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# Ab Initio MCSCF Study on Electronically Excited Singlet States of Fulvalene Systems: Energy Component Analysis of the Pseudo-Jahn−Teller Effect

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Geometry optimizations of the lowest (second) excited singlet states of the fulvalene systems were carried out by using the ab initio MCSCF method with the 6-31G(d) basis set. The electronically excited molecules are found to undergo a pseudo-Jahn−Teller (JT) distortion from $D_{2h}$ to $C_{2v}$. On the basis of the results obtained, an energy component analysis of the total energy has been carried out to elucidate the physical picture of the pseudo-JT effect. Inspection of the energy components comprised in the total energy reveals that the stability of a less symmetric structure ($C_{2v}$) is attributable commonly to the energy lowerings of the internuclear repulsion term and the interelectronic repulsive and kinetic terms due to $\sigma$ electrons. These observations are consistent with an expansion of the carbon skeleton brought about by the pseudo-JT bond distortion. It is further found that in triafulvalene and heptafulvalene the nuclear−electron attractive and interelectronic repulsive terms due to $\pi$ electrons contribute to the pseudo-JT stabilization, respectively. In pentafulvalene and 7,7′-bis(bicyclo[4.1.0]hepta-1,3,5-trienylidene), on the other hand, both the nuclear−electron attractive and interelectronic repulsive terms due to $\pi$ electrons contribute to the energetic stability of the $C_{2v}$ structure. Subsequently, heptafulvalene undergoes a pseudo-JT effect from the planar $C_{2v}$ to a nonplanar $C_s$ structure. Interestingly, the stability of nonplanar $C_s$ structure results from the energy lowering of the nuclear−electron attractive term. Moreover, the structural and electronic properties inherent in the less symmetric $C_{2v}$ and $C_s$ nuclear arrangements of the electronically excited molecules are discussed.

## Introduction

It is at present a general notion that an excited molecule is not just a ground-state molecule with a lot of energy, but it is rather a quite different molecule with its own physical and chemical properties. In comparison with the ground-state molecule, the excited molecule has in general a different equilibrium structure and, hence, has a different dipole moment, a different chemical reactivity, different acid and base strengths, and so on.[1−6] Such differences can be interpreted as being a reflection of the different electron distribution in the electronically excited state. In this sense, the chemical behavior of electronically excited molecules has been intriguing subjects from both theoretical and experimental viewpoints. Spectroscopic measurements of absorption and emission spectra provide valuable information concerning differences in geometrical structures between the ground and electronically excited states of a molecule. In pentalene and heptalene,[7−16] belonging to the so-called catacondensed nonalternant hydrocarbons, it has been observed that the electronic spectrum exhibits a long absorption tail throughout the visible region. In this respect, it has been suggested that such an anomaly should be an effect arising from large differences in geometrical structures between the ground and lowest excited singlet states.[17,18] Namely, the geometrical structure of the former state takes a skew $C_{2h}$ structure with alternate short and long bonds in the molecular periphery[19] and that of the latter state a symmetric $D_{2h}$ one with almost equal CC bond lengths.

In this context, cyclic cross-conjugated molecules termed fulvalene systems, in which two odd-membered rings are joined by a double bond, are of interest theoretically since the absorption spectra of pentafulvalene and heptafulvalene exhibit a relatively broad band in the longest wavelength region.[20,21] In this paper, we thus examine the geometrical structures of electronically excited singlet states in the fulvalene systems (Figure 1) by using the ab initio MCSCF method with 6-31G(d) basis set.[22−26] The electronic states under consideration are the lowest excited singlet state for triafulvalene (**1**), pentafulvalene (**2**), and heptafulvalene (**3**) and the second excited singlet state for 7,7′-bis(bicyclo[4.1.0]hepta-1,3,5-trienylidene) (**4**).[27,28] On the basis of the results obtained, we carry out an energy component analysis of the total energy[29,30] to understand the physical picture of the pseudo-Jahn−Teller (JT) effect[6,31−33] in the electronically excited singlet state of the fulvalene systems.

It is noted that heptafulvalene is known experimentally to take a nonplanar $C_{2h}$ structure in the ground state. That is, the X-ray structural analysis by Thomas and Coppens[34] reveals that the molecule has an S-shape when viewed sideways. Quite recently, Scott et al.[35] have examined theoretically the energetically favorable ground-state structures of the fulvalene systems by means of the ab initio MO method. They have indicated that the underlying reason for heptafulvalene adopting a nonplanar $C_{2h}$ conformation is the proximity of two pairs of hydrogen atoms within the molecule which promotes a distortion

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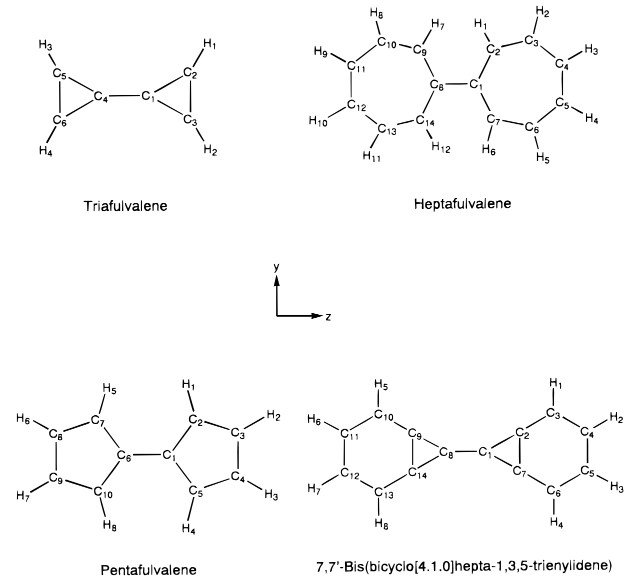

**Figure 1.** Molecular skeletons, numbering of atoms, and choice of molecular axes.

of the rings away from planarity at the central fulvenic CC double bond.[36,37] By considering this point, we also examine whether heptafulvalene takes a nonplanar conformation in the lowest excited singlet state, and, if such is the case, an account is given for the cause of nonplanarity by analysis of the energy components comprised in the total energy.

## Methods of Calculation

Since the traditional restricted Hartree−Fock method is not adequate for describing electronically excited states properly, we employ here the fully optimized reaction space (FORS) multiconfiguration self-consistent field (MCSCF) method with 6-31G(d) basis set.[22−26] It should be mentioned that for **1** and **2** the MCSCF active space includes all inner valence $\pi$ orbitals and all $\pi$ electrons. For **3** and **4**, however, since the molecular systems are rather large, the active space includes only 10 $\pi$ orbitals and eight $\pi$ electrons. Namely, the reduced 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.

