

# 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

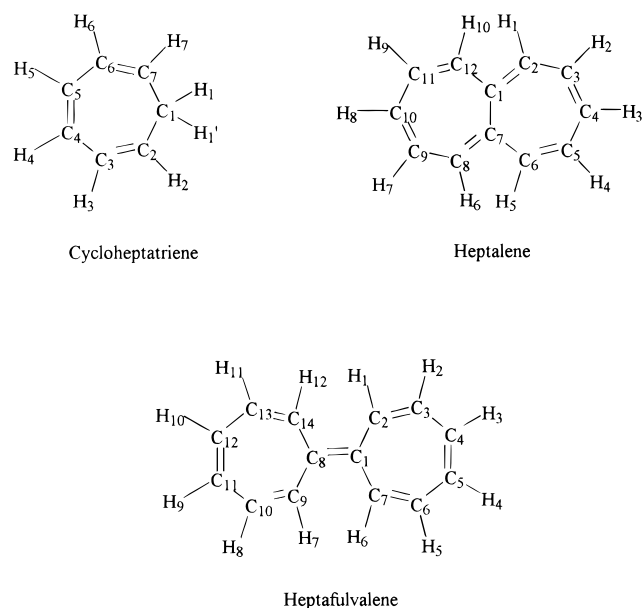
The Jahn–Teller (JT) effect is a stabilization that arises from the geometric instability of degenerate electronic states in nonlinear polyatomic molecules.<sup>1–3</sup> In this connection, the pseudo-JT effect is the stabilization which occurs when a certain asymmetric distortion mixes two electronic states which are nearly degenerate in the symmetric nuclear configuration of the ground or of an electronically excited state.<sup>4,5</sup> 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.<sup>6,7</sup> In the works, the structural changes were examined within planar conformations in order to clarify the roles of  $\pi$  and  $\sigma$  electrons in the pseudo-JT distortion. As a result, it was shown that a contraction or an expansion of  $\pi$ -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.<sup>8–25</sup> 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.<sup>26–28</sup>

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**),<sup>9</sup> heptalene (**2**),<sup>29</sup> and heptafulvalene (**3**),<sup>30</sup> and obtain a physical picture for the stability of nonplanar structure in the ground state (Figure 1).

It is noted that Scott et al.<sup>31</sup> 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**.<sup>32,33</sup> 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,<sup>4</sup> 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.<sup>34–38</sup> 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  $\pi$  orbitals as well as the two orbitals of bonding and antibonding  $\pi$  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  $\pi$  orbitals, i.e., 12  $\pi$  orbitals and 12  $\pi$  electrons. For **3**, the active space includes eight  $\pi$  electrons and 10  $\pi$  orbitals. That is, the active space is fixed such that the lower three occupied  $\pi$  orbitals and the highest unoccupied  $\pi$  orbital are excluded from the 14  $\pi$  orbitals, and accordingly six  $\pi$  electrons involved in the former orbitals are excluded from 14  $\pi$  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,<sup>39–44</sup> we employ here the energy partitioning scheme of the total energy presented by Ichikawa.<sup>43</sup> 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  $\sigma$ - and  $\pi$ -electrons as  $T_\sigma$ ,  $T_\pi$ ,  $V_{\sigma,en}$ ,  $V_{\pi,en}$ ,  $V_{\sigma,ee}$ , and  $V_{\pi,ee}$ , respectively. It is remarked that the  $V_{\sigma,ee}$  term should comprise two interaction energies arising from between pure  $\sigma$  electrons and between  $\sigma$  and  $\pi$  electrons and the  $V_{\pi,ee}$  term the energies arising from between pure  $\pi$  electrons and between  $\pi$  and  $\sigma$  electrons.

At the symmetric and less symmetric structures corresponding to the equilibrium nuclear arrangements, the respective total energies should satisfy the molecular virial theorem,<sup>45–48</sup>  $E = -T = V/2$ . The less symmetric structure is lower in energy than the symmetric one, and the energy difference  $\Delta E$  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 GAMESS<sup>34</sup> 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**,<sup>49</sup> 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.

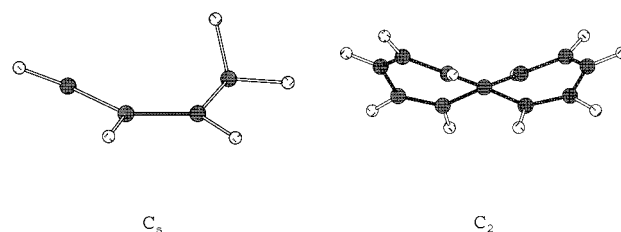
**TABLE 1: Optimized Geometrical Parameters at the Symmetric and Distorted Structures of Cycloheptatriene, Heptalene, and Heptafulvalene**

molecule	structure	geometrical parameters <sup>a</sup>
<b>1</b>	$C_{2v}$	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, $\angle C5-C3-C4-C6 = 60.4$ , $\angle C3-C4-C6-C8 = 5.0$ , $\angle C4-C6-C8-C9 = 30.8$
<b>2</b>	$D_{2h} (^1B_{3g})^c$	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, $\angle C2-C1-C7-C6 = 38.2$ , $\angle C2-C1-C7-C8 = 145.5$
<b>3</b>	$D_{2h}$	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, $\angle C2-C1-C8-C9 = 6.3$ , $\angle C2-C1-C8-C14 = 180$

