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Ab Initio MCSCF Study on Eight π-Electron Heterocyclic Conjugated Systems: Energy Component Analysis of the Pseudo-Jahn−Teller Distortion from Planarity

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To clarify the origin of nonplanarity in eight π-electron heterocyclic conjugated systems, an energy component analysis was carried out for the ground states by using ab initio MCSCF method with 6-31++G(d,p) basis set. Inspection of the energy components comprised in the total energy reveals that the type of pseudo-JT stabilization is classified into two groups, one in which the stability of nonplanar structure arises from a lowering of the interelectronic and internuclear repulsion energies and the other in which the stability results from a lowering of the electron−nuclear attraction energy. This sharp distinction in energy changes is accounted for in terms of an expansion or contraction of the molecular skeleton and a proximity among the nuclei and the electron clouds owing to a folding of the six-membered ring. Besides, it is shown that the theoretical structural characteristics for 1,2-dihydro- and 1,4-dihydro-1,2,4,5-tetrazines are in good agreement with available experimental facts.

Introduction

Pyramidalizations in nonplanar hydrocarbons have attracted much attention for their structural characteristics, physicochemical properties, and chemical reactions, and the topics have been reviewed on pyramidalized alkenes, strained bridgehead alkenes, and related compounds.[1−6] Further, the planarity or nonplanarity of conjugated dienes, especially of the second stable conformer of 1,3-butadiene, aroused considerable discussion both theoretically and experimentally.[7−11] On the other hand, a conformational criterion for aromaticity and antiaromaticity was put forth by Raber et al. such that, relative to planar reference geometries, a folding of the molecular skeleton in aromatic and antiaromatic systems results in large endothermic and exothermic changes, respectively.[12] On the basis of the criterion, a series of eight π-electron, six-membered ring systems examined are shown to be highly flexible and therefore classified as nonaromatic rather than antiaromatic within ab initio RHF calculations with the 6-21G basis set.

Among eight π-electron monocyclic compounds, cyclooctatetraene is the prototype that takes a nonplanar tub structure of D_{2d} symmetry with alternate long and short bonds.[13,14] It is so far believed that a planar bond-alternated structure of D_{4h} symmetry should be deformed into the tub structure to relax the bond angle strain in the eight-membered ring and the internuclear repulsion between vicinal hydrogen atoms. We made previously an energy component analysis of the pseudo-Jahn−Teller (JT) distortion from planarity to elucidate the origin for energetic stability of the nonplanar tub structure.[15,16] It is shown that the tub structure owes its stability essentially to an energy lowering of the electron−nuclear attractive term. Recently, we have studied the nature of the pseudo-JT distortion from planarity in the ground states of cycloheptatriene, heptalene, and heptafulvalene.[17] Despite their marked differences in molecular shape, it is found that the cause of nonplanarity is all ascribed to an energy lowering of the electron−nuclear attractive term. It is worth noting that Boyd et al. put forth the following question on the basis of the results obtained for the methane and borane cation radicals regarding the first-order JT distortions;[18,19] Is it generally true that the pure JT effect leads to a contraction of the electron cloud and to a concomitant decrease in the nuclear-electron attraction energy and to an increase in the interelectronic and internuclear repulsion energies?

It seems that no essential difference should exist between the first-order JT and pseudo-JT effects, at least in the sense that the former deals with the geometric instability of degenerate electronic states and the later merely with that of nearly degenerate electronic states. In this context, the purpose of this study is to examine whether an energy lowering of the electron−nuclear attractive term should be a common phenomenon when a conjugated molecule undergoes the pseudo-JT distortion from planarity. This is because the total energy of a molecule is composed of the four energy components and, accordingly, there is every reason to believe that the stability should result from an energy term other than the electron−nuclear attractive term. Using ab initio MCSCF method with 6-31++G(d,p) basis set, we explore the nature of pseudo-JT distortion from planarity by dealing with the following eight π-electron heterocyclic conjugated systems (Figure 1): hydro-pyrizinyl anion (**1**), 1,2-dihydro-1,2-diazine (**2**), 1,3-dihydro-1,3-diazine (**3**), 1,4-dihydropyrazine (**4**), 1,2-dihydro-1,2,4,5-tetrazine (**5**), and 1,4-dihydro-1,2,4,5-tetrazine (**6**). It is noted that **1**−**3** are still unknown compounds but derivatives of **4** and **5** and the parent compound **6** have been reported to take nonplanar conformations by X-ray structure analyses.[20,21]

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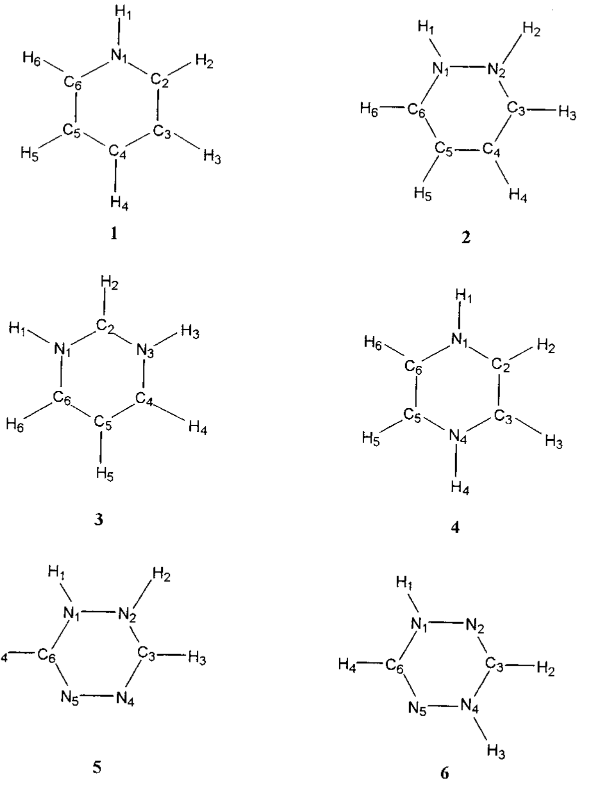


Figure 1. Molecular skeletons and numbering of atoms for **1**−**6**. The z axis is taken to be the main molecular axis in the C_{2v} and C_s point groups, to be the C_2 rotational axis in the C_2 point group, and to be perpendicular to the molecular plane in the C_{2h} point group.

