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Energy Component Analysis of the Pseudo-Jahn−Teller Effect in the Ground State of the Triafulvalene Anion, Pentafulvalene Cation, and Heptafulvalene Anion Radicals

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To understand the nature of the pseudo-Jahn−Teller (JT) effect, an energy component analysis of the total energy was carried out in the ground state of the titled ion radicals by using the MCSCF method with 6-31G(d) basis set. Examination of the energy components comprising in the total energy reveals that in the radicals the stability of a less symmetrical nuclear configuration (C_{2v}) is attributable commonly to the energy lowering of the internuclear repulsion term and the kinetic and interelectronic repulsion terms due to σ electrons. These observations are consistent with an expansion of the molecular skeleton brought about by the pseudo-JT distortion. In the triafulvalene anion radical, it is further found that the nuclear−electron attractive and interelectronic repulsive terms due to π electrons also contribute to the stability of the C_{2v} structure. In the pentafulvalene cation and heptafulvalene anion radicals, on the other hand, the interelectronic repulsive and nuclear−electron attractive terms due to π electrons contribute to the stability of the C_{2v} structure, respectively. These differences are accounted for in terms of a charge polarization attributed to the migration of π electrons. Moreover, characteristic electronic properties inherent in the radicals are discussed with much attention to the charge and unpaired spin-density distributions in the distorted C_{2v} structure.

Introduction

It is well-known that a pseudo-Jahn−Teller (JT) effect[1−4] 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 state or of an electronically excited state in nonlinear molecules. In the case where a certain molecule undergoes the pseudo-JT effect, it is in general expected that the molecule should exhibit unusual physicochemical properties. From these viewpoints, the chemistry of nonbenzenoid aromatic hydrocarbons has been of theoretical as well as synthetic interest. As a result, a number of intriguing features attributable to the pseudo-JT effect have so far been observed for such nonalternant conjugated molecules from spectroscopic measurements especially of NMR, absorption, and ESR spectra.[5−19]

In recent years, an energy component analysis of the total energy has been made to understand the physical picture of the pseudo-JT effect in bicyclic nonalternant hydrocarbons termed pentalenoid and heptalenoid systems[20] as well as in some fundamental cyclic polyenes[21] by using the ab initio MO method with 6-31G(d) basis set.[22−26] In connection with such neutral species, it is of primary importance to carry out the energy component analysis of the total energy in the charged species that should undergo the pseudo-JT distortion. This is because the pseudo-JT effect in the conjugated hydrocarbons examined is found to be profoundly related with the charge distribution in π electrons. In the present paper, we thus deal with the ion radicals of fulvalene systems (Figure 1) using the MCSCF method with 6-31G(d) basis set.[22−26] The electronic state under consideration is the ground state of the triafulvalene anion radical (**1**), the pentafulvalene cation radical (**2**), and the heptafulvalene anion radical (**3**). It will be shown that the present energy component analysis facilitates the understanding of the nature of pseudo-JT effect observed in the radicals **1**−**3**.

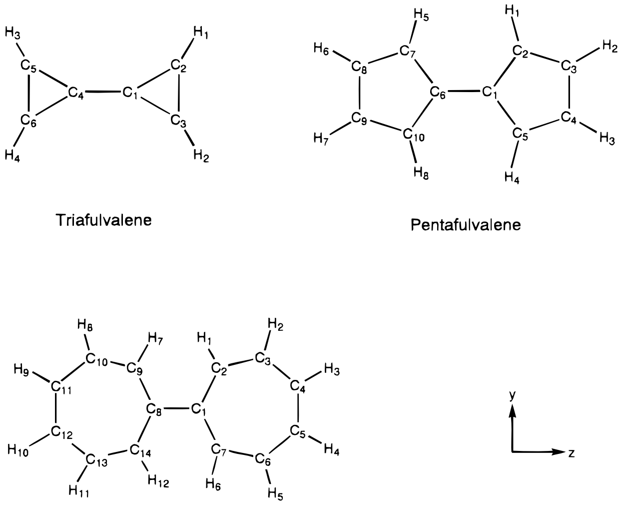

Figure 1. Molecular skeletons, numbering of atoms, and choice of molecular axes.

