

Pseudo-Jahn–Teller Distortion from Planarity in Heterocyclic Seven- and Eight-Membered Ring Systems with Eight π Electrons

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To elucidate the nature of a pseudo-Jahn–Teller (JT) distortion from planarity, ab initio MCSCF calculations with the 6-31G(d,p) basis sets were carried out in the ground states of seven- and eight-membered unsaturated heterocycles with eight π electrons. The monocyclic systems examined were found to show a variety of structural changes. Azepine and oxepin undergo the pseudo-JT distortions from a planar C_{2v} to a boat C_s conformation. In 1,5-diazocine, the pseudo-JT distortion takes place in two stages, the initial step being from a symmetric planar D_{2h} to a skew C_{2h} structure and the subsequent step from the skew C_{2h} to a tub C_2 structure. The 1,3,5,7-tetrazocine molecule undergoes pseudo-JT distortions from a symmetric planar D_{4h} to skew C_{4h} and crown-like D_{2d} structures through the respective in-plane and out-of-plane nuclear deformations. Moreover, the C_{4h} and D_{2d} structures are distorted into the same tub-shaped S_4 conformation. An inspection of the energy components comprised in the total energy reveals that the stability of nonplanar structures arises from a lowering of the electron–nuclear attraction energy. The energy variation is accounted for in terms of an electrostatic interaction and the proximity among the nuclei and electron clouds owing to a folding of the molecular skeleton. It is shown that the theoretical structural characteristics for azepine, oxepin, 1,5-diazocine, and 1,3,5,7-tetrazocine are in good agreement with available experimental facts.

Introduction

The nonplanarity of conjugated molecules has attracted much attention because of structural characteristics, physicochemical properties, and chemical reactions.^{1–7} In recent years, the magnetic properties of monocyclic conjugated systems with $4n$ π electrons have been examined in the lowest singlet and triplet states using the ab initio density functional theory by Schleyer and co-workers.⁸ On the basis of nuclear-independent chemical shifts,⁹ the problems of aromaticity were discussed for the 4π -electron, monocyclic conjugated systems. Of interest is the discovery that the cyclononatetraenyl cation adopts a helical conformation and is Möbius aromatic rather than nonaromatic.^{10,11} It is well known in the literature^{12–19} that a pseudo-Jahn–Teller (JT) effect is the stabilization that occurs when a certain asymmetric distortion mixes two electronic states that are nearly degenerate in the symmetric nuclear configuration of the ground state or of an electronically excited state in nonlinear molecules. In a previous paper,²⁰ we carried out an energy component analysis of the pseudo-JT distortion from planarity in heterocyclic six-membered ring systems with eight π electrons. Inspection of the energy components reveals that this type of pseudo-JT stabilization is classified into two cases, one in which the stability of the nonplanar structure results from a lowering of the electron–nuclear attraction energy and the other in which the associated stability arises from a reduction of the internuclear and interelectronic repulsion energies. From these results, it is concluded for the molecules that a lowering

of the electron–nuclear attraction energy should not be a common phenomenon when a molecule is subject to the pseudo-JT distortion from planarity.^{21,22}

In this context, seven- and eight-membered heterocyclic conjugated systems are intriguing because they possess a distortion of internal bond angles at a symmetric planar conformation. In such a case, it is usually believed that a molecule should change its shape from a planar to a nonplanar structure to relieve the angular strain. With a view to obtaining the physical picture of such structural changes, we carry out an energy component analysis of the total energy and hence elucidate the nature of the pseudo-JT distortion from planarity. To address this question, we deal here with the representative heterocyclic systems with eight π electrons (Figure 1) by means of the ab initio MCSCF method^{23,24} with the 6-31G(d,p) basis sets:^{25–27} azepine (**1**),^{28–30} oxepin (**2**),^{29,31–33} 1,5-diazocine (**3**),³⁴ and 1,3,5,7-tetrazocine (**4**),³⁵ the latter two being diaza and tetraaza derivatives of cyclooctatetraene, respectively. The derivatives of **1–4** are known to exist as nonplanar conformations by X-ray structure analyses.^{28–35}

MCSCF Calculations

To describe the ground state properly for heterocycles **1–4**, we employ the fully optimized reaction space (FORS) multi-configuration self-consistent field (MCSCF) method^{23,24} with the 6-31G(d,p) basis sets.^{25–27} To take into account the essential part of a static electron correlation, we include all inner valence π orbitals and all π electrons as the active space in the MCSCF calculations. Moreover, we carry out multireference second-order Moller–Plesset perturbation (MRMP2) calculations³⁶ to take into account a dynamic electron correlation by using geometrical parameters optimized by the MCSCF method.

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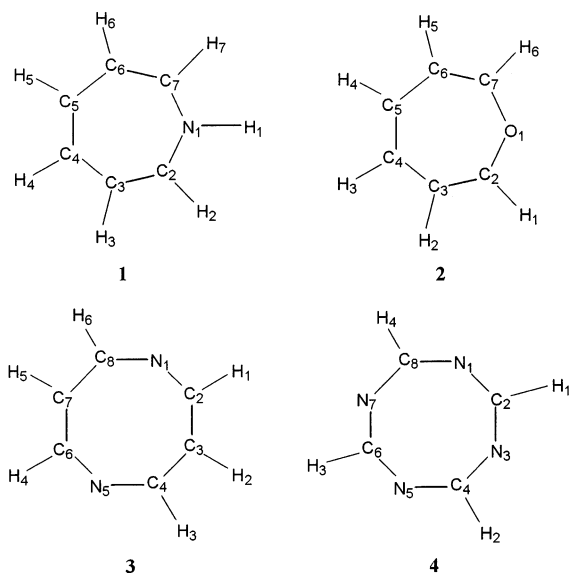


Figure 1. Molecular skeletons and numbering of atoms for **1–4**. The z axis is taken to be the main molecular axis in the C_{2v} point group, the S_4 axis in the D_{2d} point group, and perpendicular to the molecular plane in the C_{2h} , D_{2h} , C_{4h} , and D_{4h} point groups.