MCSCF Calculations

To describe the ground state properly, we make use of the full-optimized reaction space (FORS) multiconfiguration self-consistent field (MCSCF) method with the 6-31++G(d,p) basis set.[22−26] To take into account an essential part of the static correlation among π and σ electrons upon the structural change from a symmetric planar to a distorted nonplanar structure, we employ here 8 orbitals and 12 electrons as the active space in the MCSCF calculations. That is, all inner valence π orbitals are included commonly for **1**−**6** because they result in σ orbitals at the distorted nonplanar structure. As for σ orbitals, however, two orbitals are included that are lying near the π orbitals in energy: namely, they correspond to the two highest occupied σ orbitals for **1**−**4** and to the two lone-pair orbitals of N atoms for **5**−**6**.

To locate the geometrical structures corresponding to a true energy minimum, preliminary geometrical optimizations are performed by assuming the symmetric planar structures with the RHF/6-31++G(d,p) method. After geometrical optimizations, vibrational analyses are carried out to inquire as to whether each symmetric structure should be a true energy minimum on the singlet potential energy surface of the ground state. Further, structural optimizations are performed for the relevant less symmetric structures, provided that imaginary frequencies would appear in the accompanying vibrational analyses. By repetition of the procedures, we locate the true energy minimum and transition structures using the RHF method. Subsequently, all of the stationary structures are reoptimized by means of the MCSCF/6-31++G(d,p) method to see whether the above predictions should be acceptable within this level of theory. Except for frequency calculations, our discussion given below is based on the results obtained by the MCSCF calculations.

Energy Partitioning Scheme

Energy components included in the total energy are important essentially for discussing the leading terms responsible for the pseudo-JT distortion from planarity in the present molecules, and hence we give here a brief review of the energy partitioning scheme.[27] The total energy of a molecular system is expressed as the sum of the electronic energy E^{el} and the internuclear repulsion energy V_{nn}. The E^{el} term comprises the kinetic energy T and the potential energy V, the latter being further partitioned into the electron−nuclear attraction energy V_{en} and the interelectronic repulsion energy V_{ee}. That is, the total energy can be written as given below.

$$E = T + V_{en} + V_{ee} + V_{nn}$$

Following the molecular virial theorem for the stationary structures,[28−31] the energy difference between a less symmetric and a symmetric structure is readily given as $-\Delta T$ or $\Delta V/2$, the quantity being negative. In terms of the energy components comprised in the potential energy, the energy difference is expressed as given below.

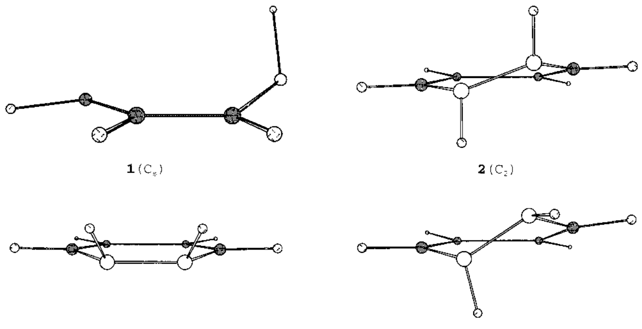
$$\Delta E = (\Delta V_{en} + \Delta V_{ee} + \Delta V_{nn})/2$$

From the leading contributor that should lead to the energy lowering of a less symmetric structure, it may be possible to classify the molecules. Namely, a molecule can be referred to as the electron−nuclear attractive, the interelectronic repulsive, or the internuclear repulsive type, as it owes its stability from an energy lowering of the corresponding energetic term. Because the kinetic energy is raised, in principle, in the pseudo-JT structural changes, no kinetic energy type should appear as the classification of the pseudo-JT stabilization.

All calculations are carried out by means of the quantum chemistry code GAMESS[22] in which new subroutines for the energy component analysis are included.

Results and Discussion

Transition and Energy Minimum Structures. The vibrational analyses with the RHF method show that at the symmetric C_{2v} structure of **1**, three imaginary frequencies corresponding to out-of-plane b_2 nuclear deformations appear. It follows that the structure optimizations starting with the three b_2 nuclear deformations all converge into the same nonplanar C_s structure. At the symmetric C_{2v} structure of **2**, there appear three imaginary frequencies corresponding to two b_2 and b_1 nuclear deformations. The structure optimizations show that the former two lead to the same nonplanar C_2 structure and the latter to a nonplanar C_s structure. Moreover, because the resulting C_s structure has one imaginary frequency corresponding to a nuclear deformation of a'' symmetry, it is distorted into a nonsymmetric C_1 structure. Comparison of the total energy finds the C_2 structure to be the real minimum and the C_1 structure to be a local minimum on the potential energy surface. The symmetric C_{2v} structure of **3** exhibits a second-order saddle point with regard to b_1 and b_2 nuclear deformations. The geometry optimizations lead to a nonplanar C_2 structure for the former and to a nonplanar C_s structure for the latter. Subsequently, the resulting C_2 and C_s structures each have one imaginary frequency corresponding to b and a'' nuclear deformations, respectively. Eventually, the geometrical optimizations starting with the respective nuclear deformations are converged into just the same C_1 structure. At the D_{2h} structure of **4**, there appear two imaginary frequencies corresponding to b_{1g} and b_{2g} nuclear deformations, i.e., the anti



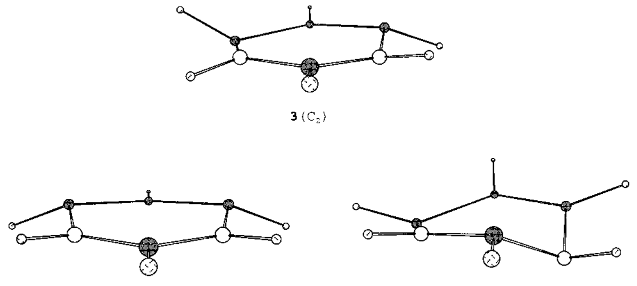
1 (C_s) **2** (C_2) **2** (C_s) **2** (C_1)

Figure 2. Side views of the C_s conformation and the C_2, C_s, and C_1 conformations obtained using the atomic coordinates of the optimized structures for **1** and **2**, respectively. Black and gray circles indicate C and N atoms, respectively.

and syn folding motions of N-hydrogens. The geometry optimizations lead to a nonplanar C_{2h} structure for the former and to a nonplanar C_{2v} structure for the latter, with the result that both structures have comparable energies (vide infra). The symmetric C_{2v} structure of **5** exhibits three imaginary frequencies corresponding to two a_2 and b_1 nuclear deformations. The former two lead to just the same C_2 structure and the latter to a C_s structure. Further, the resulting C_s structure has one imaginary frequency corresponding to a nuclear deformation of a″ symmetry, and it is transformed into the aforesaid C_2 structure by the nuclear deformation. Notice that this transformation does not correspond to the pseudo-JT structural change. Frequency analyses find the C_2 structure to be the true minimum and the C_s structure to be the transition structure for the inversion process occurring in the interconversion between the two equivalent C_2 structures. The symmetric C_{2h} structure of **6** exhibits a second-order saddle point with regard to a_u and b_g nuclear deformations and, hence, the pseudo-JT distortions lead to C_2 and C_i structures, respectively. Because all of the frequencies for the resulting C_2 and C_i structures are positive definite, both are found to be stationary points on the potential energy surface. Comparison of the total energy reveals that the C_2 structure is the global minimum and the C_i structure is a local minimum.

