

Ab Initio MCSCF Study on the Pseudo-Jahn–Teller Distortion from Planarity in Cycloheptatriene, Heptalene, and Heptafulvalene

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To elucidate the nature of a pseudo-Jahn–Teller (JT) distortion from planarity, ab initio MCSCF calculations with 6-31G(d) basis sets are carried out on the ground state of the titled molecules. Cycloheptatriene undergoes the pseudo-JT distortion from a planar C_{2v} to a boat C_s conformation. In heptalene, the pseudo-JT distortion takes place in two stages, the initial step being from a symmetric planar D_{2h} to a skew planar C_{2h} structure and the subsequent step from the skew C_{2h} to a twisted C_2 one. In heptafulvalene, the symmetric planar D_{2h} structure exhibits a third-order saddle point and, hence, the pseudo-JT distortions take place from the D_{2h} to D_2 , C_{2v} , and C_{2h} ones through the respective out-of-plane nuclear deformations. Besides, the twisted D_2 structure exhibits a second-order saddle point with respect to the syn- and anti-folding motions of the seven-membered rings and the structural changes take place from the D_2 to the C_{2v} and C_{2h} structures. A comparison of the total energy reveals that the ground state of heptafulvalene takes the anti-folded C_{2h} conformation. These structural characteristics are in good agreement with the available experimental facts. Energy component analyses reveal that in these molecules the pseudo-JT distortion from planarity should lead markedly to a lowering of the electron–nuclear attraction energy and concomitantly to raising of both the interelectronic and the internuclear repulsion energy. These energetic behaviors are accounted for in terms of the electrostatic interactions and the proximity between the nuclei and electron clouds involved in the CC and CH bonds, owing to the folding of the carbon skeleton.

Introduction

The Jahn–Teller (JT) effect is a stabilization that arises from the geometric instability of degenerate electronic states in nonlinear polyatomic molecules.^{1–3} In this connection, the pseudo-JT effect is the stabilization which occurs when a certain asymmetric distortion mixes two electronic states which are nearly degenerate in the symmetric nuclear configuration of the ground or of an electronically excited state.^{4,5} To gain insight into the nature of the pseudo-JT effect, we carried out energy component analyses for conjugated molecules in the ground and electronically excited states by means of ab initio MO method.^{6,7} In the works, the structural changes were examined within planar conformations in order to clarify the roles of π and σ electrons in the pseudo-JT distortion. As a result, it was shown that a contraction or an expansion of π -electron clouds plays an important role in the stability of a less symmetric planar structure.

A number of conjugated organic molecules have so far been prepared, some of which are known experimentally to assume nonplanar structures in the ground and electronically excited states.^{8–25} From the viewpoints of structural characteristics, chemical reactions, and physicochemical properties, a degree of pyramidalization in nonplanar conjugated molecules has attracted a good deal of attention, and the topics on measures of pyramidalization have been reviewed by several authors.^{26–28}

As will be shown below, since the total energy of a molecule can be partitioned into the four energetic components, our interest in nonplanar conjugated molecules is to elucidate what happens inside the molecule when it is subject to the pseudo-JT distortion from planarity. In such a structural change, it will be expected that non-nearest-neighbor interactions become important, according as the molecule folds its molecular skeleton. This is because with the skeletal folding the nuclei and electron clouds are brought spatially close to each other and, concomitantly, the electrostatic interactions between them are largely affected. Accordingly, we may expect that the energy component analyses for the structural changes would provide useful information to deepen our understanding of chemical bonding in nonplanar conjugated hydrocarbons. In this study, we will clarify the nature of the pseudo-JT distortion from planarity by taking cycloheptatriene (**1**),⁹ heptalene (**2**),²⁹ and heptafulvalene (**3**),³⁰ and obtain a physical picture for the stability of nonplanar structure in the ground state (Figure 1).

It is noted that Scott et al.³¹ have recently carried out ab initio calculations to determine the structures of fulvenes, fulvalenes, and related molecules by using conventional (HF/6-31G* and MP2/6-31G*) and density functional theory (B-LYP/6-31G*) methods, with particular emphasis on the cause of the distortion from planarity of **3**.^{32,33} With reference to their results, we also give an account for the cause of a deviation from planarity in **1–3** by analysis of the energy components comprised in the total energy. It will be shown that the molecules undergo the

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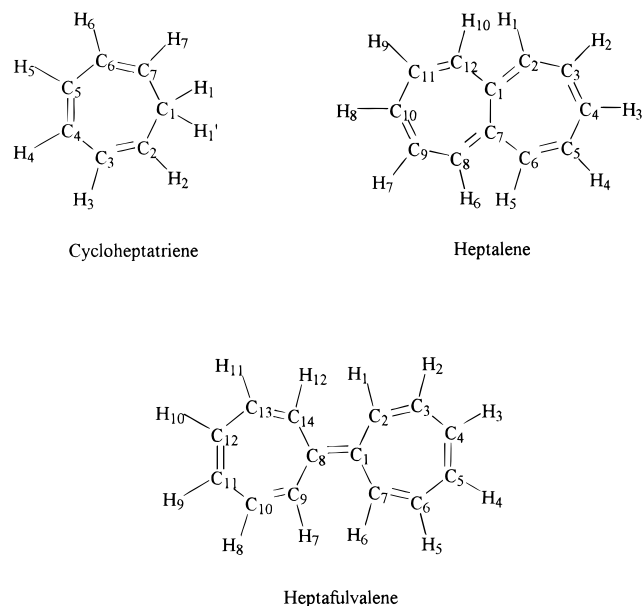


