dimensional irreducible representation component should be equal to one. However, the membership functions corresponding to other symmetry transformations of D$_{6h}$ point group will not all equal to one. But the membership functions for the MO complete set ought to be equal one.

(6) For the π MOs in the hexatomic ring of the pyridine and some azines, their main-representations according to the energy serial order are as follows: (A2u), (E1g), (E1g), (E2u), (E2u), and (B2g), the same order as that of the "pure" representations for benzene. Corresponding to the two-dimensional irreducible representations of D$_{6h}$ point group, the π MOs in a complete set are degenerate for benzene, but not degenerate for pyridine and some other azines, instead, the two π MOs have the near equal orbital energies. By means of the fuzzy D$_{6h}$ point group to analyze such π MOs of azines, the main-representations are the same two-dimensional irreducible representation, but they may belong to different one-dimensional irreducible representations of a certain subgroup of D$_{6h}$, and the energy serial order may be different.

(7) For the π MOs of pyridine and those of some azines, we may classify the symmetry transformations in D$_{6h}$ point group according to the values of their membership functions into four subsets: $G0$, $G1$, $G2$, and $G3$, in which the rotation symmetry transformations in relation to $0°$, $60°$, $2\times60°$, and $3\times60°$ are included, respectively. In a same subset, the membership functions of all the symmetry transformations are the same. In these subsets, except the rotation symmetry transformations, the transformations may be different for different molecules. For pyridine and m-diazine, the same symmetry transformations will be included in related subsets, but there are some different for the $o-$diazine. For $p-$diazine, the corresponding symmetry transformations in the subsets may be classified according to those for both the m-and o-diazines. On the other hand, for p-diazine, the membership functions of the symmetry transformations in subsets $G0$ and $G3$ are the same, and so are they in the subsets $G1$ and

$G2$. For all these molecules, the union sets $G0\cup G3$ are the same, and so are $G1\cup G2$.

(8) The pyridine hydride is a neutral but open shell molecule, a radical. It may obtain or lose an electron to become an anion or a cation. Using these species as the examples, we have probed the fuzzy symmetries of radicals and ions. As to the molecular skeletons, if we assume the atomic number as the criterion, their membership functions should be the same. Therefore, it seems that the symmetry of these molecular skeletons should be closer to D$_{6h}$ than should pyridine. However, as for the MO, the fuzzy symmetry characterizations of pyridine hydride radical and ion are different from pyridine. For the radical MO, the fuzzy symmetry characterization of different spin-state MOs will be somewhat different. There is an interesting field to explore in connection with the chemistry characterization of the radical and ion.

Acknowledgments

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