It can be pointed out that the heterocyclic conjugated molecules **1**−**6** display a variety of structural changes by the pseudo-JT effects. This should be responsible for the molecules being the eight π-electron, six-membered ring systems as given below. From the perturbational MO (PMO) approach,[32] the molecules are regarded as perturbed benzenes with eight π electrons, formed by replacement of CH-group(s) in benzene by NH-group(s) and/or N atom(s), where a degeneracy of the LUMOs in benzene is removed by such exchanges. Because the extra two π electrons are assigned to the resulting LUMO,[33] the ground state would exhibit in this sense an unfavorable electronic situation at the symmetric planar structure. Such being the case, there is good possibility for some lower electronically excited states lying at relatively lower energy regions from the ground state. Accordingly, a nuclear distortion of proper symmetry should mix the ground state and a low-lying excited state and thereby lowers the ground-state energy.[34] This is equivalent to saying that the relevant force constant becomes negative and, hence, the pseudo-JT distortion from planarity should take place spontaneously.

Structural and Electronic Characteristics. Table 1 presents the fully optimized geometrical parameters regarding bond lengths and bond angles around N (C) atoms for the various structures of **1**−**6** calculated by the MCSCF/6-31++G(d,p) method. Figures 2−5 display the side views of nonplanar structures obtained by using atomic coordinates. In Table 2 are listed atomic populations obtained at the respective structures by means of Mulliken's population analysis.[35]



3 (C_2) **3** (C_s) **3** (C_1)

Figure 3. Side views of the C_2, C_s, and C_1 conformations obtained using the atomic coordinates of the optimized structures for **3**.

The C_{2v} structure of **1** takes a so-called quinoid form with a double-bond fixation on the opposing C2−C3 and C5−C6 bonds, which is supported from the pattern of charge distribution. That is, significantly large negative charges are localized on N1 (−0.49) and C4 (−0.88).[36] On symmetry reduction from C_{2v} to C_s, a negative charge flows into C2 (C6) from C4, with the result that the negative charge of C4 is eventually reduced to one-half its initial value (Table 2). At the same time, both N1 and C4 atoms are displaced above a molecular plane of the symmetric structure, whereby the N-hydrogen is bent up on the axial position and the C4-hydrogen is pointed to the equatorial position (Figure 2). Of special notice is the finding that the sum of bond angles around N1 is 324.4°. Clearly, this angle is less than that of 328.4° in a pure sp^3-hybridized atom, and the anion **1** adopts a typical boat C_s conformation with the pseudo-JT stabilization energy of 16.7 kcal/mol.

The C_{2v} structure of **2** shows a marked double-bond fixation on C3−C4 (C5−C6), and the adjacent N atoms each carry a negative charge of −0.37. The C_s structure with almost a planar ring form exhibits a more pronounced bond fixation on the CC bond, in conjunction with an increase in negative charges on C3 (C6) and a decrease in negative charges on C4 (C5). Distortion of the C_s structure into the twisted C_1 structure is accompanied by a shortening of the NN bond, with the result that the sum of the bond angles around N1 is reduced to 326.8° from 337.2°. On going from C_{2v} to C_2, on the other hand, the NN bond is twisted relative to C4−C5, the C6−N1−N2−C3 moiety is charged negatively, and the two N-hydrogens are directed almost to the axial positions. That is, the stable C_2 structure takes a twisted boat conformation, where the sum of the bond angles around N1 is 337.9°. A marked distinction between the twisted C_2 and C_1 structures (Figure 2) is a spatial arrangement of the N1-hydrogen, so that the two appear to constitute mutually the conformational isomers arising from an inversion of the N1 atom. Relative to the symmetric C_{2v} structure, the pseudo-JT stabilization energy amounts to 9.9 kcal/mol for the C_s structure, 18.3 kcal/mol for the C_1 structure, and 21.6 kcal/mol for the C_2 structure.

The C_{2v} structure of **3** takes an antiquinoid form, possessing a rather long N3−C4 (N1−C6) and large negative charges on N1 (N3) and C4 (C6). In the C_s structure with a very shallow boat form (Figure 3), the C4- and C6-hydrogens are slightly bent downward, but a bond fixation is relaxed somewhat on N3−C4 with a decrease in negative charge on C4. Very similar features are also observed for the C_2 structure with a nearly planar ring form. In contrast, the puckered C_1 structure exhibits a pronounced structural change in comparison with those in the

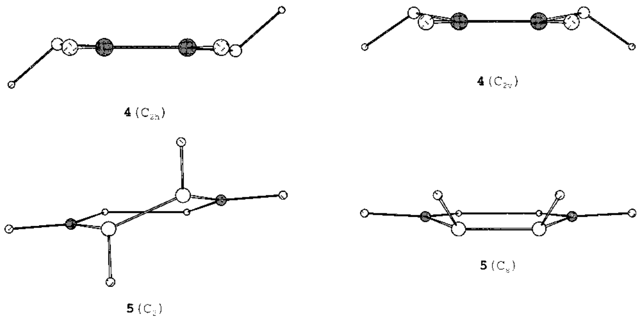


Figure 4. Side views of the C_{2v} and C_{2h} conformations and the C_2 and C_s conformations obtained using the atomic coordinates of the optimized structures for **4** and **5,** respectively.

C_s and C_2 structures. A marked bond fixation appears on the periphery of the six-membered ring, N1 takes a nearly pure sp^3-pyramidal configuration because of the sum of the associated bond angles being 330.6°, and the negative and positive charges are sizeably relaxed on C2 and C4, respectively. The stabilization energy due to the pseudo-JT effect is 2.2 kcal/mol for the C_s structure, 3.4 kcal/mol for the C_2 structure, and 15.8 kcal/mol for the C_1 structure. In the former two, the relevant energy lowerings are relatively small, which are referable to the structural changes arising mainly from out-of-plane deviations of the H atoms.