To locate the geometrical structures corresponding to a true energy minimum, geometrical optimizations are performed with the MCSCF method by assuming the symmetric planar structures. 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. Furthermore, structural optimizations are performed for the relevant less symmetric structures, provided that imaginary frequencies appear in the accompanying vibrational analyses. By repetition of the procedures, we locate the true energy minimum and transition structures for heterocycles **1–4**.

Energy Partitioning Scheme

Energy components comprised in the total energy are essentially important for discussing the leading terms responsible for the pseudo-JT distortion in the present molecules, and hence we give here a brief review of the energy partitioning scheme.³⁷

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

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

Following the molecular virial theorem for the stationary structures,^{38–41} 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 follows.

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

All calculations were carried out by means of the quantum chemistry code GAMESS⁴² in which new subroutines for the energy component analysis are included.

Results and Discussion

Location of Energy Minimum and Transition Structures.

The vibrational analyses show that the planar C_{2v} structures of **1** and **2** each have one imaginary frequency, 212.7i and 110.3i cm^{-1} , corresponding to an out-of-plane b_2 nuclear deformation, respectively. Thus, the geometry optimization starting with the relevant distorted conformation converges into a boat-shaped C_s structure for both molecules. The resulting C_s structure is shown to be a real energy minimum on the potential energy surface since all of the frequencies are positive definite. As to **3** and **4**, quite a different situation is observed for the structural changes. At the symmetric D_{2h} structure of **3**, there appears one imaginary frequency (3072.1i cm^{-1}) corresponding to an in-plane bond-stretching deformation of big symmetry. The associated geometry optimization leads to a planar C_{2h} structure with alternate short and long bonds. Moreover, since the resulting C_{2h} structure has one imaginary frequency (180.6i cm^{-1}) corresponding to an out-of-plane nuclear deformation of a_u symmetry, it is distorted into a tub-shaped C_2 structure. At the symmetric D_{4h} structure of **4**, there appear three imaginary frequencies, 12454.5i, 7305.3i, and 198.3i cm^{-1} , corresponding to nuclear deformations of b_{1u} , a_{2g} , and a_{2g} symmetry, respectively. That is, the out-of-plane b_{1u} deformation leads to a crown-like D_{2d} structure, and the two in-plane bond-stretching a_{2g} deformations lead to the same stationary point of a bond-alternated C_{4h} structure. Subsequently, the resulting D_{2d} and C_{4h} structures each have one imaginary frequency, 16763.3i and 2274.4i cm^{-1} , corresponding to a_2 and b_u nuclear deformations, respectively. Eventually, the geometrical optimizations starting with the respective nuclear deformations converge into the same stationary point of a tub-shaped S_4 structure. The vibrational analysis shows that the resulting S_4 structure is a true energy minimum because all of the frequencies are positive definite. In the symmetric D_{2h} structure of **3**, the ground state is assigned to the open-shell singlet configuration with B_{1g} symmetry instead of the closed-shell configuration with A_{1g} symmetry. This contrasts with the situation observed in the symmetric D_{4h} structure of **4**. The difference will be accounted for qualitatively as follows. In the symmetric structures of **3** and **4**, the HOMO and LUMO are confined mostly to different sets of atoms, which correspond to the doubly degenerate nonbonding MOs in the symmetric cyclooctatetraene molecule. The RHF/6-31G(d,p) calculations reveal that the HOMO is higher in energy for **3** than for **4** by about 1.9 eV but the LUMO is almost the same in energy between the two. It then follows that the energy separation between the RHF ground state and the singly excited configuration arising from the orbital jump, HOMO \rightarrow LUMO, should be smaller for **3** in comparison with that for **4**. For conjugated 4π -electron systems such as cyclobutadiene, it is observed that at the symmetric structure the open-shell singlet becomes the ground state as a result of the large correlation effects arising from dynamic spin-polarization terms.^{43–45} For the D_{2h} structure of **3**, since such correlation effects are indeed included in the MCSCF calculations, the energy ordering is reversed such that the open-shell singlet state (B_{1g}) lies below the closed-shell singlet state (A_{1g}) by 1.2 eV. In this event, this leads to a violation of Hund's multiplicity rule because the lowest excited triplet state (B_{1g}) lies above the corresponding singlet ground state by about 0.72 eV.