Figure 1. Molecular skeletons and numbering of atoms for **1–3**. The z axis is taken to be the main molecular axis in the C_{2v} point group, to be the long molecular axis in the D_{2h} and D_2 ones, and to be perpendicular to the molecular plane in the C_{2h} one.

pseudo-JT distortion from planarity, accompanied by an energy lowering of the electron–nuclear attractive term alone.

MCSCF Calculations

Since **2** exhibits a situation of quasi-open-shell structure at the symmetric D_{2h} structure,⁴ the traditional restricted Hartree–Fock (RHF) method is not adequate for describing the ground state properly. We thus employ here the full-optimized reaction space (FORS) multiconfiguration self-consistent field (MCSCF) method with 6-31G(d) basis set.^{34–38} For **1–3**, however, since the molecular systems are rather large, the MCSCF active spaces are reduced as follows. For **1**, the active space includes eight orbitals and eight electrons. This means that all of the occupied and unoccupied π orbitals as well as the two orbitals of bonding and antibonding π components arising from C1–H1 and C1–H1' bonds are included (Figure 1). For **2**, the active space includes all of the occupied and unoccupied π orbitals, i.e., 12 π orbitals and 12 π electrons. For **3**, the active space includes eight π electrons and 10 π orbitals. That is, the active space is fixed such that the lower three occupied π orbitals and the highest unoccupied π orbital are excluded from the 14 π orbitals, and accordingly six π electrons involved in the former orbitals are excluded from 14 π electrons.

To locate the geometrical structures corresponding to a true energy minimum for **1–3**, preliminary geometrical optimizations are performed by assuming the full symmetric 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, geometrical 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 for **1–3** using the RHF method. Subsequently, all of the stationary structures thus obtained are reoptimized by means of the MCSCF/6-31G(d) method to see

whether the above predictions should be acceptable within this level of theory.

Energy Partitioning Scheme

Of several types of the energy partitioning reported so far,^{39–44} we employ here the energy partitioning scheme of the total energy presented by Ichikawa.⁴³ In the scheme, the total energy is represented as the sum of the kinetic energy T and the potential energy V , the latter being partitioned into the electron–nuclear attraction energy V_{en} , the interelectronic repulsion energy V_{ee} , and the internuclear repulsion energy V_{nn} . Hence, the total energy is written as

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

In the case of a planar conjugated molecule, the kinetic energy and electronic potential energy terms V_{en} and V_{ee} can be further partitioned into the corresponding energy components of σ - and π -electrons as T_σ , T_π , $V_{\sigma,en}$, $V_{\pi,en}$, $V_{\sigma,ee}$, and $V_{\pi,ee}$, respectively. It is remarked that the $V_{\sigma,ee}$ term should comprise two interaction energies arising from between pure σ electrons and between σ and π electrons and the $V_{\pi,ee}$ term the energies arising from between pure π electrons and between π and σ electrons.

At the symmetric and less symmetric structures corresponding to the equilibrium nuclear arrangements, the respective total energies should satisfy the molecular virial theorem,^{45–48} $E = -T = V/2$. The less symmetric structure is lower in energy than the symmetric one, and the energy difference ΔE between them 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.

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

From the leading energetic term that should contribute to the energy lowering of a less symmetric structure, a classification may be possible to make between molecules. That is to say, 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. Needless to say, no kinetic energy type appears as the classification of the pseudo-JT stabilization because of the kinetic energy being always raised in the pseudo-JT structural changes.

All calculations are carried out by means of the quantum chemistry code GAMESS³⁴ in which new subroutines for the energy component analysis are included.

Results and Discussion

Transition Structures and Energy Minimum Ones. The vibrational analyses within the RHF method show that at the symmetric C_{2v} structure of **1**, one imaginary frequency corresponding to an out-of-plane b_1 nuclear deformation appears. At the symmetric D_{2h} structure of **2**,⁴⁹ there appear two imaginary frequencies corresponding to nuclear deformations of b_{3g} and a_u symmetry. That is, the D_{2h} structure exhibits a second-order saddle point, indicating that the in-plane CC bond stretching b_{3g} deformation leads to a planar C_{2h} structure with alternate long and short bonds and the out-of-plane b_{1u} deformation to a twisted D_2 one. Further, the D_{2h} structure of **3** exhibits a third-order saddle point with regard to a_u , b_{3u} , and b_{2g} nuclear deformations and, hence, the pseudo-JT distortions should lead to nonplanar D_2 , C_{2v} , and C_{2h} ones, respectively.