The symmetric D_{2h} structure of **4** adopts a quinoid form, showing that the two opposite CC bonds have double bond character and N1 (N4) is charged negatively with a value of −0.54. In the distorted C_{2h} and C_{2v} structures, the structural parameters regarding bond distances as well as the bond angles around N1 are almost the same between the two: the former takes almost a planar ring form with anti-folded positions of N-hydrogens, while the latter does a very shallow boat form with syn-folded positions of N-hydrogens (Figure 4). It is notable that relative to the D_{2h} structure, the negative charge on N1 is reduced by 0.121 and 0.125 for the C_{2h} and C_{2v} structures, respectively. Concomitantly, the pseudo-JT stabilization energies are calculated to be 6.2 and 6.4 kcal/mol for the C_{2h} and C_{2v} structures, respectively. Because the two structures have comparable energies, a preferred structure is not conceivable within the present MCSCF calculations.[37,38] Besides, the activation energy of the interconversion reaction between the two structures is rather small, and the pseudo-JT effect may be of a dynamical rather than a static nature. It is noted, however, that a tetraaryl derivative of **4** is known to take a boat conformation by X-ray structure analysis.[21,39,40]

The symmetric C_{2v} structure of **5** exhibits a double-bond fixation on the N2−C3−N4 (N1−C6−N5) moiety, but in the C_s and C_2 structures the bond fixation is smoothed out on N2−C3 (N1−C6) and the sum of the bond angles around N1 is about 339°. One of the differences between the C_s and C_2 structures is a spatial arrangement of the two N-hydrogens (Figure 4). In the C_s structure with a nearly planar ring form, both N-hydrogens are bent upward, while in the C_2 structure with a twisted boat conformation, they are on the axial positions, one tending upward and the other downward. The stabilization energies which favor the less symmetric C_s and C_2 structures are calculated to be 7.1 and 17.1 kcal/mol, respectively. In this context, the activation energy is estimated to be 10.0 kcal/mol for the isodynamic inversion process occurring in the interconversion between the two equivalent C_2 structures. The geometrical parameters for the C_2 structure are in qualitatively accord with the values observed for its diphenyl derivative.[20]

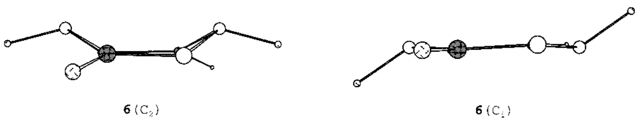


Figure 5. Side views of the C_2 and C_i conformations obtained using the atomic coordinates of the optimized structures for **6**.

The symmetric C_{2v} structure of **6** shows a double-bond fixation on the N2−C3−N4 (N1−C6−N5) moiety, while in the C_i and C_2 structures the bond fixation is entirely smoothed out on C3−N4 (N1−C6). In the C_i structure with a nearly planar ring form (Figure 5), the two N-hydrogens are displaced above and below from a molecular plane of the symmetric structure, respectively. On the other hand, the C_2 structure takes a boat conformation, where both the pyrrole-type N atoms are displaced above from the molecular plane. The stabilization energy which favors a less symmetric structure is calculated to be 2.5 kcal/mol for the C_i structure and 8.0 kcal/mol for the C_2 structure. In detail, the experimental boat structure shows a slight distortion from C_2 to C_1, but this may be responsible for crystal packing forces, as is often the case. For all that, the theoretical geometrical parameters regarding bond distances in the C_2 structure reproduce the X-ray experimental data considerably well.[20] Moreover, the sum of the calculated bond angles around N1 (N4) is 337.3°, in good agreement with the observed value of 339°.

Rehybridization of Nitrogen. It will be pertinent to refer to a possible relationship between the rehybridization of nitrogen and the pseudo-JT distortion from planarity. As noted above, each N atom carries a large negative charge in the symmetric planar structure as compared in the less symmetric structure. In some detail, the negative charge is larger for pyrrole-type nitrogen than for pyridine-type nitrogen in **5** and **6**. Moreover, the sum of bond angles around pyrrole-type nitrogen is less than 360°, which gives a strong indication of the sp^3-pyramidal hybridization. Upon rehybridization from sp^2 to sp^3, a reorganization of the σ and π electron clouds occurs around the relevant N atom. Since the resulting lone-pair electron cloud should be oriented far apart from the nearest neighbor electron clouds in CN and NH bonds, the rehybridization will bring about a decrease in the interelectronic repulsive interactions between them. Further relief may be afforded to the repulsive interactions, provided that the excess charge density on pyrrole-type nitrogen is reduced to some extent. This is equivalent to an expansion of the electron cloud to other sites,[41] so that with a negative charge relaxation the molecule will change its shape from the planar to the nonplanar structure. As typical examples belonging to this category, **4** and **6** can be cited. In the C_{2v} structure of **4**, the sum of bond angles around nitrogen is reduced by 21.2°, relative to the D_{2h} structure, with a decrease in charge density by about 0.13 (e). In this sense, it appears that a charge relaxation on nitrogen should plays an important role in the pseudo-JT distortion from planarity. A similar change in hybridization is observed on the carbon of **1**. In the structural change from C_{2v} to C_s, the sum of bond angles around C4 is reduced by 6.4° with a decrease in charge density by about 0.44 (e). But, it should be emphasized that the rehybridization itself is not necessarily the decisive factor for the overall pseudo-JT stabilization as given below, because a pyramidalization causes a skeletal folding and hence leads to an enhancement of the interelectronic repulsive interactions by virtue of the proximity between the electron clouds in bonds.

Energy Component Analysis of the Ground States. Table 3 shows the total and partitioned energies at the symmetric and less symmetric structures as well as the relative energy differences between them. In general, it is seen that the energy terms

TABLE 1: Optimized Geometrical Parameters at the Symmetric and Less Symmetric Nuclear Configurations of 1−6