The energy components comprised in the total energy are important essentially for discussing the leading terms responsible for the pseudo-JT effect in the present molecules, and accordingly we give here a brief review of the energy partitioning scheme.[38] The total energy of a molecular system is expressed as the sum of the electronic energy ($E^{\mathrm{el}}$) and the internuclear repulsion energy ($E^{\mathrm{N}}$). The $E^{\mathrm{el}}$ term comprises the kinetic ($E^{\mathrm{T}}$) and potential energies, the latter being further partitioned into the nuclear−electron attraction energy ($E^{\mathrm{V}}$) and the interelectronic repulsion energy ($E^{\mathrm{J}}$). In the case of a planar conjugated molecule, the $E^{\mathrm{el}}$ and its partitioned energies can be further partitioned into $\sigma$ electron ($E_\sigma$) and $\pi$-electron ($E_\pi$) energies. Within this framework, the total energy can be expressed as follows:

$$E_{\mathrm{total}} = E^{\mathrm{N}} + E^{\mathrm{T}}{}_{\sigma} + E^{\mathrm{V}}{}_{\sigma} + E^{\mathrm{J}}{}_{\sigma} + E^{\mathrm{T}}{}_{\pi} + E^{\mathrm{V}}{}_{\pi} + E^{\mathrm{J}}{}_{\pi}$$

It is remarked that the $E^{\mathrm{J}}{}_{\sigma}$ term should comprise two interaction energies arising from between pure $\sigma$ electrons and between $\sigma$ and $\pi$ electrons and the $E^{\mathrm{J}}{}_{\pi}$ term the energies arising from between pure $\pi$ electrons and between $\pi$ and $\sigma$ electrons. All calculations are carried out by means of the quantum chemistry code GAMESS[22] to which new subroutines for the energy component analysis are added.

## Results and Discussion

**Low-Lying Singlet States in the Full Symmetric $D_{2h}$ Structure.** The molecular forms of **1−4** are assumed to be planar, and each geometrical structure of low-lying two singlet states for them is optimized with the MCSCF scheme under the constraint of $D_{2h}$ symmetry.

It is predicted for **1−3** that the lowest excited singlet state is of $\mathrm{B_{2u}}$ symmetry and the second excited singlet state is of $\mathrm{B_{3g}}$ symmetry, the energy separations between the two state being only 0.09, 0.01, and 0.17 eV, respectively. As for **4**, the second excited singlet state is of $\mathrm{B_{2u}}$ symmetry and the third excited singlet state is of $\mathrm{B_{3g}}$ symmetry, the energy separation being 0.05 eV. The finding that these energy separations are considerably small can be regarded as being an electronic characteristic common to the present fulvalene systems. An account of the appearance of such near degenerate excited states is given as follows: In the simple HMO picture, a pair of the degenerate orbitals occurs in the lowest unoccupied MO (LUMO) for **1** and **3**, while a similar degeneracy appears in the highest occupied MO (HOMO) for **2**. Besides, such an accidental doubly degeneracy takes place in the next LUMO for **4**. Accordingly, the two electronically excited states arising from MO transitions from HOMO to LUMOs, from HOMOs to LUMO, and from HOMO to next LUMOs should become doubly degenerate for **1** and **3**, **2**, and **4**, respectively. It is apparent that when electron correlation is included, this accidental degeneracy should be lifted, but the associated energy separation is in general small, as is actually shown above. Since the two excited singlet states are almost degenerate in energy with each other, it follows from symmetry arguments for **1−3** and **4** that the lowest and second excited singlet states should suffer a pseudo-JT bond distortion from the conventional $D_{2h}$ structure to a less symmetric $C_{2v}$ structure through an in-plane nuclear deformation of $\mathrm{b_{1u}}$ ($\mathrm{B_{2u}} \times \mathrm{B_{3g}}$) symmetry, respectively.

Taking these predictions into account, the geometry optimizations of **1−4** are performed by using the MCSCF method[22−26] under $C_{2v}$ symmetry constraint, and the results are given below regarding the structural and concomitant properties of the electronically excited states.

**Structural and Electronic Characteristics.** Table 1 presents the fully optimized geometrical parameters for the symmetric ($D_{2h}$) and less symmetric ($C_{2v}$) nuclear configurations of the fulvalene systems examined (Figure 1). Atomic populations are obtained at both structures by means of Mulliken's population analysis,[39] which are summarized in Table 2 together with $\sigma$- and $\pi$-electron components. Table 3 shows the total and partitioned energies at the $D_{2h}$ and $C_{2v}$ structures of the electronically excited singlet states.[40]

For **1**, Table 1 indicates that the lengths of CC bonds in the $D_{2h}$ structure are almost as smoothed out in the three-membered rings as those in benzene. On the other hand, the $C_{2v}$ structure has an extremely short CC bond of 1.321 Å in one of the rings and a moderate double-bond fixation in the other ring. The stabilization energy due to the pseudo-JT effect, defined as the difference in total energy between the two structures, is calculated to be 15.4 kcal/mol. Examination of the atomic populations reveals that in the $C_{2v}$ structure a migration of the $\sigma$ and $\pi$ electrons takes place from one side of the rings to the other, the directions being opposite from each other. The

**TABLE 1: Optimized Geometrical Parameters of the Electronically Excited Singlet States at the Symmetric and Less Symmetric Nuclear Configurations of the Fulvalene Systems**