TABLE 1: Optimized Geometrical Parameters at the Symmetric and Distorted Structures of Cycloheptatriene, Heptalene, and Heptafulvalene

molecule	structure	geometrical parameters ^a
1	C_{2v}	C1–C2 = 1.507, C2–C3 = 1.346, C3–C4 = 1.467, C4–C5 = 1.349, C1–H1 = 1.095, C1–H1' = 1.095, C2–H2 = 1.079, C3–H3 = 1.077, C4–H4 = 1.077
	C_s^b	C1–C2 = 1.511, C2–C3 = 1.347, C3–C4 = 1.466, C4–C5 = 1.355, C1–H1 = 1.111, C1–H1' = 1.084, C2–H2 = 1.077, C3–H3 = 1.078, C4–H4 = 1.077, $\angle C5-C3-C4-C6 = 60.4$, $\angle C3-C4-C6-C8 = 5.0$, $\angle C4-C6-C8-C9 = 30.8$
2	$D_{2h} (^1B_{3g})^c$	C1–C2 = 1.418, C2–C3 = 1.403, C3–C4 = 1.398, C1–C7 = 1.510, C2–H1 = 1.075, C3–H2 = 1.076, C4–H3 = 1.076, H1–H10 = 1.973
	C_{2h}	C1–C2 = 1.370, C2–C3 = 1.457, C3–C4 = 1.347, C4–C5 = 1.455, C5–C6 = 1.351, C6–C7 = 1.483, C1–C7 = 1.490, C2–H1 = 1.075, C3–H2 = 1.076, C4–H3 = 1.076, C5–H4 = 1.077, C6–H5 = 1.075, H1–H10 = 1.978
	C_2	C1–C2 = 1.355, C2–C3 = 1.462, C3–C4 = 1.351, C4–C5 = 1.462, C5–C6 = 1.348, C6–C7 = 1.486, C1–C7 = 1.489, C2–H1 = 1.078, C3–H2 = 1.077, C4–H3 = 1.077, C5–H4 = 1.077, C6–H5 = 1.077, H1–H10 = 2.462, $\angle C2-C1-C7-C6 = 38.2$, $\angle C2-C1-C7-C8 = 145.5$
3	D_{2h}	C1–C2 = 1.482, C2–C3 = 1.353, C3–C4 = 1.460, C4–C5 = 1.326, C1–C8 = 1.369, C2–H1 = 1.067, C3–H2 = 1.077, C4–H3 = 1.076, H1–H12 = 1.726
	D_2	C1–C2 = 1.480, C2–C3 = 1.353, C3–C4 = 1.462, C4–C5 = 1.326, C1–C8 = 1.368, C2–H1 = 1.069, C3–H2 = 1.077, C4–H3 = 1.077, H1–H12 = 1.815, $\angle C2-C1-C8-C9 = 15.2$, $\angle C2-C1-C8-C14 = 164.8$
	C_{2v}	C1–C2 = 1.484, C2–C3 = 1.348, C3–C4 = 1.465, C4–C5 = 1.330, C1–C8 = 1.340, C2–H1 = 1.076, C3–H2 = 1.077, C4–H3 = 1.077, H1–H12 = 2.185, $\angle C2-C1-C8-C9 = 0$, $\angle C2-C1-C8-C14 = 176.4$
	C_{2h}	C1–C2 = 1.482, C2–C3 = 1.349, C3–C4 = 1.465, C4–C5 = 1.330, C1–C8 = 1.340, C2–H1 = 1.076, C3–H2 = 1.077, C4–H3 = 1.077, H1–H12 = 2.452, $\angle C2-C1-C8-C9 = 6.3$, $\angle C2-C1-C8-C14 = 180$

^a Numbering of atoms is shown in Figure 1. Bond lengths, nonbonded atomic distances between hydrogen atoms, and dihedral angles are in angstroms and degrees, respectively. Bond angles are omitted for simplicity.⁶¹ ^b In the C_s structure, H1 is on an axial position and H1' on an equatorial position. ^c The ground state is an open-shell structure at the D_{2h} structure.

Subsequently, vibrational analyses using the optimized distorted structures were carried out to see whether each of them should be an energy minimum. For **1**, it is shown that the C_s structure is a real energy minimum on the potential energy surface because of all the frequencies being positive definite.⁹ In contrast, a quite different situation is observed for **2** and **3**. For **2**, the C_{2h} and D_2 structures exhibit one imaginary frequency: namely, the vibrational mode is an out-of-plane a_u deformation for the former and a CC bond stretching b_2 deformation for the latter. The geometry optimizations starting with the distorted conformations are actually converged into the same stationary point of the nonplanar C_2 structure with alternate long and short bonds, indicating that it is a true energy minimum on the potential surface of the ground state.^{13–17} As for **3**, the twisted D_2 structure exhibits two imaginary frequencies corresponding to nuclear deformations of b_3 and b_2 symmetry, i.e., syn- and anti-folding motions of the seven-membered rings and, accordingly, the structural changes take place from the D_2 to the C_{2v} and C_{2h} ones, respectively. A comparison of the total energy indicates that the former is an energy minimum and the latter a true energy minimum on the potential energy surface of the ground state. In short, the predictions by the RHF calculations are in agreement with those by the MCSCF calculations, except that the twisted D_2 structure of **2** should not be a real saddle point in the latter level of theory. Therefore, our discussion below will be based on the results obtained by the MCSCF calculations.