molecule	structure	geometrical parameters[a]
1	C_{2v}	N1−C2 = 1.430, C2−C3 = 1.359, C3−C4 = 1.446, N1−H1 = 0.987, C2−H2 = 1.075, C3−H3 = 1.081, C4−H4 = 1.074, H1−N1−C2 = 120.6, C2−N1−C6 = 118.7, H4−C4−C3 = 122.5, C3−C4−C5 = 115.0
	C_s	N1−C2 = 1.445, C2−C3 = 1.368, C3−C4 = 1.433, N1−H1 = 1.010, C2−H2 = 1.078, C3−H3 = 1.083, C4−H4 = 1.078, H1−N1−C2 = 107.8, C2−N1−C6 = 108.6, H4−C4−C3 = 120.0, C3−C4−C5 = 113.6
2	C_{2v}	N1−N2 = 1.413, N2−C3 = 1.382, C3−C4 = 1.344, C4−C5 = 1.483, N1−H1 = 0.986, C3−H3 = 1.073, C4−H4 = 1.072, H1−N1−N2 = 116.8, N2−N1−C6 = 119.2, H1−N1−C6 = 123.9
	C_s	N1−N2 = 1.445, N2−C3 = 1.412, C3−C4 = 1.340, C4−C5 = 1.472, N1−H1 = 0.998, C3−H3 = 1.074, C4−H4 = 1.073, H1−N1−N2 = 109.0, N2−N1−C6 = 117.4, H1−N1−C6 = 110.8
	C_1	N1−N2 = 1.408, N2−C3 = 1.398, C3−C4 = 1.349, C4−C5 = 1.469, C5−C6 = 1.346, N1−C6 = 1.435, N1−H1 = 1.009, N2−H2 = 0.994, C3−H3 = 1.075, C4−H4 = 1.073, C5−H5 = 1.075, C6−H6 = 1.074, H1−N1−N2 = 109.5, N2−N1−C6 = 108.8, H1−N1−C6 = 108.5, H2−N2−C3 = 117.2, C3−N2−N1 = 115.2, H2−N2−N1 = 111.0
	C_2	N1−N2 = 1.405, N2−C3 = 1.420, C3−C4 = 1.344, C4−C5 = 1.467, N1−H1 = 1.000, C3−H3 = 1.075, C4−H4 = 1.074, H1−N1−N2 = 109.1, N2−N1−C6 = 116.3, H1−N1−C6 = 112.5
3	C_{2v}	N1−C2 = 1.296, N3−C4 = 1.482, C4−C5 = 1.367, N1−H1 = 0.991, C2−H2 = 1.076, C4−H4 = 1.064, C5−H5 = 1.077, H1−N1−C2 = 118.2, C2−N1−C6 = 121.7, H1−N1−C6 = 120.1, H2−C2−N1 = 118.7, N1−C2−N3 = 122.7, H4−C4−N3 = 116.2, N3−C4−C5 = 114.6, H4−C4−C5 = 129.2
	C_2	N1−C2 = 1.304, N3−C4 = 1.479, C4−C5 = 1.386, N1−H1 = 0.994, C2−H2 = 1.076, C4−H4 = 1.073, C5−H5 = 1.076, H1−N1−C2 = 117.3, C2−N1−C6 = 121.9, H1−N1−C6 = 118.7, H2−C2−N1 = 118.7, N1−C2−N3 = 122.6, H4−C4−N3 = 112.8, N3−C4−C5 = 113.3, H4−C4−C5 = 123.0
	C_s	N1−C2 = 1.304, N3−C4 = 1.481, C4−C5 = 1.385, N1−H1 = 0.993, C2−H2 = 1.075, C4−H4 = 1.071, C5−H5 = 1.077, H1−N1−C2 = 117.9, C2−N1−C6 = 122.1, H1−N1−C6 = 119.5, H2−C2−N1 = 118.7, N1−C2−N3 = 122.7, H4−C4−N3 = 113.3, N3−C4−C5 = 112.9, H4−C4−C5 = 122.2
	C_1	N1−C2 = 1.428, C2−N3 = 1.346, N3−C4 = 1.355, C4−C5 = 1.458, C5−C6 = 1.346, N1−C6 = 1.439, N1−H1 = 0.997, C2−H2 = 1.072, C3−H3 = 0.996, C4−H4 = 1.072, C5−H5 = 1.074, C6−H6 = 1.073, H1−N1−C2 = 110.3, C2−N1−C6 = 108.9, H1−N1−C6 = 120.1, H2−C2−N1 = 117.5, N1−C2−N3 = 113.7, H2−C2−N1 = 117.3, H3−N3−C4 = 118.4, C4−N3−C2 = 124.0, H3−N3−C2 = 117.3, H4−C4−N3 = 116.3, N3−C4−C5 = 113.9, H4−C4−C5 = 122.0, H5−C5−C6 = 120.3, C4−C5−C6 = 118.3, H5−C5−C6 = 121.2, H6−C6−C5 = 124.0, C5−C6−N1 = 118.2, H6−C6−N2 = 117.6
4	D_{2h}	N1−C2 = 1.405, C2−C3 = 1.341, N1−H1 = 0.988, C2−H2 = 1.071, C2−N1−C6 = 118.0, H1−N1−C2 = 121.0
	C_{2h}	N1−C2 = 1.417, C2−C3 = 1.339, N1−H1 = 0.998, C2−H2 = 1.073, C2−N1−C6 = 112.7, H1−N1−C2 = 112.7
	C_{2v}	N1−C2 = 1.417, C2−C3 = 1.339, N1−H1 = 0.998, C2−H2 = 1.072, C2−N1−C6 = 112.5, H1−N1−C2 = 113.8
5	C_{2v}	N1−N2 = 1.401, N2−C3 = 1.367, C3−N4 = 1.272, N4−N5 = 1.429, N1−H1 = 0.988, C3−H2 = 1.074, H1−N1−N2 = 118.8, N2−N1−C6 = 116.3, H1−N1−C6 = 124.9
	C_s	N1−N2 = 1.398, N2−C3 = 1.404, C3−N4 = 1.274, N4−N5 = 1.402, N1−H1 = 1.000, C3−H2 = 1.075, H1−N1−N2 = 111.7, N2−N1−C6 = 114.6, H1−N1−C6 = 112.8
	C_2	N1−N2 = 1.427, N2−C3 = 1.394, C3−N4 = 1.269, N4−N5 = 1.419, N1−H1 = 0.998, C3−H2 = 1.075, H1−N1−N2 = 110.7, N2−N1−C6 = 113.5, H1−N1−C6 = 114.5
6	C_{2h}	N1−N2 = 1.391, N2−C3 = 1.272, C3−N4 = 1.375, N1−H1 = 0.988, C3−H2 = 1.073, H1−N1−N2 = 115.4, N2−N1−C6 = 121.9, H1−N1−C6 = 122.7
	C_i	N1−N2 = 1.401, N2−C3 = 1.270, C3−N4 = 1.397, N1−H1 = 0.995, C3−H2 = 1.073, H1−N1−N2 = 111.0, N2−N1−C6 = 118.6, H1−N1−C6 = 116.6
	C_2	N1−N2 = 1.395, N2−C3 = 1.271, C3−N4 = 1.392, N1−H1 = 0.994, C3−H2 = 1.074, H1−N1−N2 = 109.1, N2−N1−C6 = 114.1, H1−N1−C6 = 114.1

[a] Numbering of atoms is shown in Figure 1. Bond lengths and bond angles are in angstroms and degrees.[46]

are highly sensitive to changes in molecular geometry and have mutually opposite signs to the pseudo-JT stabilization.