It is remarked here that the parent triafulvalene molecule is still an unknown compound, but its dibenzo derivatives[27] and the parent pentafulvalene and heptafulvalene molecules[15] were prepared together with the ion radicals.[16,28,29] Among other

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things, of special note is the ESR spectrum of the radical **3** observed by Sevilla and others,[16] which indicates that the unpaired spin density is not delocalized throughout the molecule, but it is localized essentially on a single seven-membered ring. A similar anomaly in spin-density distribution has also been observed in the trianion radical of heptafulvalene by Bauld et al.[17]

Methods of Calculation

Since the ground state of the radicals **1**−**3** is an open-shell structure, we employ here full-optimized reaction space (FORS) multiconfiguration self-consistent field (MCSCF) method with 6-31G(d) basis set.[22−26] It should be noted that for the radicals **1** and **2** the MCSCF active space includes all inner valence π orbitals and all π electrons. For the anion radical **3**, however, the MCSCF active space includes only nine π electrons in 10 active π orbitals. That is, the reduced 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 hence six π electrons occupying in the former orbitals are excluded from 15 π electrons involved in the anion radical.

The energy components comprising in the total energy are important essentially for discussing the leading terms responsible for the pseudo-JT stabilization in the present charged species, and accordingly we give here a brief review of the energy partitioning scheme.[30] The total energy of a molecular system is expressed as the sum of the electronic energy (E^{el}) and the internuclear repulsion energy (E^{N}). The E^{el} term comprises the kinetic (E^{T}) and potential energies, the latter being further partitioned into the nuclear−electron attraction energy (E^{V}) and the interelectronic repulsion energy (E^{J}). In the case of a planar conjugated molecule, the E^{el} and its partitioned energies can be further partitioned into σ-electron (E_σ) and π-electron (E_π) 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 σ electrons and between σ and π electrons and the $E^{\mathrm{J}}{}_{\pi}$ term the energies arising from between pure π electrons and between π and σ electrons. All these 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 Doublet States in the Symmetric D_{2h} Structure. Molecular geometries for the radicals **1**−**3** are assumed to be planar.[31] The low-lying doublet states of the radicals have been examined using the optimized D_{2h} geometrical structures in the ground state. It is predicted for the radicals **1** and **3** that the ground state is of $\mathrm{B_{1g}}$ symmetry and the lowest excited doublet state is of $\mathrm{A_u}$ symmetry, the energy separations between the two states being 0.12 and 0.43 eV, respectively. As for the radical **2**, the ground state is of $\mathrm{A_u}$ symmetry and the lowest excited doublet state is of $\mathrm{B_{1g}}$ symmetry, the associated energy separation being 0.15 eV. It is often observed that such a small energy gap is a crucial factor for the occurrence of the pseudo-JT effect in the ground state.[32] A qualitative account can be given of the appearance of near-degeneracy in the ground state as follows: In the simple HMO picture, an accidental doubly degeneracy takes place in the lowest unoccupied MO (LUMO) in triafulvalene and heptafulvalene, while a similar orbital degeneracy occurs in the highest occupied MO (HOMO) in pentafulvalene. Hence, it is readily expected that addition of an electron to or removal of an electron from the relevant neutral molecule to produce the anion or cation radical should lead to the degenerate ground state in the corresponding ion radical. Needless to say, when electron repulsion is included, this accidental degeneracy is lifted, but in the resultant electronic states the energy separation of interest is in general small, as is actually shown above. It is mentioned that for the present radicals the second excited doublet state with $\mathrm{B_{3u}}$ symmetry lies relatively high above the ground state in energy. Since the ground state is nearly degenerate with the lowest excited doublet state, it is suggested from symmetry arguments that the in-plane nuclear deformation of $\mathrm{b_{1u}}$ ($\mathrm{B_{1g}} \times \mathrm{A_u}$) symmetry should cause a strong vibronic interaction between them. As a result, the ground-state nuclear arrangement of the radicals **1**−**3** is expected to undergo a pseudo-JT bond distortion from D_{2h} to C_{2v}. This means that no conventional D_{2h} nuclear configuration of the radicals represents a minimum but a saddle point of the ground-state potential energy surface. In what follows, we will give the structural and concomitant properties of the D_{2h} and C_{2v} structures that have been obtained by the MCSCF geometry optimizations with 6-31G(d) basis set.