Structural and Electronic Characteristics. Table 1 lists the optimized geometrical parameters of the various structures obtained by the MCSCF/6-31G(d) calculations and Figures 2 and 3 represent the side views of the nonplanar structures obtained using the atomic coordinates. The atomic and CC bond populations are obtained at the respective structures by means of Mulliken's population analysis,⁵⁰ which are summarized in

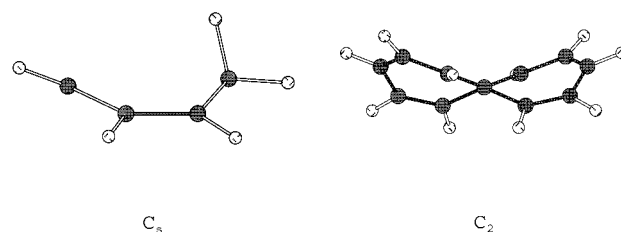


Figure 2. Side views of the C_s and C_2 conformations obtained using the atomic coordinates of the optimized structures for **1** and **2**, respectively.

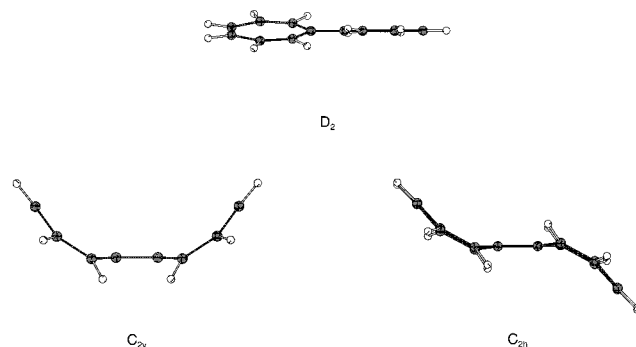


Figure 3. Side views of the D_2 , C_{2v} , and C_{2h} conformations obtained using the atomic coordinates of the optimized structures for **3**.

Table 2 together with π -electron components for the D_{2h} and C_{2h} structures of **2**. Table 3 shows the total and partitioned energies at the symmetric and distorted structures as well as the relative energy differences between them.

The C_{2v} structure of **1** exhibits a moderate bond-length alternation in the molecular periphery, and a large negative charge is located on the methylene carbon atom. In the C_s

TABLE 2: Atomic and CC Bond Populations at the Symmetric and Distorted Structures of Cycloheptatriene, Heptalene, and Heptafulvalene^a

molecule	atom and bond	structure (point group)			
		C_{2v}	C_s		
1^b	C1	6.3466	6.3410		
	C2	6.1653	6.1802		
	C3	6.1824	6.1705		
	C4	6.1850	6.1941		
	H1	0.8291	0.8349		
	H1'		0.8296		
	H2	0.8280	0.8168		
	H3	0.8204	0.8168		
	H4	0.8163	0.8188		
	C1–C2	0.3442	0.3466		
	C2–C3	0.6293	0.6211		
	C3–C4	0.3952	0.4051		
	C4–C5	0.6222	0.6149		
	2^c	C1	5.9319 (0.9858)	5.9243 (0.9706)	5.9742
C2		6.2269 (0.9948)	6.2702 (1.0319)	6.2234	
C6			6.1986 (0.9919)	6.1945	
C3		6.1959 (1.0224)	6.2039 (0.9773)	6.1797	
C5			6.1959 (1.0224)	6.1778	
C4		6.1737 (0.9799)	6.1830 (0.9992)	6.1912	
H1		0.8099	0.8129	0.8136	
H5			0.8109	0.8080	
H2		0.8110	0.8111	0.8126	
H4			0.8118	0.8127	
H3		0.8071	0.8084	0.8124	
C1–C2		0.4915 (0.1118)	0.5829 (0.1973)	0.6095	
C2–C3		0.4856 (0.1045)	0.3902 (0.0190)	0.6151	
C3–C4		0.5017 (0.1065)	0.6164 (0.2099)	0.6151	
C4–C5		0.5017 (0.1065)	0.3976 (0.0132)	0.4004	
C5–C6		0.4856 (0.1045)	0.6040 (0.2111)	0.6008	
C6–C7		0.4915 (0.1118)	0.3902 (0.0190)	0.3900	
C1–C7	0.3845 (−0.0086)	0.4117 (0.0166)	0.3914		
3	C1	6.0192	6.0127	6.0263	6.0199
	C2	6.1738	6.1769	6.1795	6.1910
	C3	6.2042	6.2032	6.1819	6.1836
	C4	6.1847	6.1856	6.1939	6.1948
	H1	0.8163	0.8070	0.8084	0.7989
	H2	0.8152	0.8147	0.8132	0.8122
	H3	0.8063	0.8065	0.8100	0.8097
	C1–C2	0.3985	0.3965	0.3914	0.3964
	C2–C3	0.6090	0.6075	0.6090	0.5972
	C3–C4	0.3969	0.3939	0.4001	0.3998
	C4–C5	0.6695	0.6696	0.6673	0.6666
	C1–C8	0.6576	0.6509	0.6896	0.6879