*The Hydropyrizinyl Anion (**1**).* Distortion of the planar C_{2v} structure to the boat C_s structure is accompanied by a small amount of the totally symmetric expansion of the six-membered ring. The associated changes in bond length are given below,

TABLE 2: Atomic and Bond Populations at the Symmetric and Distorted Structures of 1−6

molecule	position	structure (point group)			
1		C_{2v}	C_s		
	N1	7.4903	7.4576		
	C2	6.1559	6.3257		
	C3	5.9723	5.9651		
	C4	6.8773	6.4416		
	H1	0.7118	0.7659		
	H2	0.9267	0.9365		
	H3	0.9405	0.9560		
	H4	0.9297	0.9682		
2		C_{2v}	C_s	C_1	C_2
	N1	7.3681	7.3064	7.3514	7.3320
	N2			7.3047	
	C3	6.0733	6.1820	6.1727	6.2918
	C6			6.2089	
	C4	6.1627	6.0766	6.0967	5.9658
	C5			6.0252	
	H1	0.6538	0.7055	0.6942	0.6762
	H2			0.6758	
	H3	0.8787	0.8717	0.8751	0.8795
	H6			0.8702	
	H4	0.8633	0.8578	0.8604	0.8548
	H5			0.8646	
3		C_{2v}	C_s	C_2	C_1
	N1	7.4306	7.4442	7.4249	7.4198
	N3				7.3854
	C2	5.6944	5.7188	5.7208	5.9717
	C4	6.3415	6.2516	6.2784	6.0551
	C6				6.2386
	C5	6.0221	6.0437	6.0250	6.0540
	H1	0.6479	0.6424	0.6511	0.6960
	H3				0.6500
	H2	0.8367	0.8378	0.8422	0.8786
	H4	0.8657	0.8184	0.9170	0.9039
	H6				0.8795
	H5	0.8753	0.8866	0.8692	0.8673
4		D_{2h}	C_{2h}	C_{2v}	
	N1	7.5449	7.4240	7.4197	
	C2	6.0306	6.0790	6.0795	
	H1	0.6585	0.6880	0.6908	
	H2	0.8677	0.8650	0.8653	
5		C_{2v}	C_s	C_2	
	N1	7.4091	7.3433	7.3930	
	C3	5.8391	5.8998	5.9309	
	N4	7.2617	7.2151	7.1594	
	H1	0.6352	0.6905	0.6633	
	H3	0.8548	0.8514	0.8535	
6		C_{2h}	C_i	C_2	
	N1	7.5016	7.4064	7.3336	
	N2	7.1608	7.1583	7.2066	
	C3	5.8565	5.9112	5.9408	
	H1	0.6403	0.6795	0.6751	
	H2	0.8408	0.8445	0.8439	

where the signs + and − denote, respectively, a lengthening and a shortening of the bonds relative to the C_{2v} structure: N1−C2 (+0.015 Å), C2−C3 (+0.009 Å), and C3−C4 (−0.013 Å). Because of a folding of the molecular skeleton, the nuclei and the electron cloud should become spatially close together and, hence, the electrostatic interactions should be largely enhanced in the C_s structure. In conformity with this expectation, the distortion leads to large energy changes of the attractive and repulsive interaction terms. Actually, the former term is lowered in energy, while the latter terms are raised in energy. Further, it is observed that the kinetic term is slightly raised in energy, in accord with the requirement arising from the molecular virial theorem. This is briefly accounted for in terms of the kinetic energy pressure of electrons:[42−45] the less room the electron has to move about in, the higher will be the kinetic energy. Since a folding of the molecular skeleton brings about a confinement of the electron movement, it results in an energy raise of the kinetic term in comparison with the C_{2v} structure. In conclusion, it can be said that the boat C_s structure of **1** owes its energetic stability to the energy lowering of the electron−nuclear attractive term V_{en} and the other terms are in the opposite direction to the stability.

*1,2-Dihydro-1,2-diazine (**2**).* As noted in the preceding section, the molecule suffers two types of the pseudo-JT effects, one being from C_{2v} to C_1 and the other from C_{2v} to C_2. (i) On distortion from C_{2v} to C_1, the structural changes take place in two stages. As a whole, the first step ($C_{2v}\rightarrow C_s$) is attributable to an expansion of the six-membered ring, holding the ring to almost planar: N1−N2 (+0.032 Å), N2−C3 (+0.030 Å), C3−C4 (−0.004 Å), C4−C5 (−0.016 Å), C1−H1 (+0.010 Å), C3−H3 (+0.001 Å), and C4−H4 (+0.001 Å). Evidently, this will lead to the prediction that the repulsive terms V_{nn} and V_{ee} should be lowered in energy, whereas the attractive term V_{en} should be raised in energy. Interestingly, the second step ($C_s\rightarrow C_1$) offers a contrast with the first one in that the net structural change presents a contraction of the six-membered ring coupled with its folding. A simple analysis with regard to the bond distances between the C_s and C_1 structures reveals that N1−N2 is shortened by 0.037 Å, N2−C3 is lengthened by 0.005 Å, C3−C4 is lengthened by 0.008 Å, and C4−C5 is shortened by 0.003 Å in a totally symmetric fashion. Besides, the asymmetric a″ nuclear deformation is operative such that N2−C3 is shortened by 0.019 Å, C3−C4 is lengthened by 0.002 Å, and the remaining two bonds are lengthened and shortened so that each set of the displacement vectors may satisfy the symmetry. However, N1−N2 and C4−C5 remain unchanged in length by symmetry. Accordingly, the skeletal folding accompanied by a contraction of the electron cloud should give rise to the energy changes of the individual terms opposite to those in the first step. Indeed, it is seen that the attractive term V_{en} is lowered in energy, whereas the repulsive terms V_{nn} and V_{ee} are raised in energy. Regarding the overall distortion from C_{2v} to C_1, it may be safely said that the molecular skeleton is contracted in a totally symmetric fashion, the associated changes in bond length being given as follows: N1−N2 (−0.005 Å), N2−C3 (−0.067 Å), C3−C4 (+0.004 Å), and C4−C5 (−0.014 Å). Comparison of each term in energy between the C_{2v} and C_1 structures reveals that the skeletal contraction is actually reflected in an energy lowering of the attractive term. From this viewpoint, it can be said that the stability of C_1 structure originates from an energy lowering of the electron−nuclear attractive term V_{en}. (ii) On the structural changes from C_{2v} to C_2, N2−C3 is lengthened by 0.038 Å, while the remaining peripheral bonds are slightly shortened. This shows that almost no net changes in bond distance take place regarding the peripheral bonds, while a negative charge is transferred to the twisting C3−N2−N1−C6 moiety. On account of a twisting of the six-membered ring, the nuclei should come to lie in close proximity to the electron clouds. As is to be expected, this is virtually reflected on an energy lowering of the attractive term. Thus, it is concluded that the energetic stability of C_2 structure should arise from the electron−nuclear attractive term V_{en}.