As described above, **1–4** show a variety of structural changes by the pseudo-JT effects. These should be largely responsible for the molecules being the 8π -electron heterocyclic systems as given below. From a perturbational MO approach, **1–4** are

TABLE 1: Optimized Geometrical Parameters at the Symmetric and Distorted Structures of 1–4

molecule	structure (point group)	geometrical parameters ^a
1	C_{2v}	N1–C2 = 1.393, C2–C3 = 1.343, C3–C4 = 1.478, C4–C5 = 1.346, N1–H1 = 0.990, C2–H2 = 1.075, C3–H3 = 1.075, C4–H4 = 1.077, C5–C4–H4 = 117.5, C4–C3–H3 = 115.8, C3–C2–H2 = 118.3, C2–N1–H1 = 115.9, C5–C4–C3 = 127.5, C4–C3–C2 = 128.8, C3–C2–N1 = 129.6, C2–N1–C7 = 128.2, C6–C5–C4–C3 = 0.0, C5–C4–C3–C2 = 0.0, C4–C3–C2–N1 = 0.0, C3–C2–N1–C7 = 0.0
	C_s	N1–C2 = 1.408, C2–C3 = 1.342, C3–C4 = 1.473, C4–C5 = 1.347, N1–H1 = 0.993, C2–H2 = 1.077, C3–H3 = 1.076, C4–H4 = 1.077, C5–C4–H4 = 118.2, C4–C3–H3 = 116.9, C3–C2–H2 = 119.5, C2–N1–H1 = 112.5, C5–C4–C3 = 125.9, C4–C3–C2 = 126.2, C3–C2–N1 = 125.7, C2–N1–C7 = 120.2, C6–C5–C4–C3 = 0.0, C5–C4–C3–C2 = 27.3, C4–C3–C2–N1 = –0.1, C3–C2–N1–C7 = –48.0
2	C_{2v}	O1–C2 = 1.361, C2–C3 = 1.340, C3–C4 = 1.473, C4–C5 = 1.344, C2–H1 = 1.073, C3–H2 = 1.076, C4–H3 = 1.076, C5–C4–H1 = 118.4, C4–C3–H2 = 116.1, C3–C2–H1 = 120.0, C5–C4–C3 = 126.0, C4–C3–C2 = 129.9, O1–C2–C3 = 131.3, C2–O1–C7 = 125.7, C6–C5–C4–C3 = 0.0, C5–C4–C3–C2 = 0.0, C4–C3–C2–O1 = 0.0, C3–C2–O1–C7 = 0.0
	C_s	O1–C2 = 1.370, C2–C3 = 1.339, C3–C4 = 1.469, C4–C5 = 1.340, C2–H1 = 1.074, C3–H2 = 1.076, C4–H3 = 1.077, C5–C4–H1 = 118.6, C4–C3–H2 = 117.7, C3–C2–H1 = 122.2, C5–C4–C3 = 124.9, C4–C3–C2 = 125.3, O1–C2–C3 = 124.2, C2–O1–C7 = 116.6, C6–C5–C4–C3 = 0.0, C5–C4–C3–C2 = 28.2, C4–C3–C2–O1 = 4.4, C3–C2–O1–C7 = –59.9
3	$D_{2h}(B_{1g})^b$	N1–C2 = 1.334, C2–C3 = 1.412, C2–H1 = 1.077, C3–H2 = 1.077, C8–N1–C2 = 130.8, N1–C2–C3 = 135.6, C2–C3–C4 = 137.9, 23 N1–C2–H1 = 111.6, C2–C3–H2 = 111.1, C8–N1–C2–C3 = 0.0, C8–N1–C2–H1 = 180.0, N1–C2–C3–C4 = 0.0, N1–C2–C3–H2 = 180.0
	C_{2h}	N1–C2 = 1.404, C2–C3 = 1.349, C3–C4 = 1.481, C4–N5 = 1.273, C2–H1 = 1.075, C3–H2 = 1.077, C4–H3 = 1.081, C8–N1–C2 = 130.0, N1–C2–C3 = 136.2, C2–C3–C4 = 137.7, C3–C4–N5 = 136.1, N1–C2–H1 = 109.5, C2–C3–H2 = 112.3, C3–C4–H3 = 110.8, C8–N1–C2–C3 = 0.0, N1–C2–C3–C4 = 0.0, C2–C3–C4–N5 = 0.0, 8-N1–C2–H1 = 180.0, C8–N1–C2–C3–H2 = 180.0, C2–C3–C4–H3 = 180.0
	C_2	N1–C2 = 1.408, C2–C3 = 1.341, C3–C4 = 1.485, C4–N5 = 1.274, C2–H1 = 1.076, C3–H2 = 1.077, C4–H3 = 1.081, C8–N1–C2 = 121.4, N1–C2–C3 = 126.6, C2–C3–C4 = 125.2, C3–C4–N5 = 127.9, N1–C2–H1 = 113.1, C2–C3–H2 = 118.3, C3–C4–H3 = 116.0, C8–N1–C2–C3 = 59.5, N1–C2–C3–C4 = 2.9, C2–C3–C4–N5 = 60.5, C3–C4–N5–C6 = –0.5, C8–N1–C2–H1 = 127.7, N1–C2–C3–H2 = 117.1, C2–C3–C4–H3 = –121.6
4	D_{4h}	N1–C2 = 1.326, C2–H1 = 1.078, C2–N3–C4 = 131.3, N3–C2–N1 = 138.7, N3–C2–H1 = 110.6, N3–C4–H2 = 110.6, C4–N3–C2–N1 = 0.0, N5–C4–N3–C2 = 0.0, C6–N5–C4–N3 = 0.0
	D_{2d}	N1–C2 = 1.318, C2–H1 = 1.078, C2–N3–C4 = 129.0, N3–C2–N1 = 132.5, N3–C2–H1 = 113.4, N3–C4–H2 = 113.4, C4–N3–C2–N1 = 30.5, N5–C4–N3–C2 = 30.5, C6–N5–C4–N3 = 30.5
	C_{4h}	N1–C2 = 1.410, C2–N3 = 1.268, C2–H1 = 1.076, C2–N3–C4 = 133.5, N3–C2–N1 = 136.5, N3–C2–H1 = 109.1, N3–C4–H2 = 114.4, C4–N3–C2–N1 = 0.0, N5–C4–N3–C2 = 0.0, C6–N5–C4–N3 = 0.0
	S_4	N1–C2 = 1.404, C2–N3 = 1.270, C2–H1 = 1.076, C2–N3–C4 = 119.8, N3–C2–N1 = 126.8, N3–C2–H1 = 114.4, N3–C4–H2 = 118.6, C4–N3–C2–N1 = 5.0, N5–C4–N3–C2 = 64.6, C6–N5–C4–N3 = –5.0