^a Values of total atomic and bond populations. ^b In the C_s structure, H1 is on an axial position and H1' on an equatorial position. ^c Values in parentheses indicate atomic or bond populations of π -electron components.

structure with a boat conformation, the double-bond fixation is somewhat relaxed and negative charges are slightly increased on C2 and C4. Anet^{9a} and Jensen and Smith^{9b} measured the temperature-dependent ¹H NMR spectrum of **1** and obtained about 6 kcal/mol as the activation energy for the isodynamic inversion process occurring in the interconversion between the two equivalent boat conformations. The theoretical activation energy obtained with the MCSCF method is 7.7 kcal/mol (Table 3), in good agreement with the experimental value. Further, the geometrical parameters regarding CC bond distances are quite in accord with the experimental values^{10,11} as well as the theoretical ones obtained by Scott et al.³¹

At the symmetric D_{2h} structure of **2**, the ground state is not a closed-shell structure with A_{1g} symmetry but an open-shell one with B_{3g} symmetry.⁴⁹ The D_{2h} structure exhibits fairly equal CC bond lengths except for a quite long transannular bond of 1.510 Å. Atomic populations of π electrons reveal that positive charges appear on C1, C2, and C4 and a negative charge on C3. Upon the structural changes from D_{2h} to C_{2h} , the stabilization energy is calculated to be 11.2 kcal/mol. The skew C_{2h} structure exhibits a substantial bond-length alternation along the molecular periphery and the transannular bond is shortened by 0.020 Å. Moreover, the nonplanar C_2 structure shows a pronounced double-bond fixation in the carbon periphery, exhibiting a situation of charge relaxation in comparison with the planar D_{2h} and C_{2h} ones and hence a rather uniform charge distribution. Note that each of the seven-membered rings takes a shallow boat conformation in the C_2 structure (Figure 2).¹⁶ This may be reflected in a rather small amount of the stabilization energy of 3.9 kcal/mol (Table 3). So far, it is supposed that steric hindrance due to the two pairs of the nonbonded hydrogen atoms of peri positions is the most probable factor that is responsible for the nonplanar C_2 structure of **2**. The calculations show that the atomic distance between H1 and H10 is 1.973, 1.978, and 2.462 Å in the D_{2h} , C_{2h} , and C_2 structures, respectively. In the former two, the atomic distance is shorter than the sum of their van der Waals radii, 2.0–2.4 Å.^{51–53} From this point of view, it seems as if a reduction of the repulsive interaction arising from the two pairs of the nonbonded hydrogen atoms should play an important role in the pseudo-JT distortion from planarity. Whether this is true or not will be discussed below from the energy component analysis, in conjunction with the similar feature observed in **3**. Vogel et al. measured the temperature-dependent ¹³C NMR spectrum of **2** and obtained about 3.5 kcal/mol as the activation energy for the isodynamic double-bond shift occurring in the interconversion between the two nonplanar Kekulé type structures.¹⁷ The theoretical activation energy within the MCSCF calculations is about 15.1 kcal/mol,⁵⁴ which is appreciably larger than the experimental value but is quite smaller than the theoretical values thus far reported.^{49c} The geometrical parameters regarding CC bond distances are in agreement with the X-ray experimental values of the heptalene derivatives.^{15,16}

As to **3**, the planar D_{2h} structure is almost the same as the twisted D_2 one with respect to CC bond lengths, both possessing a short C4–C5 bond of 1.326 Å and a rather long cross bond of 1.369 Å. The occurrence of such a long CC bond seems to be largely responsible for relieving the steric repulsion between the two pairs of the nonbonded hydrogen atoms ortho to the cross bond. This is because the nonbonded atomic distance between H1 and H12 is 1.726 Å in the D_{2h} structure, which is markedly shorter than the sum of their van der Waals radii. Upon symmetry reduction from D_{2h} to D_2 , the nonbonded atomic distance is lengthened by 0.089 Å, while the cross bond is shortened by 0.001 Å. This negligibly small shortening may be ascribed qualitatively to the opposing two factors given below. That is, a relaxation of the nonbonded repulsive interaction helps to shorten the bond, while a disruption of π conjugation between the two seven-membered rings by torsion around the cross bond results in a lengthening of the bond. On the other hand, the syn-folded C_{2v} structure is quite different from the D_{2h} and D_2 ones but is almost the same as the anti-folded C_{2h} one with regard to CC bond lengths. Closer examination indicates that the C_{2v} and C_{2h} structures possess a considerably short cross bond of 1.340 Å, the shortening amounting to about 0.03 Å. This shortening may be ascribed to a relaxation of the non-