| molecule | structure | geometrical params[a] |
|---|---|---|
| **1** | $D_{2h}$ ($^1B_{2u}$) | C1−C2 = 1.3946, C2−C3 = 1.3898, C1−C4 = 1.4235, C2−H1 = 1.0640, C1−C2−C3 = 60.1, C4−C1−C2 = 150.1, C1−C2−H1 = 149.5, C2−C1−C3 = 59.8 |
| | $C_{2v}$ ($^1B_2$) | C1−C2 = 1.3595, C2−C3 = 1.4724, C1−C4 = 1.4373, C4−C5 = 1.4369, C5−C6 = 1.3209, C2−H1 = 1.0614, C5−H3 = 1.0674, C1−C2−C3 = 57.2, C4−C1−C2 = 147.2, C2−C1−C3 = 65.6, C1−C4−C5 = 152.6, C4−C5−C6 = 62.6, C5−C3−C6 = 54.7, C1−C2−H1 = 150.8, C4−C5−H3 = 148.8 |
| **2** | $D_{2h}$ ($^1B_{2u}$) | C1−C2 = 1.4182, C2−C3 = 1.4158, C3−C4 = 1.4157, C1−C6 = 1.4809, C2−H1 = 1.0719, C3−H2 = 1.0719, C1−C2−C3 = 108.6, C6−C1−C2 = 126.4, C2−C3−C4 = 107.8, C2−C1−C5 = 107.2, C1−C2−H1 = 126.0, C2−C3−H2 = 126.0 |
| | $C_{2v}$($^1B_2$) | C1−C2 = 1.4383, C2−C3 = 1.3700, C3−C4 = 1.4791, C1−C6 = 1.4866, C6−C7 = 1.4002, C7−C8 = 1.4664, C8−C9 = 1.3574, C2−H1 = 1.0720, C3−H2 = 1.0723, C7−H5 = 1.0723, C8−H6 = 1.0720, C1−C2−C3 = 108.2, C6−C1−C2 = 126.2, C2−C3−C4 = 107.9, C2−C1−C5 = 107.7, C1−C6−C7 = 126.6, C6−C7−C8 = 108.9, C7−C8−C9 = 107.7, C7−C6−C10 = 106.8, C1−C2−H1 = 125.5, C2−C3−H2 = 126.9, C6−C7−H5 = 126.3, C7−C8−H6 = 125.0 |
| **3** | $D_{2h}$ ($^1B_{2u}$) | C1−C2 = 1.4100, C2−C3 = 1.3989, C3−C4 = 1.3978, C4−C5 = 1.3780, C1−C8 = 1.4970, C2−H1 =1.0656, C3−H2 = 1.0764, C4−H3 = 1.0760, C8−C1−C2 = 119.0, C1−C2−C3 = 131.3, C2−C3−C4 = 131.0, C3−C4−C5 = 126.8, C1−C2−H1 = 117.4, C3−C4−H3 = 116.0, C2−C1−C7 = 121.7 |
| | $C_{2v}$ ($^1B_2$) | C1−C2 = 1.3916, C2−C3 = 1.4415, C3−C4 = 1.3581, C4−C5 = 1.4512, C1−C8 = 1.5396, C8−C9 = 1.4119, C9−C10 = 1.3757, C10−C11 = 1.4469, C11−C12 = 1.3354, C2−H1 = 1.0665, C3−H2 = 1.0774, C4−H3 = 1.0758, C9−H7 = 1.0680, C10−H8 = 1.0754, C11−H9 = 1.0765, C1−C2−C3 = 131.0, C2−C3−C4 = 131.5, C3−C4−C5 = 126.2, C8−C1−C2 = 118.7, C2−C1−C7 = 122.6, C1−C8−C9 = 119.4, C8−C9−C10 = 132.4, C9−C10−C11 = 129.8, C10−C11−C12 = 127.0, C9−C8−C14 = 121.3, C1−C2−H1 = 118.0, C2−C3−H2 = 113.9, C3−C4−H3 = 117.3, C8−C9−H7 = 116.4, C9−C10−H8 = 115.2, C10−C11−H9 = 115.3 |
| | $C_s$ ($^1A''$) | C1−C2 = 1.3927, C2−C3 = 1.4334, C3−C4 = 1.3542, C4−C5 = 1.4308, C1−C8 = 1.5288, C8−C9 = 1.4371, C9−C10 = 1.3696, C10−C11 = 1.4573, C11−C12 = 1.3302, C2−H1 = 1.0673, C3−H2 = 1.0775, C4−H3 = 1.0760, C9−H7 = 1.0704, C10−H8 = 1.0759, C11−H9 = 1.0767, C8−C1−C2 = 118.0, C1−C2−C3 = 130.0, C2−C3−C4 = 131.4, C3−C4−C5 = 126.7, C1−C8−C9 = 119.6, C8−C9−C10 = 130.7, C9−C10−C11 = 129.3, C10−C11−C12 = 126.9, C9−C8−C14 = 120.4, C1−C2−H1 = 117.8, C2−C3−H2 = 113.0, C3−C4−H3 = 116.9, C8−C9−H7 = 116.2, C9−C10−H8 = 115.7, C10−C11−H9 = 115.3, C9−C8−C1−C2 = 178.2, C8−C1−C2−H1 = 2.9, C1−C2−C3−H2 = 178.8, C2−C3−C4−H3 = 179.6, C3−C4−C5−H4 = 179.3, C1−C8−C9−C10 = 165.4, C8−C9−C10−C11 = 3.1, C9−C10−C11−C12 = 16.6, C1−C8−C9−H7 = 16.1, C8−C9−C10−H8 = 179.3, C9−C10−C11−H9 = 165.2, C10−C11−C12−H10 = 178.2 |
| **4** | $D_{2h}$ ($^1B_{2u}$) | C1−C8 = 1.4236, C1−C2 = 1.3600, C2−C3 = 1.3932, C2−C7 = 1.4261, C3−C4 = 1.3870, C4−C5 = 1.4474, C3−H1 = 1.0736, C4−H2 = 1.0747, C8−C1−C2 = 148.4, C1−C2−C3 = 178.4, C1−C2−C7 = 58.4, C2−C3−C4 = 113.8, C3−C4−C5 = 122.9, C2−C3−H1 = 124.0, C3−C4−H2 = 119.4, C2−C1−C7 = 63.2 |
| | $C_{2v}$ ($^1B_2$) | C1−C8 = 1.4365, C1−C2 = 1.3442, C2−C3 = 1.4156, C2−C7 = 1.4686, C3−C4 = 1.3706, C4−C5 = 1.5112, C3−H1 = 1.0747, C4−H1 = 1.0744, C8−C9 = 1.3836, C9−C10 = 1.3765, C9−C14 = 1.3870, C10−C11 = 1.4149, C11−C12 = 1.3853, C10−H5 = 1.0727, C11−H6 = 1.0754, C8−C1−C2 = 146.9, C1−C2−C3 = 179.5, C1−C2−C7 = 56.9, C2−C3−C4 = 115.0, C3−C4−C5 = 122.6, C2−C1−C7 = 66.2, C1−C8−C9 = 149.9, C8−C9−C10 = 176.0, C8−C9−C14 = 59.9, C9−C8−C14 = 60.2, C9−C10−C11 = 112.7, C10−C11−C12 = 123.0, C3−C4−H2 = 120.0, C2−C3−H1 = 123.2, C9−C10−H5 = 124.9, C10−C11−H6 = 118.7 |