Structural Characteristics and Electronic Properties. Table 1 presents the fully optimized geometrical parameters for the symmetric (D_{2h}) and less symmetric (C_{2v}) nuclear configurations of the radicals **1**−**3**. Atomic populations are obtained at the D_{2h} and C_{2v} structures by means of Mulliken's population analysis,[33] which are summarized in Table 2 together with σ- and π-electron components. In Table 3 are shown the total and partitioned energies at the D_{2h} and C_{2v} structures of the radicals examined .

As to the radical **1** with D_{2h} symmetry, Table 1 shows that there exists a marked double-bond fixation in both the three-membered rings. In the C_{2v} structure, on the other hand, an extremely short CC bond of 1.317 Å appears in one of the rings, while the lengths of the CC bonds are nearly equalized 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 14.0 kcal/mol. Examination of the atomic populations reveals that despite a negatively charged species, all the hydrogen atoms are charged positively in both the structures. In the C_{2v} structure, a migration of the π-electrons is observed from one side of the rings to the other, whereas the σ-electrons are transferred to the direction opposite to the π-electron migration. The amount of electron migration is larger for the former than for the latter, with the result that the large negative charge (−0.70 e) is localized in the ring with the nearly equalized CC bonds in length. This aspect may be equivalent to saying that the pseudo-JT effect brings about a contraction of the π-electron cloud. The charge distributions in σ and π electrons can also be discussed from a slightly different viewpoint: Taking the atomic populations in the D_{2h} structure as reference values, a charge alternation[34] can be observed with regard to the σ and π electrons along the long molecular axis (z) in the C_{2v} structure (Figure 1). This situation differs markedly from those observed in pentalene and heptalene.[21] In the molecules, a charge alternation appears along the carbon periphery in the symmetric D_{2h} structure, while in the less symmetric C_{2h} structure it is relaxed largely by migration of the π electrons. Of special interest is the distribution of unpaired spin densities, because the two rings are no more equivalent in the C_{2v} structure. By means of the usual restricted open-shell Hartree−Fock (ROHF) method with 6-31G(d) basis set,[22] the unpaired spin densities on carbon atoms are calculated at the D_{2h} and C_{2v} structures in cooperation with the geometry

TABLE 1: Optimized Geometrical Parameters at the Symmetric and Less Symmetric Nuclear Configurations of the Ion Radicals