TABLE 3: Total and Partitioned Energies at the Symmetric and Distorted Structures of Cycloheptatriene, Heptalene, and Heptafulvalene^a

molecule	component	structure (point group)			
		C_{2v}	C_s	D_{2h}	C_{2h}
1	E_{total}	-269.768403	-269.780693		
	Δ^b	0	-7.71		
	T	269.567033	269.580670		
	V_{en}	-1160.124061	-1167.868618		
	V_{ee}	354.707402	358.609114		
	V_{nn}	266.081223	269.898141		
molecule	component	structure (point group)			
		D_{2h}	C_{2h}	C_2	
2^c	E_{total}	-460.291525	-460.309373	-460.315522	
	Δ	0	-11.20	-15.05	
	T	459.910427 (12.729307)	459.926765 (12.757881)	459.932152	
	V_{en}	-2279.445804 (-223.143831)	-2278.155631 (-223.184794)	-2292.455825	
	V_{ee}	755.391077 (102.678728)	754.752850 (102.664049)	762.022783	
	V_{nn}	603.852776	603.166644	610.185368	
	molecule	component	structure (point group)		
D_{2h}			D_2	C_{2v}	C_{2h}
3	E_{total}	-537.125382	-537.128430	-537.136819	-537.140587
	Δ	0	-1.91	-7.18	-9.54
	T	536.678622	536.685212	536.691070	536.698209
	V_{en}	-2764.993114	-2767.151549	-2796.548156	-2788.724808
	V_{ee}	933.938132	935.029926	949.900312	945.952475
	V_{nn}	757.250976	758.307989	772.819961	768.933549

^a Energies are in hartrees. ^b Differences of the total energy in kcal/mol relative to the symmetric structure. ^c In the planar D_{2h} and C_{2h} structures of **2**, values in parentheses indicate the respective energy components of π electrons.

bonded repulsive interaction between the hydrogen atoms of interest, because in the C_{2v} and C_{2h} structures the nonbonded atomic distances of 2.185 and 2.452 Å are longer than the sum of their van der Waals radii. In this case too, it seems likely that a reduction of the repulsive interaction arising from the nonbonded hydrogen atoms should play an essential role in the pseudo-JT distortion from planarity. This will be discussed below by analysis of the energy components involved in the total energy. A comparison of the atomic populations indicates that the largest atomic charge on C3 in the D_{2h} and D_2 structures is relaxed in the C_{2v} and C_{2h} ones, with the result that the negative charges are quite uniformly delocalized on the two hexatriene-like moieties. Note that the twisted D_2 structure corresponds to the transition (or bifurcation) structure for the isomerization between the anti-folded C_{2h} and syn-folded C_{2v} ones.³¹ The associated activation energy from the anti- to the syn-folded structure is calculated to be about 7.6 kcal/mol (Table 3). The present theoretical CC bond distances for the anti-folded C_{2h} structure are in good agreement with the X-ray experimental ones observed by Thomas and Coppens¹⁹ as well as the theoretical ones obtained by Scott et al.³¹ In this connection, it is remarked that, according to the X-ray crystal structure analyses, the perchloroheptafulvalene molecule takes an anti-folded C_{2h} conformation,⁵⁵ whereas a tetrachlorotetraphenyl derivative of **3** takes a syn-folded one, in which the two seven-membered rings are bent up facing each other.⁵⁶

Energy Component Analysis of the Total Energy in the Ground States. *Cycloheptatriene (1).* When the planar C_{2v} structure undergoes the pseudo-JT distortion to the boat C_s conformation, there occurs a small amount of the totally symmetric expansion of the carbon skeleton. The associated changes in bond length are given as follows, where the signs + and - denote, respectively, a lengthening and a shortening of the bonds relative to the C_{2v} structure: C1–C2 (+0.004 Å),

C2–C3 (+0.001 Å), C3–C4 (-0.001 Å), and C4–C5 (+0.006 Å). This means that on the structural changes the carbon atoms are displaced above or below a molecular plane of the symmetric structure almost keeping the CC bond lengths intact. Owing to the folding of seven-membered ring, the nuclei and electron clouds should become spatially close together (Figure 2) and hence the electrostatic interactions should be largely enhanced in the C_s structure. In conformity with this expectation, Table 3 indicates that the structural change 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. It is notable that the kinetic term is slightly increased in energy, in accordance with the requirement ($\Delta T > 0$) arising from the molecular virial theorem.^{45–48} This energy change can be interpreted as the effect due to a raising of the so-called kinetic energy pressure of electrons.^{57–61} In brief, it can be said that a folding of the molecular skeleton brings about a confinement of the electron movement and, hence, a raising of the kinetic energy. As a result, it is concluded that the stability of C_s structure should originate from the energy lowering of the electron–nuclear attractive term V_{en} and the other energy terms are in the opposite direction to the stability.