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

**TABLE 2: Atomic Populations of the Electronically Excited Singlet States at the Symmetric and Distorted Structures**

| | | symmetric structure, $D_{2h}$ | | | distorted structure, $C_{2v}$ | | | |
|---|---|---|---|---|---|---|---|---|
| molecule | atom | total | $\sigma$ | $\pi$ | total | $\sigma$ | $\pi$ | $C_s$[a] |
| **1** | C1 | 5.9411 | 5.0085 | 0.9326 | 5.8250 | 5.0228 | 0.8022 | |
| | C4 | | | | 6.0553 | 4.9867 | 1.0686 | |
| | C2, C3 | 6.2536 | 5.2199 | 1.0337 | 6.3280 | 5.1785 | 1.1495 | |
| | C5, C6 | | | | 6.1742 | 5.2591 | 0.9150 | |
| | H1, H2 | 0.7758 | 0.7758 | | 0.7906 | 0.7906 | | |
| | H3, H4 | | | | 0.7670 | 0.7670 | | |
| **2** | C1 | 6.0134 | 5.0170 | 0.9964 | 5.9929 | 5.0935 | 0.8994 | |
| | C6 | | | | 6.0287 | 4.9467 | 1.0820 | |
| | C2, C5 | 6.1928 | 5.1883 | 1.004 | 6.2053 | 5.1197 | 1.0856 | |
| | C7, C10 | | | | 6.1815 | 5.2561 | 0.9254 | |
| | C3, C4 | 6.2073 | 5.2100 | 0.9973 | 6.2039 | 5.2266 | 0.9773 | |
| | C8, C9 | | | | 6.2070 | 5.1860 | 1.0210 | |
| | H1, H4 | 0.7974 | 0.7974 | | 0.8089 | 0.8089 | | |
| | H5, H8 | | | | 0.7878 | 0.7878 | | |
| | H2, H3 | 0.7958 | 0.7958 | | 0.7989 | 0.7989 | | |
| | H6, H7 | | | | 0.7958 | 0.7958 | | |
| **3** | C1 | 5.9518 | 4.9847 | 0.9672 | 5.8735 | 4.9713 | 0.9022 | 5.8594 |
| | C8 | | | | 6.0434 | 4.9465 | 1.0969 | 6.0133 |
| | C2, C7 | 6.2285 | 5.2142 | 1.0144 | 6.2882 | 5.2024 | 1.0858 | 6.2971 |
| | C9, C14 | | | | 6.1666 | 5.2432 | 0.9234 | 6.1749 |
| | C3, C6 | 6.1848 | 5.1989 | 0.9859 | 6.1545 | 5.1895 | 0.9649 | 6.1432 |
| | C10, C13 | | | | 6.2136 | 5.1861 | 1.0275 | 6.2032 |
| | C4, C5 | 6.1971 | 5.1809 | 1.0162 | 6.1940 | 5.1810 | 1.0130 | 6.2128 |
| | C11, C12 | | | | 6.1796 | 5.1938 | 0.9858 | 6.1864 |
| | H1, H6 | 0.7992 | 0.7992 | | 0.8120 | 0.8120 | | 0.8108 |
| | H7, H12 | | | | 0.7954 | 0.7954 | | 0.7987 |
| | H2, H5 | 0.8088 | 0.8088 | | 0.8153 | 0.8153 | | 0.8106 |
| | H8, H11 | | | | 0.8084 | 0.8084 | | 0.8101 |
| | H3, H4 | 0.8057 | 0.8057 | | 0.8111 | 0.8111 | | 0.8102 |
| | H9, H10 | | | | 0.8029 | 0.8029 | | 0.8056 |
| **4** | C1 | 5.9974 | 5.0275 | 0.9699 | 5.9054 | 5.0612 | 0.8442 | |
| | C8 | | | | 6.0722 | 4.9826 | 1.0896 | |
| | C2, C7 | 6.0025 | 5.0461 | 0.9564 | 6.1022 | 5.0224 | 1.0798 | |
| | C9, C14 | | | | 5.9290 | 5.0624 | 0.8666 | |
| | C3, C6 | 6.1967 | 5.1568 | 1.0399 | 6.1510 | 5.1514 | 0.9996 | |
| | C10, C13 | | | | 6.2320 | 5.1693 | 1.0627 | |
| | C4, C5 | 6.2146 | 5.1959 | 1.0187 | 6.2176 | 5.1827 | 1.0349 | |
| | C11, C12 | | | | 6.1989 | 5.2094 | 0.9895 | |
| | H1, H4 | 0.7868 | 0.7868 | | 0.7976 | 0.7976 | | |
| | H5, H8 | | | | 0.7786 | 0.7786 | | |
| | H2, H3 | 0.8007 | 0.8007 | | 0.8126 | 0.8126 | | |
| | H5, H8 | | | | 0.7786 | 0.7786 | | |

[a] Values of total atomic population.

amount of electron migration is larger for the latter (0.10 electrons) than for the former (0.04 electrons), with the result that a negative pole of the charge (−0.06 e) is situated on the ring with the moderate double-bond fixation. This indicates that the pseudo-JT effect brings about a contraction of the $\pi$ electron cloud on the ring. The charge distributions in $\sigma$ and $\pi$ electrons can also be discussed from a slightly different viewpoint: Taking the respective atomic populations in the $D_{2h}$ structure as the reference values, those in the $C_{2v}$ structure exhibit a charge alternation with regard to the $\sigma$ and $\pi$ electrons along the long molecular axis ($z$) (Figure 1). This situation is very similar to those observed in the ion radicals of fulvalene systems,[41] but it is markedly different from those observed in pentalene and heptalene.[29] In the latter molecules, a charge alternation appears along the carbon periphery at the symmetric $D_{2h}$ structure, while it is relaxed largely by migration of the $\pi$ electrons at the less symmetric $C_{2h}$ structure. Owing to the unsymmetrical charge distribution in the $C_{2v}$ structure, the lowest excited singlet state of **1** is predicted to have a dipole moment of 2.85 D, reflecting a rather large charge polarization in $\pi$ electrons.

As for **2,** the lengths of CC bonds in the $D_{2h}$ structure are considerably equalized in both the five-membered rings. In the $C_{2v}$ structure, however, one of the rings has a butadiene-like skeleton with a bond-length alternation and the other ring a relatively short CC bond of 1.357 Å. The stabilization energy which favors the distorted $C_{2v}$ nuclear configuration is calculated to be 11.0 kcal/mol. The atomic populations in Table 2 indicate that in the $C_{2v}$ structure a charge polarization takes place in $\sigma$ and $\pi$ electrons and a negative pole of the charge (−0.03 e) is situated on the ring with the butadiene-like skeleton. Taking the atomic charges at the $D_{2h}$ structure as the reference values, a charge alternation can be observed in the $C_{2v}$ structure along the long molecular axis with regard to the $\sigma$ and $\pi$ electrons. In this case too, the phase of the two charge alternations is opposite in sign with each other. As a result, this aspect is shown to be well-reflected in the small magnitude of dipole moment, which is actually calculated to be 0.55 D.