^a Numbering of atoms is shown in Figure 1. Bond lengths and bond and dihedral angles are in angstroms and degrees. ^b The ground state is an open-shell singlet configuration in the D_{2h} structure of 1,5-diazocine.

regarded as perturbed seven- and eight-membered ring systems with eight π electrons, formed by the replacement of CH group(s) in relevant carbocyclic systems of the type $(CH)_n$ with an NH group, an O atom, or N atoms, where a degeneracy of the HOMOs in the unperturbed systems is lifted by such a change. In the perturbed planar conformation, since two π electrons are assigned to the resulting HOMO, the ground state would exhibit in this sense an unfavorable electronic situation. Such being the case with 1–4, there is a good possibility of some lower electronically excited states lying at lower energy regions relative to the ground state. Accordingly, it is very provable that a nuclear distortion of proper symmetry would mix the ground state and a low-lying excited state and would thereby

lower the ground-state energy. This is equivalent to saying that the relevant force constant becomes negative and, hence, the pseudo-JT distortion should occur spontaneously in the ground state.

Table 1 presents the fully optimized geometrical parameters regarding bond lengths and bond angles for the various structures of 1–4 calculated by the MCSCF/6-31(d,p) method. Figures 2 and 3 display the side views of nonplanar structures obtained by using atomic coordinates. Table 2 lists atomic populations obtained at the respective structures by means of Mulliken's population analysis.⁴⁶ Table 3 shows the total and partitioned energies at the symmetric and distorted structures as well as the relative energy difference between them.

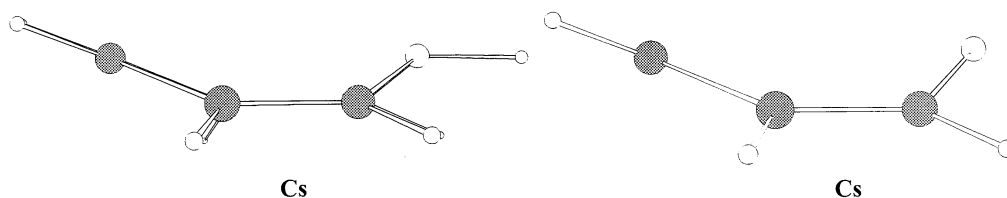


Figure 2. Side views of the boat C_s conformations obtained using the atomic coordinates of the optimized structures for **1** (left) and **2** (right), where gray circles indicate C atoms.

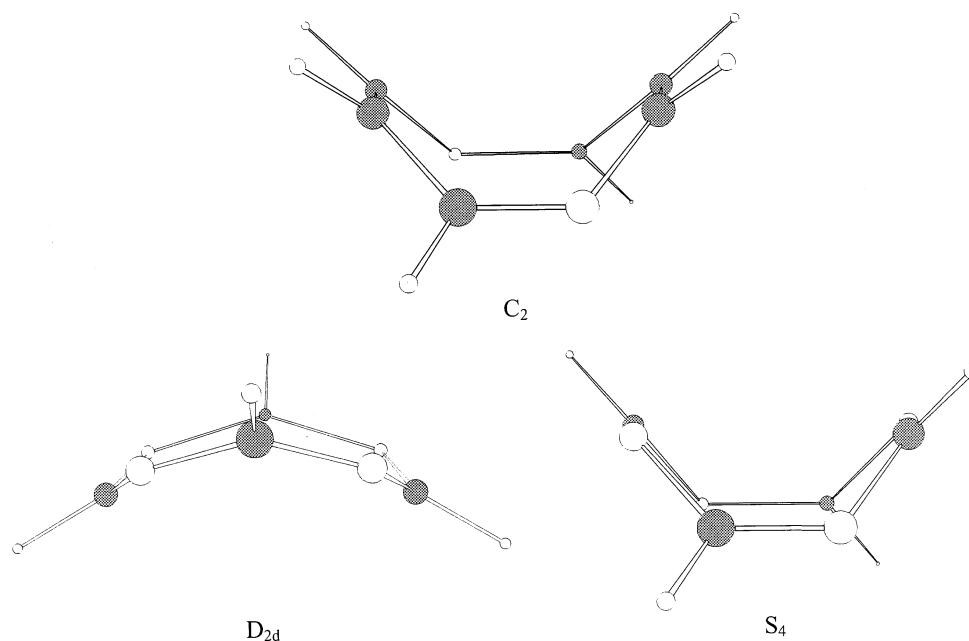


Figure 3. Side views of the tub C_2 conformation and of the crown-like D_{2d} and tub S_4 conformations obtained using the atomic coordinates of the optimized structures for **3** (upper) and **4** (lower), respectively, where gray circles indicate C atoms.