Heptalene (2). First, the D_{2h} structure undergoes the pseudo-JT distortion to the C_{2h} one. Except for the transannular bond, the carbon skeleton of C_{2h} structure is expanded to some extent symmetrically relative to the D_{2h} one and the associated changes in bond length are given as follows: transannular bond (-0.020 Å), C1–C2 (+0.009 Å), C2–C3 (+0.001 Å), and C3–C4 (+0.003 Å). At the same time, the b_{3g} nuclear deformation is operative such that C1–C2 is shortened by 0.057 Å, C2–C3 is lengthened by 0.053 Å, C3–C4 is shortened by 0.054 Å, and the successive peripheral CC bonds are alternately lengthened and shortened by lengths that correspond to the changes for the former three bonds. In this case, the transannular bond

remains unchanged by symmetry. In accordance with a symmetric expansion of the carbon skeleton, the three repulsive terms V_{nn} , $V_{\sigma,ee}$, and $V_{\pi,ee}$ should be lowered in energy, whereas the two attractive terms $V_{\sigma,en}$ and $V_{\pi,en}$ should be raised in energy. As expected, Table 3 shows that all of the repulsive terms are more or less lowered and one attractive term $V_{\sigma,en}$ is raised in energy. Contrary to expectation, however, the other attractive term $V_{\pi,en}$ is slightly lowered in energy. An explanation about how such an energy change should take place in the term $V_{\pi,en}$ may be given as follows. Since all of the CC bond populations of σ electrons exhibit no essential changes, an expansion of the carbon skeleton should raise the electron–nuclear attractive energy $V_{\sigma,en}$. Further, the CC bond populations of π electrons along the molecular periphery change alternately such that the populations on the double bonds increase while those on the single bonds decrease and the amounts of changes are almost the same in magnitude in both the cases. From these changes in π bond populations, no essential energy change in the term $V_{\pi,en}$ should be expected. However, it can be pointed out that the value of the π bond population on the transannular bond changes from -0.009 (D_{2h}) to $+0.017$ (C_{2h}), with a shortening of the bond length by 0.020 Å. It may therefore be presumed that a small energy lowering of the attraction term $V_{\pi,en}$ should originate from the effect brought about by the two factors through the electrostatic attractive interaction. A part of the stabilization for the C_{2h} structure arises from the energy lowering of the electron–nuclear attractive term $V_{\pi,en}$ but the magnitude of the energy lowering is less than about one-tenth of those of the repulsive terms V_{nn} and $V_{\sigma,ee}$. It can thus be said that the preference for the bond-alternated C_{2h} structure should arise from the lowering of the repulsive terms V_{nn} , $V_{\sigma,ee}$, and $V_{\pi,ee}$, the attractive term $V_{\pi,en}$, and the kinetic term T_{σ} . The leading energy components correspond to the two repulsive terms V_{nn} and $V_{\sigma,ee}$, in order of importance.

Second, the planar bond-alternated C_{2h} structure undergoes the pseudo-JT distortion to the nonplanar C_2 one. In that case, the main geometrical changes take place such that C1–C2 is shortened by 0.015 Å and C4–C5 lengthened by 0.007 Å. Concomitantly, the dihedral angles $\angle C2-C1-C7-C6$ and $\angle C2-C1-C7-C8$ are changed from 0° and 180° to 38.2° and 145.5° , respectively. The structural change in dihedral angles distorts the molecular carbon skeleton in a helical fashion (Figure 2), leading to the proximity between the nuclei and electron clouds. It is thus expected that the electrostatic interactions should be enhanced in the nonplanar C_2 structure. In agreement with this expectation, Table 3 indicates that the repulsive terms V_{nn} and V_{ee} are largely raised in energy, while the attractive term V_{en} is greatly lowered in energy. It is noted that the kinetic term T increases in energy to a negligibly small extent. It is therefore concluded that the stability of the nonplanar C_2 structure should benefit from a lowering of the electron–nuclear attractive term V_{en} and all the other energy components are in the opposite direction to the stability.

Heptafulvalene (3). The D_{2h} structure suffers pseudo-JT distortion to the twisted D_2 one, which further undergoes geometrical changes to the C_{2v} and C_{2h} ones. As **3** changes its molecular shape from D_{2h} to D_2 and from D_2 to C_{2v} and C_{2h} , the total energy of the distorted structures is lowered in the order (Table 3). The associated energy changes are given briefly as follows: The kinetic energy T changes to a small extent. The repulsive terms V_{nn} and V_{ee} are raised in energy, while the attractive term V_{en} is lowered in energy. It is of interest to note that, in spite of the total energy being lower for the anti-folded C_{2h} structure than for the syn-folded C_{2v} one, the electron–

nuclear attraction energy is appreciably lower for the latter than for the former. Evidently, this should be readily ascribed to the fact that in the latter the distances between the nuclei and electron clouds are shorter than those in the former (Figure 3). Concomitantly, the repulsive terms are raised in energy for the latter than those for the former. 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 exceeds in absolute value the energy raising due to the internuclear and interelectronic repulsive terms upon distortion from planarity. In conclusion, it can be said that the anti-folded C_{2h} structure of **3** owes its energetic stability to the energy lowering of the electron–nuclear attractive term V_{en} and the other energy components are in the opposite direction to the stability.