In the $D_{2h}$ structure of **3**, there exists little double-bond fixation in both the seven-membered rings. In the $C_{2v}$ structure, on the other hand, a marked double-bond fixation occurs in the two rings. Closer examination indicates that one of the rings has a butadiene-like moiety and the other a hexatriene-like one with an extremely short CC bond of 1.335 Å. The striking aspect of the results is that the cross-bond should assume a length of CC single bonds in ordinary saturated hydrocarbons,

**TABLE 3: Total and Partitioned Energies and Their Energy Differences between the Symmetric and Distorted Structures at the Electronically Excited Singlet States of the Fulvalene Systems**[a]

| molecule | component | symmetric | distorted | difference[b] |
|---|---|---|---|---|
| **1**[c] | | $D_{2h}$ | $C_{2v}$ | |
| | $E_{\text{total}}$ | −229.214 725 | −229.239 226 | −0.024 501 |
| | $E^{\text{N}}$ | 175.019 490 | 174.458 163 | −0.561 327 |
| | $E^{\text{T}}{}_{\sigma}$ | 222.381 234 | 222.310 008 | −0.071 226 |
| | $E^{\text{V}}{}_{\sigma}$ | −807.552 132 | −806.383 825 | +1.168 307 |
| | $E^{\text{J}}{}_{\sigma}$ | 216.904 918 | 216.406 136 | −0.498 782 |
| | $E^{\text{T}}{}_{\pi}$ | 6.691 186 | 6.776 453 | +0.085 267 |
| | $E^{\text{V}}{}_{\pi}$ | −76.197 317 | −76.346 538 | −0.149 221 |
| | $E^{\text{J}}{}_{\pi}$ | 33.537 913 | 33.540 353 | +0.002 440 |
| **2**[c] | | $D_{2h}$ | $C_{2v}$ | |
| | $E_{\text{total}}$ | −383.301 456 | −383.319 026 | −0.017 570 |
| | $E^{\text{N}}$ | 440.441 819 | 439.903 649 | −0.538 170 |
| | $E^{\text{T}}{}_{\sigma}$ | 372.324 620 | 372.295 406 | −0.029 214 |
| | $E^{\text{V}}{}_{\sigma}$ | −1605.443 193 | −1604.406 443 | +1.036 750 |
| | $E^{\text{J}}{}_{\sigma}$ | 490.231 019 | 489.755 551 | −0.475 468 |
| | $E^{\text{T}}{}_{\pi}$ | 10.703 995 | 10.746 485 | +0.042 490 |
| | $E^{\text{V}}{}_{\pi}$ | −168.335 650 | −168.359 362 | −0.023 712 |
| | $E^{\text{J}}{}_{\pi}$ | 76.775 956 | 76.745 689 | −0.030 267 |
| **3**[c] | | $D_{2h}$ | $C_{2v}$ | |
| | $E_{\text{total}}$ | −537.018 726 | −537.051 918 | −0.033 192 |
| | $E^{\text{N}}$ | 760.444 552 | 756.864 470 | −3.580 082 |
| | $E^{\text{T}}{}_{\sigma}$ | 522.522 972 | 522.239 348 | −0.238 624 |
| | $E^{\text{V}}{}_{\sigma}$ | −2497.014 596 | −2490.286 545 | +6.728 051 |
| | $E^{\text{J}}{}_{\sigma}$ | 809.627 728 | 806.594 919 | −3.032 809 |
| | $E^{\text{T}}{}_{\pi}$ | 14.071 189 | 14.376 252 | +0.305 063 |
| | $E^{\text{V}}{}_{\pi}$ | −273.810 209 | −273.746 472 | +0.063 737 |
| | $E^{\text{J}}{}_{\pi}$ | 127.139 625 | 126.906 111 | −0.233 514 |
| | | $C_{2v}$ | $C_s$ | |
| | $E_{\text{total}}$ | −537.051 918 | −537.055 841 | −0.003 923 |
| | $E^{\text{N}}$ | 756.864 470 | 758.275 719 | +1.411 249 |
| | $E^{\text{T}}$ | 536.615 600 | 536.619 583 | +0.003 983 |
| | $E^{\text{V}}$ | −2764.033 017 | −2766.810 660 | −4.033 017 |
| | $E^{\text{J}}$ | 933.501 030 | 934.859 522 | +1.358 492 |
| **4**[c] | | $D_{2h}$ | $C_{2v}$ | |
| | $E_{\text{total}}$ | −534.485 486 | −534.526 753 | −0.041 267 |
| | $E^{\text{N}}$ | 697.919 342 | 695.891 596 | −2.027 746 |
| | $E^{\text{T}}{}_{\sigma}$ | 519.543 346 | 519.350 173 | −0.193 173 |
| | $E^{\text{V}}{}_{\sigma}$ | −2374.060 699 | −2370.218 850 | +3.841 849 |
| | $E^{\text{J}}{}_{\sigma}$ | 750.569 772 | 748.889 134 | −1.680 638 |
| | $E^{\text{T}}{}_{\pi}$ | 14.556 792 | 14.781 458 | +0.224 666 |
| | $E^{\text{V}}{}_{\pi}$ | −265.756 257 | −265.844 434 | −0.088 177 |
| | $E^{\text{J}}{}_{\pi}$ | 122.742 208 | 122.624 172 | −0.118 036 |

[a] Energies are in hartrees. [b] The minus sign means that the energy term is lower in energy for the distorted structure than for the symmetric one. [c] The total $D_{2h}$ ground-state energies for **1**−**4** are −229.356 839, −383.394 738, −537.125 382, and −534.667 770 hartree, respectively.

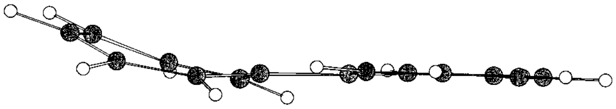

**Figure 2.** Side view of the nonplanar $C_s$ structure for the lowest excited singlet state of heptafulvalene.

i.e., about 1.54 Å: Relative to the $D_{2h}$ structure, the lengthening amounts to 0.04 Å in the $C_{2v}$ structure. Presumably, the significant lengthening should be largely responsible for relieving the steric repulsion between the two pairs of the neighboring hydrogen atoms across the cross-bond within the planar conformation. This is because the nonbonded atomic distance between H1 and H7 is 1.694 Å in the optimized $D_{2h}$ structure, which is markedly shorter than the sum of their van der Waals radii, 2.0−2.40 Å.[42,43] The stabilization energy due to the pseudo-JT distortion is calculated to be 20.8 kcal/mol. A comparison of the atomic populations between the $D_{2h}$ and $C_{2v}$ structures indicates that in the latter a charge alternation appears along the long molecular axis with regard to the $\sigma$ and $\pi$ electrons. A small negative pole of the charge (−0.02 e) is situated on the ring with the butadiene-like moiety. This indicates a contraction of the $\pi$-electron cloud on the ring, and the dipole moment is calculated to be 0.75 D.