Structural and Electronic Characteristics. In the C_{2v} structure of **1**, the CN bond is indicative of some π -electron delocalization because the distance of 1.393 Å is longer than the experimental value of pyrrole, 1.370 Å.⁴⁷ Of interest is the finding that all of the internal bond angles are comparable to the average angle of 128.6° in a planar heptagon. Upon a structural change from C_{2v} to C_s , an elongation of the CN bond occurs by 0.015 Å, followed by a slight migration of the negative charge from N1 to C2. Concomitantly, the dihedral angles $\angle C3-C2-N1-C7$ and $\angle C5-C4-C3-C2$ are changed significantly from 0 to 48.0 and -27.3° , respectively. The changes in the dihedral angles distort the molecular skeleton in a concave fashion, and hence the C_s structure assumes a boat form with N1-hydrogen in an equatorial position (Figure 2). At the same time, a reduction of the internal bond angles of the seven-membered ring occurs. Among other things, the bond angle at N1 decreases from 128.2 to 120.2°. Since the sum of the bond angles around N1 is less than 360° by 14.8°, it takes to an appreciable extent the sp^3 pyramidal configuration in the C_s structure. The theoretical bond distances in the C_s structure reproduce fairly well the X-ray experimental data of 1-(4-bromophenylsulfonyl)-1H-azepine with a boat conformation.²⁸ The stabilization energy associated with the pseudo-JT effect (i.e., the activation energy for the isodynamic inversion process occurring in the interconversion between the two equivalent boat conformations) is calculated to be 1.4 kcal/mol by MCSCF and 3.0 kcal/mol by MRMP2. Note that the present activation energy for the interconversion process is smaller than the observed value of cycloheptatriene, ca. 6 kcal/mol.⁴⁸ In this connection, a closer examination of Table 3 reveals that the individual energy components vary largely in energy, indicating that the above

TABLE 2: Atomic Populations at the Symmetric and Distorted Structures of 1–4

molecule	position	structure (point group)			
1		C_{2v}	C_s		
	N1	7.7661	7.6815		
	C2	5.8453	5.9007		
	C3	6.1905	6.1697		
	C4	6.1287	6.1285		
	H1	0.6991	0.7124		
	H2	0.8631	0.8680		
	H3	0.8702	0.8672		
2		C_{2v}	C_s		
	O1	8.6472	8.6353		
	C2	5.7877	5.8034		
	C3	6.1959	6.1779		
	C4	6.1249	6.1273		
	H1	0.8517	0.8593		
	H2	0.8578	0.8549		
	H3	0.8584	0.8595		
3		D_{2h}	C_{2h}	C_2	
	N1	7.5031	7.5211	7.4592	
	C2	5.8963	5.9032	5.9073	
	C4	5.8963	5.8536	5.8842	
	C3	6.1394	6.1539	6.2001	
	H1	0.8551	0.8517	0.8463	
	H2	0.8547	0.8575	0.8480	
	H3	0.8551	0.8590	0.8549	
4		D_{4h}	D_{2d}	C_{4h}	S_4
	N1	7.5745	7.5665	7.4945	7.4724
	N3	5.6013	5.6083	5.6737	5.6990
	H1	0.8242	0.8252	0.8318	0.8286

TABLE 3: Total and Partitioned Energies (hartrees) and Total Energy Differences (kcal/mol) between the Symmetric and Distorted Structures of 1–4^a

molecule	component	structure (point group)			
1		C_{2v}	C_s		
	E_{total}	-285.761147	-285.763373		
	Δ^b	0	-1.4 (-3.0) ^c		
	T	285.451242	285.463733		
	V_{en}	-1208.440114	-1212.208456		
	V_{ec}	366.244965	368.143840		
2		C_{2v}	C_s		
	E_{total}	-305.580480	-305.584109		
	Δ	0	-2.3 (-3.3)		
	T	305.209578	305.219372		
	V_{en}	-1258.955176	-1265.284173		
	V_{ec}	375.986830	379.217165		
3		D_{2h}	C_{2h}	C_2	
	E_{total}	-339.596824	-339.612767	-339.641476	
	Δ	0	-10.0 (-9.2)	-28.0 (-29.7)	
	T	339.198341	339.213490	339.243791	
	V_{en}	-1439.398758	-1438.402559	-1459.399383	
	V_{ec}	437.089742	436.604531	447.169796	
4		D_{4h}	D_{2d}	C_{4h}	S_4
	E_{total}	-371.562095	-371.574174	-371.603421	-371.655145
	Δ	0	-7.6 (-16.7)	-25.9 (-7.4)	-58.4 (-44.2)
	T	370.986019	370.987100	371.002291	371.107169
	V_{en}	-1536.364430	-1548.596297	-1531.270234	-1560.362980
	V_{ec}	459.859328	465.965731	457.346352	471.787352
	V_{nn}	333.956987	340.069292	331.318170	345.813313

^a 1 hartree = 627.0898 kcal/mol. ^b Differences of the total energy relative to that of the fully symmetric structure. ^c Difference of the total energy obtained by the MRMP2 method.

stabilization energy is in competition between the two contributions, one arising from energy components that favor the planar C_{2v} structure and the other from the one that favors the boat C_s structure. It can be said commonly for **1–4** that the energy terms are highly sensitive to changes in molecular geometry and have mutually opposite signs to the pseudo-JT stabilization.