Origin of Nonplanarity. The cause of nonplanarity in **3** has been a controversial problem^{31–33} and discussed from steric hindrance arising from the two pairs of nonbonded hydrogen atoms and bond angle strain in the seven-membered rings. One approach to the origin of nonplanarity would be to study how geometrical parameters of interest vary upon the pseudo-JT structural changes. Recently, Scott et al.³¹ submitted that the primary cause for the nonplanarity of **3** is the intramolecular overcrowding due to the close contacts of the hydrogen atoms ortho to the cross bond. To be sure, it seems likely from the changes in geometrical parameters that the nonplanarity should arise from the effect for relieving the repulsive interactions between the two pairs of nonbonded hydrogen atoms. This is because the atomic distances of question are made longer in the distorted C_{2h} structure and hence the relevant repulsive interactions should be relieved. Besides, most $\angle CCC$ bond angles are actually decreased more or less from the average angle of 128.6° in a planar heptagon when **1–3** undergo the pseudo-JT distortion from planarity.^{31,62} These changes in bond angle can also be rationalized in terms of a relief of the angular strain in the seven-membered ring. But, it is also to be emphasized that the folding of the seven-membered rings by virtue of the two factors should bring about an enhancement of the other repulsive interactions because of the proximity between the nuclei and between the electron clouds involved in the CC and CH bonds. This suggests strongly that it is preferable to judge from the overall energy changes in the respective energy components whether a deviation from planarity should occur in a molecule. That is, another approach to the origin of nonplanarity would be to examine how the individual energy components vary in energy upon the pseudo-JT structural changes. On the basis of this viewpoint, we have so far carried out the energy component analyses of the pseudo-JT distortion in conjugated molecules.^{6,7} As is acutely shown numerically in Table 3, since all the repulsive terms are raised in energy, it can be safely said that the cause of nonplanarity in **3** should be ascribed to the energy lowering of the electron–nuclear attractive term. This feature is accounted for in terms of the proximity between the nuclei and electron clouds owing to the folding of the seven-membered rings. That is, since the energy lowering due to the nuclear–electron attractive term is actually larger in absolute value than the energy raising due to the internuclear and interelectronic repulsive terms, the pseudo-JT distortion from planarity should take place spontaneously in **1–3**. In this connection, it is noted that cyclooctatetraene (**4**) is known experimentally to be a puckered, nonplanar form of D_{2d} symmetry. It is usually considered that because of angle strain in the eight-membered ring and steric repulsion between vicinal hydrogen atoms, a planar D_{4h} structure with alternate

long and short bonds is less stable than a nonplanar D_{2d} one. The previous analysis^{6b} shows that the energy component responsible for the distortion in **4** is just the same as that observed in **1–3** when it is distorted into the D_{2d} from the D_{4h} structure through the out-of-plane nuclear deformation of b_{1u} symmetry.^{6b,63}

Conclusions

This study indicates that the energy component analysis is highly informative to elucidate what happens inside the molecule when it is subject to the pseudo-JT distortion. From the above considerations, it has become apparent for **1–3** that the variation of both the attractive and repulsive components involved in the potential energy is considerably large in energy but they are out of phase with each other. In contrast, the variation of the total energy as well as the kinetic energy is quite small upon the pseudo-JT distortion from planarity. Despite their marked differences in molecular shape, it is shown that the cause of nonplanarity is all ascribed to an energy lowering of the electron–nuclear attractive term. This interpretation is given such that in the nonplanar structure most distances between the nuclei and electron clouds are shortened relative to those in the planar structure and, hence, the electron–nuclear attractive interactions are enhanced largely. From a slightly different point of view, it may be said that such through-space interactions in the molecules should play an essential role in maintaining their molecular frameworks in a variety of nonplanar conformations. In view of the classification for the pseudo-JT stabilization introduced here, the present molecules as well as cyclooctatetraene can be referred to as the electron–nuclear attractive type. For all that, it will be premature to conclude that the stability of the pseudo-JT distortion from planarity should all originate from the electron–nuclear attractive term alone. 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 other energy terms than the electron–nuclear attractive one. With this background, we are now undertaking an investigation by dealing with a series of eight π -electron heterocyclic systems,⁶⁴ in which the stability of nonplanar structure results mainly from an energy lowering of the interelectronic repulsive term, the internuclear repulsive term, or the combined two repulsive terms.⁶⁵

Finally, it is noted that it may be desirable to use a more large basis set than 6-31G(d) basis set for properly representing electronic structures of the present molecules. However, since the differences of total energy and its components between the symmetric and less symmetric structures are considered in this work, we conjecture that the likely effects on the energy terms at the different structures should be virtually canceled when estimating the relevant energy differences.^{3,66} We are in the hope that the essence of the present conclusions would not be impaired even if more flexible basis sets larger than 6-31G(d) basis set are used in the MCSCF calculations for the present molecules.

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