In the optimized $C_{2v}$ structure of **3**, the nonbonded atomic distance between H1 and H7 is 1.717 Å, the hydrogen atoms being far apart by 0.023 Å in comparison with those in the $D_{2h}$ structure. Note that the distance is still shorter than the sum of their van der Waals radii. In view of nonbonded repulsive interactions, it is most probable that **3** should further undergo a pseudo-JT distortion from the planar $C_{2v}$ to a nonplanar $C_s$ structure. This expectation is confirmed as follows: The geometry optimization starting with a nonplanar conformation is actually converged into a stationary point corresponding to the nonplanar $C_s$ structure.[44] The optimized geometrical parameters are also listed in Table 1. Figure 2 shows the side view of the nonplanar $C_s$ structure obtained using the atomic coordinates. The structural analysis reveals that, relative to the planar $C_{2v}$ structure, the double and single bonds in the seven-membered ring with a hexatriene-like moiety are respectively shortened and lengthened, the bond lengths almost corresponding to those in ordinary polyolefinic hydrocarbons. In accordance with the strong double-bond fixation, the present seven-membered ring is deformed into a shallow half-chair conformation (Figure 2). On the other hand, the other ring possessing a butadiene-like moiety exhibits a rather moderate double-bond fixation in its carbon periphery, almost taking a planar conformation. It is seen that the degree of folding in the former ring is small in comparison with that observed for the ground state of the heptafulvalene molecule.[34] This may be reflected in such a small amount of the stabilization energy due to the nonplanarity, which is calculated to be 2.5 kcal/mol. In the nonplanar $C_s$ structure, the nonbonded atomic distance between H1 and H7 is increased to 1.797 Å,[45] but the distance is shorter than the sum of their van der Waals radii. However, it is noticeable that the distance is comparable to those between nonbonded hydrogen atoms observed with tetra-*tert*-butylcyclobutadiene by Irngartinger and Nixdorf.[46] Upon the structural changes from $C_{2v}$ to $C_s$, the changes of atomic populations are relatively small. It thus follows that the dipole moment is calculated to be 0.81 D in the $C_s$ structure, the magnitude being almost the same as that in the $C_{2v}$ structure.

As to the $D_{2h}$ structure of **4**, a double-bond fixation is observed with the three-membered rings, i.e., in the regions of C1−C2 and C8−C9. In the $C_{2v}$ structure, C1−C2 is shortened to 1.344 Å, while C8−C9 is lengthened to 1.384 Å. Besides, C4−C5 is lengthened to 1.511 Å. The remaining CC bonds also exhibit a moderate bond-length alternation. The cross-bond in the $C_{2v}$ structure assumes a length of 1.437 Å. Relative to the $D_{2h}$ structure, the lengthening amounts only to 0.01 Å in the $C_{2v}$ structure, and the change in bond length is almost the same as that seen in **1**. The stabilization energy due to the pseudo-JT distortion is calculated to be 25.9 kcal/mol. A comparison of the atomic populations between the $D_{2h}$ and $C_{2v}$ structures indicates that in the latter a charge alternation appears along the long molecular axis with regard to the $\sigma$ and $\pi$ electrons. Concomitantly, a contraction of the $\pi$-electron cloud takes place appreciably on the ring with the two short and long CC bonds. This aspect should be well-reflected in the magnitude of dipole moment, which amounts actually to as much as 2.42 D in the present MCSCF method.

In connection with the above charge distributions, it is of interest to refer to the properties of electronically excited singlet states qualitatively in view of occupation numbers of natural orbitals.[47] Analysis of natural orbitals in the $C_{2v}$ structure reveals that these excited states exhibit two natural orbitals with values close to 1: **1**, 1.000 and 0.989; **2**, 1.012 and 1.011; **3**, 0.993 and 0.991; and **4**, 0.996 and 0.994. Interestingly, the associated two orbitals in **2** show a complete localization on the different five-membered rings. That is, the orbital of occupation number 1.012 is localized only on C1 and C3−C4 regions, while the one of occupation number 1.011 is only on C7−C8 and C9−C10 regions. Accordingly, it can be said that the lowest excited singlet state should possess a biradical character rather than an ionic one. A quite similar localization is also observed with the relevant two orbitals of the remaining molecules, suggesting that they should exhibit biradical characters in the excited singlet state of interest.

Now that the energetically favorable molecular shapes of the electronically excited singlet states have become clear, an explanation is given about how a characteristic long absorption tail appears in the longest wavelength absorption band for pentafulvalene and heptafulvalene.[20,21] Since the geometrical structure of the lowest excited singlet state differs markedly from that of the ground state in molecular shape, it is thus evident that the equilibrium points are far apart for the potential energy curves with each other. This suggests that the absorption spectrum should exhibit long vibrational progressions along the nontotally symmetric nuclear displacement that is active to the pseudo-JT distortion, together with the totally symmetric nuclear displacement. In pentafulvalene, for example, the electronic transition energies from the $D_{2h}$ ground state to the vertical $^1B_{2u}$ excited state, the energy minimum $^1B_{2u}$ excited state, and the energy minimum $^1B_2$ excited state are calculated to be 3.57, 2.54, and 2.06 eV, respectively. Hence, it can be said that the molecule should exhibit a relatively long absorption spectrum for the transition to the lowest excited singlet state.

On the basis of these results, we now discuss the leading factors responsible for the stability of less symmetric nuclear configuration.