In the C_{2v} structure of **2**, the CO bond length of 1.361 Å is very close to the experimental value of furan, 1.362 Å.⁴⁹ Upon symmetry reduction from C_{2v} to C_s , the dihedral angles $\angle\text{C3–C2–O1–C7}$ and $\angle\text{C5–C4–C3–C2}$ are changed from 0 to 59.9 and -28.2° , respectively. Just as in the case of **1**, the changes in dihedral angles result in the formation of the boat form. Concomitantly, the internal bond angles of the seven-membered ring are reduced with a slight lengthening of the CO bond. Of notice is the variation in the bond angles at O1 and C2, which are changed from 125.7 and 131.3 to 116.6 and 124.2°, respectively. Obviously, the angle change at O1 leads to a contraction of the atomic distance between C2 and C7 in the boat form, implying that **2** has a latent tendency of valence isomerization into benzene oxide.²⁹ Despite the relatively large change in molecular shape, the stabilization energy due to the pseudo-JT effect is small: 2.3 kcal/mol by MCSCF and 3.3 kcal/mol by MRMP2. Oxepin **2** and its derivatives are known to exist in equilibrium with valence tautomers of benzene oxides.²⁹ However, 2,7-diphenyloxepin has been reported to take a boat conformation by X-ray structure analysis.³³ The theoretical bond distances in the boat C_s structure are in qualitative accord with the values observed for the diphenyl derivative. The D_{2h} structure of **3** shows that the CN bond length of 1.334 Å is comparable to the experimental value of 1.338 Å in pyridine and that the CC bonds exhibit normal atomic distances in ordinary aromatic hydrocarbons.⁵⁰ Population analysis shows that a marked charge alternation appears along the periphery of the D_{2h} , C_{2h} , and C_2 structures. Namely, N1 and C3 carry

negative charges, whereas C2 and C4 have positive charges. On distortion from the D_{2h} to the skew C_{2h} structure, a substantial bond-length alternation appears along the molecular periphery, with the internal bond angles remaining essentially unchanged (Table 1). On going from the skew C_{2h} to the tub C_2 structure, however, the internal bond angles at N1, C2, C3, and C4 are reduced greatly, the decrements ranging from 8.2 to 12.2°. The stabilization energies arising from the first step ($D_{2h} \rightarrow C_{2h}$) and the second step ($C_{2h} \rightarrow C_2$) are calculated to be 10.0 and 18.0 kcal/mol, respectively. Accordingly, the overall energy lowering amounts to 28.0 kcal/mol, which is almost comparable to the value obtained by the MRMP2 calculations. The X-ray structure analysis shows that the ring of 2,6-dimethyl-3,7-dibromo-4,8-diphenyldiazocine has a tub-shaped configuration and contains alternating double and single bonds.³⁴

For the D_{4h} structure of **4**, the CN bond length of 1.326 Å is slightly shorter than the experimental values in aromatic pyridinyl compounds.⁴⁹ This molecule is interesting in the sense that the pseudo-JT distortion from the planar D_{4h} to the tub S_4 conformation occurs through two different paths, one via the planar bond-alternated C_{4h} structure and the other via the crown-like D_{2d} structure. Notice that in the D_{2d} structure the four N atoms form a symmetric plane; a pair of the opposite two C atoms lies above the plane, and another pair lies below it (Figure 3). On symmetry reduction from D_{4h} to S_4 , the overall structural changes are appreciable regarding bond distances and bond angles. Thus, a substantial bond-length alternation occurs along the molecular periphery, and the bond angles at N1 and C2 are reduced to 119.8 and 126.8 from 134.3 and 138.7°, respectively. The crystal structure of 2,4,6,8-tetramorpholino-1,3,5,7-tetrazocine indicates that the ring adopts a tub conformation with the CN bond lengths in the range of 1.30 to 1.40 Å and the internal bond angles at N and C atoms in the ranges of 116.6 to 119.7 and 124.4 to 127.20°, respectively.³⁵ A comparison

shows that the theoretical geometrical parameters in the S_4 structure (Table 1) reproduce the experimental data very well. The stabilization energies owing to the pseudo-JT effect from D_{4h} to C_{4h} and from C_{4h} to S_4 are respectively 25.9 and 32.5 kcal/mol, whereas those from D_{4h} to D_{2d} and from D_{2d} to S_4 are respectively 7.6 and 50.8 kcal/mol. After all, the pseudo-JT distortion from D_{4h} to S_4 gives an overall energy lowering of 58.4 kcal/mol. Unlike the cases in **1–3**, the MRMP2 calculations for **4** lead to a reduction of the overall energy lowering by about 14 kcal/mol and, concomitantly, lead to a reversal of the relative stability such that the D_{2d} structure is lower in energy than the C_{4h} structure (Table 3).

Obviously, one approach to the cause of nonplanarity is to examine how geometrical parameters vary upon pseudo-JT structural changes. From this viewpoint, it appears that the nonplanarity arises from the effect for relieving the angular strain in the planar conformation. This is because most bond angles are actually decreased more or less from the average angles in a regular heptagon or octagon when **1–4** undergo the pseudo-JT distortions from planarity. However, it is observed that a folding of the ring from the angular strain should bring about an enhancement of the repulsive interactions because of the proximity between the nuclei and between the electron clouds. This suggests that it is preferable to examine the cause of nonplanarity from the overall energy changes in the respective energy components. Namely, another approach to the cause of nonplanarity is to examine how the individual energy components vary upon pseudo-JT structural changes. Below, we are concerned with the dominant energy components responsible for the pseudo-JT distortion.