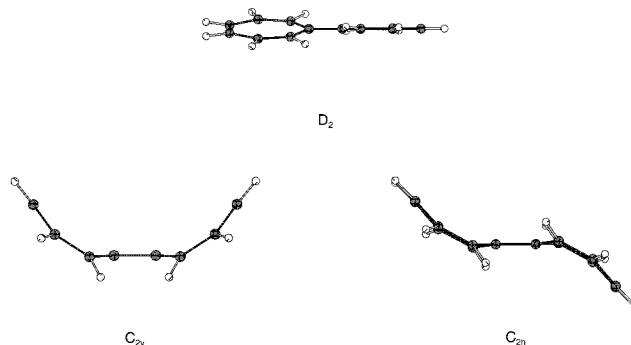
<sup>a</sup> Numbering of atoms is shown in Figure 1. Bond lengths, nonbonded atomic distances between hydrogen atoms, and dihedral angles are in angstroms and degrees, respectively. Bond angles are omitted for simplicity.<sup>61</sup> <sup>b</sup> In the  $C_s$  structure, H1 is on an axial position and H1' on an equatorial position. <sup>c</sup> 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.<sup>9</sup> 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.<sup>13–17</sup> 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,<sup>50</sup> 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  $\pi$ -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<sup>a</sup>**

molecule	atom and bond	structure (point group)			
		$C_{2v}$	$C_s$		
<b>1<sup>b</sup></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		
molecule	atom and bond	structure (point group)			
		$D_{2h}$	$C_{2h}$	$C_2$	
<b>2<sup>c</sup></b>	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	
molecule	atom and bond	structure (point group)			
		$D_{2h}$	$D_2$	$C_{2v}$	$C_{2h}$
<b>3</b>	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

<sup>a</sup> Values of total atomic and bond populations. <sup>b</sup> In the  $C_s$  structure, H1 is on an axial position and H1' on an equatorial position. <sup>c</sup> Values in parentheses indicate atomic or bond populations of  $\pi$ -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<sup>9a</sup> and Jensen and Smith<sup>9b</sup> measured the temperature-dependent <sup>1</sup>H 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<sup>10,11</sup> as well as the theoretical ones obtained by Scott et al.<sup>31</sup>

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.<sup>49</sup> The  $D_{2h}$  structure exhibits fairly equal CC bond lengths except for a quite long transannular bond of 1.510 Å. Atomic populations of  $\pi$  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).<sup>16</sup> 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.<sup>51–53</sup> 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 <sup>13</sup>C 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.<sup>17</sup> The theoretical activation energy within the MCSCF calculations is about 15.1 kcal/mol,<sup>54</sup> which is appreciably larger than the experimental value but is quite smaller than the theoretical values thus far reported.<sup>49c</sup> The geometrical parameters regarding CC bond distances are in agreement with the X-ray experimental values of the heptalene derivatives.<sup>15,16</sup>

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  $\pi$  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<sup>a</sup>**

molecule	component	structure (point group)	
		$C_{2v}$	$C_s$
<b>1</b>	$E_{\text{total}}$	−269.768403	−269.780693
	$\Delta^b$	0	−7.71
	$T$	269.567033	269.580670
	$V_{\text{en}}$	−1160.124061	−1167.868618
	$V_{\text{ee}}$	354.707402	358.609114
	$V_{\text{nn}}$	266.081223	269.898141

molecule	component	structure (point group)		
		$D_{2h}$	$C_{2h}$	$C_2$
<b>2<sup>c</sup></b>	$E_{\text{total}}$	−460.291525	−460.309373	−460.315522
	$\Delta$	0	−11.20	−15.05
	$T$	459.910427 (12.729307)	459.926765 (12.757881)	459.932152
	$V_{\text{en}}$	−2279.445804 (−223.143831)	−2278.155631 (−223.184794)	−2292.455825
	$V_{\text{ee}}$	755.391077 (102.678728)	754.752850 (102.664049)	762.022783
	$V_{\text{nn}}$	603.852776	603.166644	610.185368

molecule	component	structure (point group)			
		$D_{2h}$	$D_2$	$C_{2v}$	$C_{2h}$
<b>3</b>	$E_{\text{total}}$	−537.125382	−537.128430	−537.136819	−537.140587
	$\Delta$	0	−1.91	−7.18	−9.54
	$T$	536.678622	536.685212	536.691070	536.698209
	$V_{\text{en}}$	−2764.993114	−2767.151549	−2796.548156	−2788.724808
	$V_{\text{ee}}$	933.938132	935.029926	949.900312	945.952475
	$V_{\text{nn}}$	757.250976	758.307989	772.819961	768.933549

<sup>a</sup> Energies are in hartrees. <sup>b</sup> Differences of the total energy in kcal/mol relative to the symmetric structure. <sup>c</sup> In the planar  $D_{2h}$  and  $C_{2h}$  structures of **2**, values in parentheses indicate the respective energy components of  $\pi$  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.<sup>31</sup> 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 Coppens<sup>19</sup> as well as the theoretical ones obtained by Scott et al.<sup>31</sup> 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,<sup>55</sup> whereas a tetrachlorotetraphenyl derivative of **3** takes a syn-folded one, in which the two seven-membered rings are bent up facing each other.<sup>56</sup>

**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.<sup>45–48</sup> This energy change can be interpreted as the effect due to a raising of the so-called kinetic energy pressure of electrons.<sup>57–61</sup> 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  $V_{\text{en}}$  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  $\sigma$  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  $\pi$  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  $\pi$  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  $\pi$  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  $T_{\sigma}$ . 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  $0^\circ$  and  $180^\circ$  to  $38.2^\circ$  and  $145.5^\circ$ , 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<sup>31–33</sup> 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.<sup>31</sup> 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  $128.6^\circ$  in a planar heptagon when **1–3** undergo the pseudo-JT distortion from planarity.<sup>31,62</sup> 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.<sup>6,7</sup> As is actually 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<sup>6b</sup> 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.<sup>6b,63</sup>

## 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  $\pi$ -electron heterocyclic systems,<sup>64</sup> 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.<sup>65</sup>

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.<sup>3,66</sup> 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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