**Energy Component Analysis of the Total Energy in the Excited Singlet States.** *Triafulvalene (**1**).* An analysis with regard to the CC and CH bonds in length between the $D_{2h}$ and $C_{2v}$ structures reveals that, in addition to the $b_{1u}$ nuclear deformation of interest, the totally symmetric nuclear deformation is operative. 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 $D_{2h}$ structure: the cross-bond, +0.014 Å; C1−C2, +0.004 Å; C2−C3, −0.007 Å; and C1−H1, $+0.000_4$ Å. At the same time, the bond-length changes due to the $b_{1u}$ nuclear deformation are given as follows: C1−C2, −0.039 Å; C2−C3, +0.076 Å; and C1−H1, −0.003 Å. Here the remaining bonds are shortened or lengthened by the lengths above in absolute values so that each set of their displacement vectors should satisfy the symmetry of $b_{1u}$ nuclear deformation. It is mentioned that the displacement vector of cross-bond is zero by symmetry in the $b_{1u}$ nuclear deformation. It should be remarked that when the excited triafulvalene molecule settles at the $C_{2v}$ equilibrium structure, an expansion of the molecular skeleton takes place in a totally symmetric fashion. Hence, it is expected that the repulsive terms should be lowered in energy. As is listed in Table 3, this is actually true for the two repulsive terms $E^N$ and $E^J{}_\sigma$. But, another term $E^J{}_\pi$ is raised in energy, and an account of the energy raising will be given below. In marked contrast, the expansion of molecular skeleton should generally lead to the energy raising of the nuclear−electron attractive terms. As noted in the preceding section, however, a contraction of the $\pi$-electron cloud occurs on the ring with the nearly equal CC bonds in length. In such a case, it is often observed that the nuclear−electron attractive term $E^V{}_\pi$ is lowered in energy. This suggests that the energy changes of $E^V{}_\pi$ and $E^J{}_\pi$ should depend on a competition between the two opposing factors mentioned above. That the term $E^V{}_\pi$ is indeed lowered and the term $E^J{}_\pi$ is raised in energy can thus be attributable to the fact that the contribution from the contraction of the $\pi$-electron cloud is larger than that from the expansion of molecular skeleton. The energy changes of the kinetic terms due to $\sigma$ and $\pi$ electrons are small, the absolute values being almost equal. As a consequence, it can be concluded for the lowest excited singlet state of triafulvalene that the stability of the $C_{2v}$ structure should arise from the energy lowerings of the terms $E^N$, $E^J{}_\sigma$, $E^V{}_\pi$, and $E^T{}_\sigma$, and the other terms change in energy in the opposite direction to the stability. The leading energy terms to the stability come from the former three terms, in order of importance.

*Pentafulvalene (**2**).* Upon the pseudo-JT distortion from $D_{2h}$ to $C_{2v}$, it is found that the molecular skeleton is expanded in a totally symmetric fashion. The associated changes in bond length are given as follows: the cross-bond, +0.006 Å; C1−C2, +0.001 Å; C2−C3, +0.002 Å; C3−C4, +0.003 Å; C2−H2, $+0.000_3$ Å; and C3−H3, $+0.000_3$ Å. At the same time, the bond-length changes due to the $b_{1u}$ nuclear deformation are given as follows: C1−C2, +0.019 Å; C2−C3, −0.048 Å; C3−C4, +0.061 Å; C2−H2, $-0.000_2$ Å; and C3−H3, $+0.000_2$ Å. As a result, an expansion of the carbon skeleton should be reflected in a decrease in the internuclear and interelectronic repulsion energies. Table 3 shows clearly that all the repulsive terms $E^N$, $E^J{}_\sigma$, and $E^J{}_\pi$ are actually lowered in energy. In contrast, the nuclear−electron attractive terms should be raised in energy because of the expansion of molecular skeleton. As is shown in Table 3, this is actually true for the attractive term $E^V{}_\sigma$, but another term $E^V{}_\pi$ is slightly lowered in energy. The latter situation will be attributable to the fact that a contraction of the $\pi$-electron cloud contributes to the energy lowering of the term $E^V{}_\pi$. In more detail, this is because the large $\pi$-electron densities resulting from a contraction of the $\pi$-electron cloud reside on the atoms forming C8−C9 and, hence, enhance the nuclear−electron attractive interactions to some extent. As to the kinetic terms due to $\sigma$ and $\pi$ electrons, the energy changes are small, the absolute values being almost equal. As a consequence, it can be said for the lowest excited singlet state of pentafulvalene that the preference for the $C_{2v}$ structure should originate from the energy lowerings of the terms $E^N$, $E^J{}_\sigma$, $E^J{}_\pi$, $E^V{}_\pi$, and $E^T{}_\sigma$. The other energy terms contribute to the direction opposite from the stability of distorted structure.

*Heptafulvalene (**3**).* Relative to the $D_{2h}$ structure, the molecular skeleton of the $C_{2v}$ structure is expanded symmetrically, and the associated changes in bond length are given as follows: the cross-bond, +0.043 Å; C1−C2, −0.008 Å; C2−C3, +0.010 Å; C3−C4, +0.005 Å; C4−C5, +0.015 Å; C2−H2, +0.002 Å; C3−H3, $+0.000_0$ Å; and C4−H4, $+0.000_2$ Å. At the same time, the bond-length changes due to the $b_{1u}$ nuclear deformation are given as follows: C1−C2, −0.010 Å; C2−C3, +0.033 Å; C3−C4, −0.044 Å; C4−C5, +0.015 Å; C2−H2, −0.001 Å; C3−H3, +0.001 Å; and C4−H4, $-0.000_4$ Å. In conformity with a symmetric expansion of the carbon skeleton, Table 3 shows clearly that all the repulsive terms $E^N$, $E^J{}_\sigma$, and $E^J{}_\pi$ are actually lowered in energy. Further, the symmetric expansion of molecular skeleton leads to the energy changes that the nuclear−electron attractive terms are raised in energy. Slightly amazing, this is true for the two attractive terms

$E^{V}_{\sigma}$ and $E^{V}_{\pi}$. It should be noted here that the term $E^{V}_{\pi}$ is lowered in energy in **1** and **2**, but it is raised in energy in **3**. The energy change in the latter seems not to be consistent with the contraction of the $\pi$-electron cloud, and this distinction may be explained as follows. In the former, the contraction of the $\pi$-electron cloud takes place on the carbon atoms forming a CC bond, but in the latter it occurs on the carbon ones forming no CC bond. For this reason, the nuclear−electron attractive interactions in heptafulvalene are not so strongly enhanced as to lower the energy of the attractive term $E^{V}_{\pi}$ in the distorted structure. It is remarked that the energy changes of the kinetic terms due to $\sigma$ and $\pi$ electrons are rather large, the former being lowered and the latter raised in energy. Consequently, it can be concluded for the lowest excited singlet state of heptafulvalene that the energetic stability of the $C_{2v}$ structure results from the energy lowerings of the terms $E^{N}$, $E^{J}_{\sigma}$, $E^{J}_{\pi}$, and $E^{T}_{\sigma}$. The large contributions come from the former two terms, in order of importance.