Energy Component Analysis of the Total Energy. Azepine

(1). The pseudo-JT distortion from the planar C_{2v} to the boat C_s structure leads to a folding of the seven-membered ring accompanied by a small amount of the totally symmetric expansion of the ring. The associated changes in bond lengths are given below, where the signs + and – denote, respectively, a lengthening and a shortening of the bonds relative to those of the C_{2v} structure: N1–C2(+0.015 Å), C2–C3(–0.001 Å), C3–C4(–0.005 Å), and C4–C5(+0.001 Å). The structural changes indicate that the energy variation of the attractive and repulsive terms should be affected by the opposing two factors. In such a case, it is hard in general to predict the overall energy changes in the respective energy components. This is because, for example, a folding of the ring lowers the electron–nuclear attraction energy, whereas an expansion of the ring raises the energy. As shown in Table 3, however, that the attractive term is indeed largely lowered in energy and the two repulsive terms are raised in energy can be attributable to the fact that the contribution from skeletal folding is much larger than that from skeletal expansion. Qualitatively, this is consistent with the above finding that the angle changes surpass in magnitude the expansion of the ring. A concave folding of the ring should lead to a proximity between the nuclei and electron clouds spatially, and hence, the electrostatic attractive interactions are largely enhanced in the C_s structure. Furthermore, it is observed that the kinetic term is slightly raised in energy, in accordance with the requirement arising from the molecular virial theorem. This can be accounted for in terms of the kinetic energy pressure of electrons.^{51,52} The less space that the electron has to move about in, the higher the kinetic energy will be. Since a folding of the molecular skeleton brings about a confinement of the electron motion, it results in an energy increase in the kinetic term relative to that of the C_{2v} structure. These energetic behaviors indicate that the nonplanarity should in fact be

achieved through such a competition that the energy lowering due to the electron–nuclear attractive term V_{en} exceeds in absolute value the energy increase due to the internuclear and interelectronic repulsive terms V_{nn} and V_{ee} . It can thus be concluded 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 that the other terms are in the opposite direction to the stability.

Oxepin (2). The seven-membered ring undergoes a folding upon distortion from the C_{2v} to the C_s structure. Concomitantly, a slight totally symmetric expansion of the seven-membered ring occurs. The associated changes in bond length are given as follows: O1–C2(+0.009 Å), C2–C3(–0.001 Å), C3–C4(–0.004 Å), and C4–C5(+0.005 Å). By reference to **1**, it may be presumed for **2** that for the energy variation of the terms of interest the contribution from a folding of the seven-membered ring should be larger than that from an expansion of the ring. From this point of view, the attractive term should be lowered in energy, and the repulsive terms should be raised in energy. As listed in Table 3, the assumption that a folding of the molecular skeleton should greatly affect the energy variation also holds for this case. A closer examination of the respective energy terms between **1** and **2** reveals that the energy change of the attractive term is about twice as large in magnitude for the latter as for the former upon symmetry reduction from C_{2v} to C_s . Also, for the two repulsive terms, very similar changes in energy are observed between the two molecules. This distinction can be ascribed mostly to the degree of folding of the molecular skeleton: the dihedral angle is larger for $\angle C3-C2-O1-C7$ than for $\angle C3-C2-N1-C7$ by about 12°, indicating that the folding is much larger for **2** than for **1** (Figure 2). In conclusion, it can be said for **2** that the stability of the boat C_s structure arises from an energy decrease in the electron–nuclear attractive term V_{en} and the other terms are in the opposite direction to the stability.

1,5-Diazocine (3). As noted in the preceding section, the pseudo-JT distortion takes place in two stages, the initial step being from a symmetric planar D_{2h} to a planar skew C_{2h} structure and the subsequent step from the skew C_{2h} to a tub C_2 structure. In the initial step ($D_{2h} \rightarrow C_{2h}$), the changes in bond distances correspond to an expansion of the eight-membered ring in a totally symmetric fashion: N1–C2(+0.005 Å) and C2–C3(+0.003 Å). At the same time, the asymmetric big nuclear deformation is operative such that N1–C2 is lengthened by 0.066 Å, C2–C3 is shortened by 0.066 Å, and the remaining bonds are alternately lengthened and shortened by respective lengths so that each set of displacement vectors may satisfy the symmetry. This indicates the participation of two vibrational modes of a_{1g} and b_{1g} symmetry in this structural change. The skeletal expansion is thus predicted to lead to a reduction of the internuclear and interelectronic repulsion energies. In good accordance with this expectation, the repulsive terms V_{nn} and V_{ee} are lowered in energy, whereas the attractive term V_{en} is raised in energy. In the second step ($C_{2h} \rightarrow C_2$), although almost no net changes in bond distances take place regarding the peripheral CN and CC bonds on the whole, the C and N atoms are displaced above and below a molecular plane of the symmetric structure. Owing to a folding of the eight-membered ring into a tub form (Figure 3), the nuclei and electron clouds should become spatially close together and, hence, the electrostatic interactions should be largely enhanced in the tub C_2 structure. In conformity with this expectation, the structural change leads to large energy changes of the attractive and

repulsive interaction terms. Actually, the former is lowered in energy, and the latter terms are raised in energy. From these results, it is concluded for **3** that the pseudo-JT bond distortion within the planar forms ($D_{2h} \rightarrow C_{2h}$) takes place with an energy reduction of the repulsive terms V_{nn} and V_{ee} , whereas the pseudo-JT distortion from planarity ($C_{2h} \rightarrow C_2$) takes place with an energy lowering of the electron–nuclear attractive term V_{en} .