*1,3-Dihydro-1,3-diazine (**3**).* The pseudo-JT effects from C_{2v} to C_1 take place through two paths, one being via the C_s structure and the other via the C_2 structure. (i) In the first step ($C_{2v}\rightarrow C_s$), the changes in bond distance correspond to an expansion of the six-membered ring as given below: C2−N3 (+0.008 Å), N3−C4 (−0.001 Å), and C4−C5 (+0.018 Å). It is thus

TABLE 3: Total and Partitioned Energies and Total Energy Differences between the Symmetric and Distorted Structures of 1−6[a]

molecule	component	structure (point group)			
1		C_{2v}	C_s		
	E_{total}	−247.218726	−247.245328		
	Δ^b	0	−16.68		
	T	246.919120	246.959909		
	V_{en}	−1009.079744	−1012.921305		
	V_{ee}	303.083851	304.997838		
	V_{nn}	211.858047	213.718230		
2		C_{2v}	C_s	C_1	C_2
	E_{total}	−263.818909	−263.834742	−263.848131	−263.853319
	Δ	0	−9.94	−18.33	−21.58
	T	263.435748	263.471260	263.484340	263.486414
	V_{en}	−1066.757429	−1064.439409	−1069.582531	−1067.379414
	V_{ee}	314.267592	313.003439	315.556132	314.466603
	V_{nn}	225.235179	224.129967	226.693929	225.573078
3		C_{2v}	C_s	C_2	C_1
	E_{total}	−263.794994	−263.798464	−263.800465	−263.820135
	Δ	0	−2.17	−3.44	−15.77
	T	263.403627	263.419713	263.423591	263.457059
	V_{en}	−1068.195643	−1067.853572	−1067.839733	−1069.972875
	V_{ee}	314.730613	314.515970	314.490192	315.678867
	V_{nn}	226.266409	226.119423	226.125485	227.016814
4		D_{2h}	C_{2h}	C_{2v}	
	E_{total}	−263.868905	−263.878723	−263.879153	
	Δ	0	−6.17	−6.43	
	T	263.485122	263.520242	263.520584	
	V_{en}	−1068.311953	−1067.179848	−1067.412005	
	V_{ee}	315.013844	314.333200	314.447752	
	V_{nn}	225.944083	225.447683	225.564515	
5		C_{2v}	C_s	C_2	
	E_{total}	−295.805314	−295.816514	−295.832520	
	Δ	0	−10.04	−17.07	
	T	295.279601	295.310376	295.320785	
	V_{en}	−1154.848528	−1152.836931	−1155.832168	
	V_{ee}	332.590089	331.455468	332.935634	
	V_{nn}	231.173524	230.254574	231.743230	
6		C_{2h}	C_i	C_2	
	E_{total}	−295.839882	−295.843862	−295.852697	
	Δ	0	−2.51	−8.03	
	T	295.311814	295.327557	295.340483	
	V_{en}	−1156.944825	−1155.493897	−1158.771472	
	V_{ee}	333.594376	332.795881	334.415247	
	V_{nn}	232.198753	231.526597	233.163046	

[a] Energies are in hartrees. [b] Differences of the total energy in kcal/mol relative to the symmetric structure.

predicted that the skeletal expansion should result in an energy lowering of the internuclear and interelectronic repulsive terms. In the second step ($C_s \rightarrow C_1$), the molecular skeleton is slightly expanded symmetrically relative to the C_s structure: C2−N3 (+0.083 Å), N3−C4 (−0.084 Å), and C4−C5 (+0.017 Å). At the same time, the asymmetric a″ nuclear deformation is operative such that C2−N3 is shortened by 0.041 Å, N3−C4 is shortened by 0.042 Å, C4−C5 is lengthened by 0.056 Å, and the remaining bonds are shortened and lengthened so that each set of the displacement vectors may satisfy the symmetry. Moreover, the molecular skeleton is folded with the structural changes. This implies that the energy variation of the attractive and repulsive terms should be affected by the opposing two factors, one being an expansion of the ring and the other a folding of the skeleton. In such a case, it is hard to predict the energy variation of the terms in question. However, that the attractive term is indeed lowered and the repulsive terms are raised in energy can be presumed to be due the fact that the contribution from the latter is larger than the former. It should be remarked that, owing to the competition between the two factors, each change of the terms is rather small in energy as compared with the other cases. (ii) In another path, the first step ($C_{2v} \rightarrow C_2$) as well as the second one ($C_2 \rightarrow C_1$) cause almost the same structural and energy changes as those observed in (i). The first step indicates an expansion of the six-membered ring: C2−N3 (+0.008 Å), N3−C4 (−0.003 Å), and C4−C5 (+0.019 Å). It is thus predictable that the internuclear and interelectronic repulsive terms should be lowered in energy. In the second step, the ring is slightly expanded symmetrically relative to the C_2 structure, followed by a folding of the molecular skeleton: C2−N3 (+0.083 Å), N3−C4 (−0.082 Å), and C4−C5 (+0.016 Å). In this case too, the numerical values in Table 3 indicate clearly that to the energy variation of the individual terms, the contribution from the skeletal folding is larger than that from the skeletal expansion. In short, the stability of the C_2 structure is due to an energy lowering of the repulsive terms V_{nn} and V_{ee}, while the stability of the C_1 structure is ascribed to an energy lowering of the attractive term V_{en}. It is further noted that, irrespective of the above pathways, the overall pseudo-JT distortion from C_{2v} to C_1 gives rise to a folding of the molecular skeleton as well as a slight symmetrical expansion of the six-membered ring: C2−N3 (+0.083 Å), N3−C4

(−0.082 Å), and C4−C5 (+0.016 Å). From this viewpoint, it may be said that the stability of C_1 structure should originate from an energy lowering of the electron−nuclear attractive term V_{en}.

*1,4-Dihydropyrazine (**4**)*. Taking the bond distances at the D_{2h} structure as the reference values, it is found that the molecular skeleton of the antifolded C_{2h} structure is expanded symmetrically, with the six-membered ring being held almost planar. The associated changes in bond length are given as follows: N1−C2 (+0.012 Å), C2−C3 (−0.002 Å), N1−H1 (+0.010 Å), and C2−H2 (+0.002 Å). Because the skeletal expansion leads to an expansion of the electron cloud, the interelectronic repulsive interactions should be largely reduced in energy. As is shown in Table 3, the internuclear and interelectronic repulsive terms are actually lowered in energy, where an energy lowering of the latter term is partly responsible for a negative charge relaxation on N1 (N4). On the other hand, the electron−nuclear attractive term is raised in energy due to the factors mentioned above. The same is also found for the C_{2v} structure with regard to the structural changes as well as the associated variation of each energy term. In conclusion, it can be said that the energetic stability of C_{2h} and C_{2v} structures should arise from an energy lowering of the internuclear and interelectronic repulsive terms V_{nn} and V_{en}.