As shown in the preceding section, heptafulvalene undergoes the pseudo-JT distortion from $C_{2v}$ to $C_s$ in the lowest excited singlet state. The energy components for the nonplanar $C_s$ structure are also listed in Table 3. A comparison of the respective energy components between the two structures reveals that the nuclear−electron attractive term $E^{V}$ contributes definitely to the energetic stability of the nonplanar structure.[48,49] But the other energy terms contribute more or less to the direction opposite from the stability. Namely, the internuclear and interelectronic repulsive terms are increased greatly in energy and the kinetic energy changes to a small extent. An explanation may be given of how the two repulsive interactions are enhanced to such extents. In the nonplanar structure, most nonbonded atomic distances for the folding moiety are shortened relative to those for the planar seven-membered moiety in the $C_{2v}$ structure, and hence the internuclear interactions are increased. At the same time, since the electrons involved in the CC and CH bonds become spatially close together due to the folding, the interelectronic repulsive interactions should be increased as well. As a result, the two repulsive terms $E^{N}$ and $E^{J}$ are largely raised in energy. Concomitantly, the distances between the nuclei and electrons are shortened for the above reason, and the nuclear−electron attractive term $E^{V}$ should be largely lowered in energy. In conclusion, it can be said that in the lowest excited singlet state of heptafulvalene the nonplanar $C_s$ structure owes its energetic stability to the energy lowering of the nuclear−electron attractive term $E^{V}$.[48,49]

*7,7′-Bis(bicyclo[4.1.0]hepta-1,3,5-trienylidene) (**4**).* Taking the bond distances at the $D_{2h}$ structure as the reference values, it is found that the molecular skeleton of the $C_{2v}$ structure is expanded symmetrically, and the associated changes in bond length are given as follows: the cross-bond, +0.013 Å; C1−C2, +0.004 Å; C2−C3, +0.003 Å; C2−C7, +0.002; C3−C4, +0.006 Å; C4−C5, +0.001 Å; C3−H1, $+0.000_1$ Å; and C4−H2, $+0.000_2$ Å. At the same time, the bond-length changes due to the $b_{1u}$ nuclear deformation are given as follows: C1−C2, −0.020 Å; C2−C3, +0.020 Å; C2−C7, +0.041; C3−C4, −0.022 Å; C4−C5, +0.063 Å; C3−H1, +0.001 Å; and C4−H1, −0.001 Å. In accordance with a symmetric expansion of the carbon skeleton, Table 3 shows clearly that all the repulsive terms $E^{N}$, $E^{J}_{\sigma}$, and $E^{J}_{\pi}$ are actually lowered in energy. Further, the symmetric expansion of molecular skeleton should lead to the energy changes that the nuclear−electron attractive terms are raised in energy. This is true for the attractive term $E^{V}_{\sigma}$, but another attractive term $E^{V}_{\pi}$ is lowered in energy. As noted above, the attractive term $E^{V}_{\pi}$ is lowered in energy in **1** and **2**, but it is raised in energy in **3**. As in the former molecules, since in **4** the contraction of $\pi$-electron cloud takes place on the carbon atoms forming two CC bonds, the nuclear−electron attractive interactions are enhanced to lower the energy of the attractive term $E^{V}_{\pi}$ slightly in the distorted $C_{2v}$ structure. It should be remarked that the energy changes of the kinetic terms due to $\sigma$ and $\pi$ electrons are rather large, the former being lowered and the latter raised in energy. As a result, it can be concluded for the second excited singlet state of 7,7′-bis(bicyclo[4.1.0]hepta-1,3,5-trienylidene) that the energetic stability of the $C_{2v}$ structure results from the energy lowerings of the terms $E^{N}$, $E^{J}_{\sigma}$, $E^{T}_{\sigma}$, $E^{J}_{\pi}$, and $E^{V}_{\pi}$. The large contributions come from the former three terms, in order of importance.

## Conclusions

From the above considerations, it has become apparent that the electronically excited singlet states of the fulvalene systems examined undergo the pseudo-JT bond distortion from $D_{2h}$ to $C_{2v}$. In each molecule, the stabilization energy which favors the distorted $C_{2v}$ structure is found to be quite large, in comparison with those observed theoretically in the lowest excited singlet state of cyclobutadiene and the lowest excited triplet state of benzene.[30] A characteristic feature inherent in the present fulvalene systems is that a charge alternation in $\pi$ electrons as well as in $\sigma$ electrons appears at the less symmetric $C_{2v}$ nuclear configuration. This is equivalent to saying that a charge polarization takes place and, hence, a contraction of the $\pi$-electron cloud occurs in one of the odd-membered rings on excitation. In accordance with the unsymmetrical charge distribution, the singlet excited states under consideration possess dipole moments, which are calculated to be in the range of 0.6−2.9 D for the molecules examined. Accordingly, it follows that the relevant absorption bands should be sensitive to changes in the polarity of solvents used. This is to be expected when the ground and excited states have very different electron distributions.

In this connection, the present study indicates that the energy component analysis is informative for elucidating what happens inside the excited singlet state of the fulvalene systems when it is subject to the pseudo-JT distortion. In the electronically excited states, it is shown that, in addition to the $b_{1u}$ nuclear deformation, an expansion of the carbon skeleton takes place in a totally symmetric fashion. Hence, it is revealed that a reduction of the internuclear repulsion energy and the interelectronic repulsion energy due to the $\sigma$ electron contributes commonly to the stability of the $C_{2v}$ structure. Despite this, it is observed that in triafulvalene and pentafulvalene the nuclear−electron attraction energy of $\pi$ electrons plays a role in the stability of the $C_{2v}$ structure. This is ascribed to the behavior that the $\pi$-electron cloud is contracted to the atoms forming a CC bond by polarization of atomic charges. It is also notable that the energy change in the kinetic term $E^{T}_{\sigma}$ is almost the same in absolute value as that in the term $E^{T}_{\pi}$. It may thus be concluded that an expansion of the carbon skeleton and a charge polarization play dominant roles in the stability of a less symmetric structure. In other words, the pseudo-JT stabilization from $D_{2h}$ to $C_{2v}$ in the present fulvalene systems can be said to result mostly from the combined effects due to a structural change and a redistribution of the $\pi$-electron density through electrostatic interactions. Moreover, it is shown that **3** further suffers an out-of-plane pseudo-JT distortion from $C_{2v}$ to $C_s$. Apparently, the cause of nonplanarity seems to be due to the effect for relieving the repulsion interactions between the nonbonded hydrogen atoms. But, the analysis reveals clearly that the stability of nonplanar $C_s$ structure arises from the energy lowering of the nuclear−electron attractive term.[48,49] This aspect is accounted for in terms of the proximity between the nuclei and electron clouds, owing to the folding of the seven-membered ring with the hexatriene-like moiety. The present energetic behavior is just the same as that observed in cyclooctatetraene when it is distorted into the nonplanar bond-alternated $D_{2d}$ structure from the planar bond-alternated $D_{4h}$ one.[30,50]

Finally, we must note that it is desirable to use a larger basis set than the 6-31G(d) basis set for properly representing electronic structures of the electronically excited states. 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.[48,49,51] We hope that the essence of the present conclusions would not be impaired even if more flexible basis sets larger than the 6-31G(d) basis set are used in the MCSCF calculations for the present molecules.

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