1,3,5,7-Tetrazocine (4). As mentioned above, the pseudo-JT distortion from D_{4h} to S_4 takes place through two paths, one via the nonplanar D_{2d} structure and the other via the planar C_{4h} structure. (i) For the former path, the structural change in the first step ($D_{4h} \rightarrow D_{2d}$) corresponds to a contraction of the eight-membered ring: all of the CN bonds are shortened by 0.008 Å relative to those in the D_{4h} structure, and the molecular skeleton is folded slightly in a crown-like fashion (Figure 3). Evidently, the structural changes should lead to the results that the attractive term is lowered in energy and the repulsive terms are raised in energy, in agreement with the energy variations shown in Table 3. In the second step ($D_{2d} \rightarrow S_4$), however, the structural change is accompanied by a totally symmetric expansion of the CN bonds by 0.019 Å. At the same time, the asymmetric a_2 nuclear deformation is operative such that the successive CN bonds are alternately shortened and lengthened by 0.067 Å, leading to a strong bond-length alternation along the molecular periphery. Concomitantly, the structural change leads to a marked folding of the molecular skeleton into a tub conformation. As noted above, the energy variation of the attractive and repulsive terms is also expected to be affected by the opposing two factors upon the present structural change. In this case too, the energy component analysis reveals clearly that the attractive term is indeed lowered in energy and that the repulsive terms are raised in energy. As a result, it can be said that the pseudo-JT stabilizations from the first and second steps should arise from a decrease in the electron–nuclear attraction energy V_{en} . (ii) As for another path, the structural change in the first step ($D_{4h} \rightarrow C_{4h}$) brings about a strong bond-length alternation in the molecular periphery, keeping the eight-membered ring planar. The successive CN bonds are alternately shortened and lengthened by 0.071 Å along the periphery. At the same time, an expansion of the ring takes place in a totally symmetric fashion, each CN bond being lengthened by 0.013 Å. Because the skeletal expansion leads to an expansion of the electron clouds, the interelectronic repulsive interactions should be largely reduced in energy. In accordance with this expectation, the internuclear and interelectronic repulsive terms V_{nn} and V_{ee} are actually lowered in energy. It is thus found for **3** and **4** that the pseudo-JT bond distortion within the planar forms takes place by a reduction of the two repulsive interaction energies. In the second step ($C_{4h} \rightarrow S_4$), the structural change into the tub form is accompanied by a folding of the molecular skeleton and a shortening of the CN bonds on the whole: N1–C2(+0.002 Å) and C2–N3(–0.006 Å). As expected, these structural changes lead to an energy lowering of the attractive term and a raising of the repulsive terms. The analyses reveal that in the path via the C_{4h} structure the dominant factors contributing to the pseudo-JT stabilization are different between the two steps, the first step comprising the repulsive terms V_{nn} and V_{ee} and the second step, the attractive term V_{en} .

Conclusions

Using the ab initio MCSCF method with the 6-31G(d,p) basis sets, we carried out an energy component analysis of the total energy to understand the nature of the pseudo-JT effect in the ground states of heterocycles **1–4**. For **1** and **2**, it is found that

the stability of the boat C_s structure arises from an energy lowering of the electron–nuclear attractive term V_{en} and that the other terms are in the opposite direction to the stability. As to **3** and **4**, however, the type of pseudo-JT stabilization is classified into two cases, one in which the stability of bond-alternated planar structures results from a reduction of the internuclear and interelectronic repulsion energies V_{nn} and V_{ee} and the other in which the stability of nonplanar structures arises from a lowering of the electron–nuclear attraction energy V_{en} . An energy change of this type is observed for the parent cyclooctatetraene molecule.⁵³ Namely, when the planar D_{8h} structure suffers an in-plane bond distortion, the resulting bond-alternated D_{4h} structure owes its stability to the energy reduction of the repulsive terms V_{nn} and V_{ee} . Subsequently, when the planar D_{4h} structure undergoes an out-of-plane nuclear deformation, the stability of the tub structure with D_{2d} symmetry arises from the energy lowering of the electron–nuclear attractive term V_{en} . It is thus shown that the energy component analyses are highly informative in elucidating what happens inside the molecule when it undergoes pseudo-JT distortion: the energy variations of the attractive and repulsive terms are significant, but they are out of phase with each other. Even within a molecule, the phase relationship between the attractive and repulsive terms changes from one case to another when it settles at some stationary points by the pseudo-JT distortions. From these results, it is concluded that an energy lowering of the electron–nuclear attractive term V_{en} should not be a common phenomenon when a molecule undergoes the pseudo-JT distortion.^{21,22} However, it can be said safely that the origin of nonplanarity arises from a lowering of the electron–nuclear attraction energy V_{en} at least in **1–4**. This interpretation is given such that owing to the folding of the molecular skeleton the nuclei and electron clouds should become spatially close together and, hence, the electron–nuclear attractive interactions are largely enhanced in the nonplanar structure. As a byproduct, it is found that in the symmetric D_{2h} structure of **3** the open-shell B_{1g} singlet state is lowest in energy, the corresponding B_{1g} triplet state and the closed-shell A_{1g} singlet state being stabilized to a lesser extent by the inclusion of configuration interactions responsible for dynamic spin-polarization effects in the MCSCF calculations. Accordingly, this indicates a violation of Hund's rule, reflecting that **3** possesses an unusual electronic property inherent to the parent cyclooctatetraene molecule.^{43–45}

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