*1,2-Dihydro-1,2,4,5-tetrazine (**5**)*. Upon the pseudo-JT distortion from C_{2v} to C_s, almost all the bonds including CH and NH bonds are lengthened as given below: N1−N2 (+0.026 Å), N2−C3 (+0.027 Å), C3−N4 (−0.004 Å), N4−N5 (−0.010 Å), N1−H1 (+0.010 Å), and C3−H3 (+0.001 Å). Concurrently, the adjacent N-hydrogens are bent up from the planar six-membered ring. Owing to an expansion of the molecular skeleton, the two repulsive terms V_{nn} and V_{en} should contribute to the stability of C_s structure. In the transformation from C_s to C_2, the planar six-membered ring is deformed into a twisted conformation, the changes in bond distance being given as follows: N1−N2 (−0.029 Å), N2−C3 (+0.010 Å), C3−N4 (+0.005 Å), N4−N5 (−0.017 Å). Because the structural change corresponds to a contraction of the six-membered ring together with its twisting, it is readily predicted that the electron−nuclear attractive term is lowered in energy, while the repulsive terms are raised in energy. In accord with this expectation, the twisted C_2 structure is actually lowered in energy by the electron−nuclear attractive term V_{en}. In the pseudo-JT distortion from C_{2v} to C_2, the associated changes in bond distance are given as follows: N1−N2 (−0.003 Å), N2−C3 (+0.037 Å), C3−N4 (+0.001 Å), N4−N5 (−0.027 Å), N1−H1 (+0.012 Å), and C3−H3 (+0.001 Å). In this case, no appreciable changes in bond distance are observed on the whole, but the hydrazine moiety is twisted relative to the N4−N5 bond. Note that since a twisting of the ring brings about the proximity between the nuclei and electron clouds, the electron−nuclear attraction energy should be lowered in energy. On the contrary, the repulsive interaction terms should be raised in energy because of the proximity between the nuclei and between the electron clouds. It can be given as a conclusion that a preference of the C_2 structure over the C_{2v} structure comes from an energy lowering of the electron−nuclear attractive term V_{en}.

*1,4-Dihydro-1,2,4,5-tetrazine (**6**)*. In the pseudo-JT structural changes from C_{2h} to C_i, almost all of the bonds are lengthened, the associated changes in bond distance being given as follows: N1−N2 (+0.004 Å), N2−C3 (−0.001 Å), C3−N4 (+0.017 Å), and N1−H1 (+0.006 Å). At the same time, the two N-hydrogens are directed spatially to the antifolded positions, relative to the almost planar six-membered ring. In short, the nuclear deformation corresponding to a slight skeletal expansion should lower the interelectronic and internuclear repulsive interactions. As expected, the stability of C_i structure would arise actually from an energy lowering of the two repulsive terms V_{nn} and V_{ee}. In the pseudo-JT structural changes from C_{2h} to C_2, a skeletal expansion is also observed, the associated changes in bond distance being given as follows: N1−N2 (+0.010 Å), N2−C3 (−0.002 Å), C3−N4 (+0.022 Å), N1−H1 (+0.007 Å), and C3−H2 (+0.001 Å). In contrast with the above case ($C_{2h} \rightarrow C_i$), the pyrrole-type N1 and N4 atoms are displaced above a molecular plane of the symmetric structure, so that the six-membered ring is deformed into a shallow boat conformation, followed by a charge transfer from N1 (N4) to the nearest-neighbor atoms. Just as in the case ($C_s \rightarrow C_1$) of **3**, it may be presumed here that to the energy variation of the terms of interest, the contribution from a folding of the six-member ring should be larger than that from an expansion of the skeleton. From this standpoint, the attractive term V_{en} should be lowered in energy, while the repulsive terms V_{nn} and V_{ee} should be raised in energy. As is actually listed in Table 3, the assumption that a folding of the molecular skeleton should affect largely the energy variations is shown to hold for this case also. As a consequence, it can be said that the energetic stability of the C_2 structure arises from an energy lowering of the electron−nuclear attractive term V_{en} and the others are in the opposite direction to the stability.

Conclusion

This study shows that the energy component analyses are highly informative to elucidate what happens inside the molecule when it undergoes the pseudo-JT distortion. It is found that the variation of the attractive and repulsive terms is considerably large in energy, but they are out of phase with each other. Examination of the energy components reveals that the pseudo-JT stabilization is classified into two cases, one in which the stability of nonplanar structure results from a lowering of the electron−nuclear attraction energy and the other in which the associated stability arises from a lowering of the internuclear and interelectronic repulsion energies. For one thing, the pseudo-JT stabilization from C_{2v} to C_s in **1** originates from an energy lowering of the electron−nuclear attractive term, due to a proximity between the nuclei and electron clouds arising from a folding of the ring. For another, **4** undergoes the pseudo-JT distortions from D_{2h} to C_{2h} and C_{2v}, and the stability of both structures arises from an energy lowering of the two repulsive terms, due to an expansion of the molecular framework along with a charge relaxation on N atoms. In the remaining molecules, the case differs somewhat in several respects, but the type of pseudo-JT stabilization can be classified into one of the above two cases. As to **6**, for example, the pseudo-JT stabilization from C_{2h} to C_2 arises from an energy lowering of the electron−nuclear attractive term, whereas the distortion into the local minimum C_i structure takes place with an energy lowering of the two repulsive terms. From these results, we can draw a conclusion that an energy lowering of the electron−nuclear term should not be a common phenomenon when a molecule undergoes the pseudo-JT distortion from planarity. It is of interest to note that, as the energy terms responsible for the pseudo-JT stabilization combine, no instances other than the above two cases are in fact observed, at least in the present molecules.[47] In summary, it can be said that the dominant energy components leading to the pseudo-JT stabilization are different from molecule to molecule and, even within a molecule, they differ from one case to another when it will settle at some stationary points by the pseudo-JT distortions.

Finally, it is noted that it will be desirable for representing the ground state properly to take into account much larger active spaces than the present eight orbitals and 12 electrons in the MCSCF calculations. However, because the differences of the total energy and the components between the symmetric and distorted structures are considered in this work, we conjecture that the likely effects on the energy terms at the different structures would be virtually canceled when estimating the relevant energy differences.[18,48] We thus hope that the essence of the conclusions for **1**−**6** will not be impaired, even if much larger active spaces are included in the MCSCF calculations.

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