molecule	structure	geometrical parameters[a]
1	D_{2h} ($^2B_{1g}$)	C1−C2 = 1.4477, C2−C3 = 1.3682, C1−C4 = 1.3280, C2−H1 = 1.0679, C4−C1−C2 = 151.8, C1−C2−C3 = 61.8, C1−C2−H1 = 149.0, C2−C1−C3 = 56.4
	C_{2v} ($^2A_2$)	C1−C2 = 1.4302, C2−C3 = 1.4175, C1−C4 = 1.3285, C4−C5 = 1.4808, C5−C6 = 1.3172, C2−H1 = 1.0655, C5−H3= 1.0718, C1−C2−C3 = 60.2, C1−C2−H1 = 147.7, C2−C1−C3 = 59.4, C1−C4−C5 = 153.3, C4−C5−C6 = 63.6, C4−C5−H3 = 150.2, C5−C3−C6 = 52.8
2	D_{2h} (^2A_u)	C1−C2 = 1.4532, C2−C3 = 1.3846, C3−C4 = 1.4396 C1−C6 = 1.3630, C2−H1 = 1.0703, C3−H2 = 1.0713, C6−C1−C2 = 126.9, C1−C2−C3 = 108.2, C2−C3−C4 = 108.7, C1−C2−H1 = 125.7, C2−C3−H2 = 125.9, C2−C1−C5 = 106.2
	C_{2v} ($^2A_2$)	C1−C2 = 1.4745, C2−C3 = 1.3503, C3−C4 = 1.4949, C1−C6 = 1.3740, C6−C7 = 1.4408, C7−C8 = 1.4150, C8−C9 = 1.3923, C2−H1 = 1.0703, C3−H2 = 1.0714, C7−H5 = 1.0711, C8−H6 = 1.0715, C6−C1−C2 = 126.9, C1−C2−C3 = 108.2, C2−C3−C4 = 108.7, C1−C2−H1 = 125.7, C2−C3−H2 = 125.9, C2−C1−C5 = 106.2
3	D_{2h} ($^2B_{1g}$)	C1−C2 = 1.4632, C2−C3 = 1.3751, C3−C4 = 1.4302, C4−C5 = 1.3574, C1−C8 = 1.3881, C2−H1 =1.0668, C3−H2 = 1.0804, C4−H3 = 1.0794, C8−C1−C2 = 120.5, C1−C2−C3 = 132.0, C2−C3−C4 = 131.9, C3−C4−C5 = 126.7, C1−C2−H1 = 116.2, C2−C3−H2 = 114.0, C3−C4−H3 = 115.7, C2−C1−C7 = 118.9
	C_{2v} ($^2A_2$)	C1−C2 = 1.4428, C2−C3 = 1.4054, C3−C4 = 1.3797, C4−C5 = 1.4229, C1−C8 = 1.4165, C8−C9 = 1.4677, C9−C10 = 1.3569, C10−C11 = 1.4720, C11−C12 = 1.3246, C2−H1 = 1.0685, C3−H2 = 1.0818, C4−H3 = 1.0791, C9−H7 = 1.0700, C10−H8 = 1.0793, C11−H9 = 1.0800, C8−C1−C2 = 120.8, C1−C2−C3 = 132.0, C2−C3−C4 = 133.4, C3−C4−C5 = 125.4, C1−C2−H1 = 116.7, C2−C3−H2 = 112.5, C3−C4−H3 = 117.0, C2−C1−C7 = 118.3, C1−C8−C9 = 120.9, C8−C9−C10 = 133.4, C9−C10−C11 = 130.3, C10−C11−C12 = 127.2, C8−C9−H7 = 115.3, C9−C10−H8 = 115.7, C10−C11−H9 = 115.0, C9−C8−C14 = 118.2

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

TABLE 2: Atomic Populations at the Symmetric and Distorted Structures of the Ion Radicals

		symmetric structure (D_{2h})			distorted structure (C_{2v})		
molecule	atom	total	σ	π	total	σ	π
1	C1	6.0250	4.8690	1.1560	5.9570	4.9795	0.9775
	C4				6.0826	4.7675	1.3150
	C2,C3	6.3506	5.1786	1.1720	6.4519	5.0784	1.3735
	C5,C6				6.2470	5.2668	0.9802
	H1,H2	0.8869	0.8869		0.9183	0.9183	
	H3,H4				0.8630	0.8630	
2	C1	6.0180	5.1204	0.8976	5.9620	5.2135	0.7485
	C6				6.0781	5.0387	1.0395
	C2,C5	6.1277	5.2151	0.9126	6.1694	5.1165	1.0529
	C7,C10				6.0772	5.3084	0.7689
	C3,C46	6.1729	5.2843	0.8886	6.1802	5.2792	0.9010
	C8,C9				6.1668	5.2836	0.8832
	H1,H4	0.7253	0.7253		0.7538	0.7538	
	H5,H8				0.6999	0.6999	
	H2,H3	0.7151	0.7151		0.7322	0.7322	
	H6,H7				0.7004	0.7004	
3	C1	6.0093	4.9762	1.0331	5.8677	5.0105	0.8572
	C8				6.1797	4.8613	1.3184
	C2,C7	6.2216	5.1647	1.0569	6.3198	5.1169	1.2029
	C9,C14				6.1373	5.2086	0.9287
	C3,C6	6.2098	5.1392	1.0706	6.1603	5.1587	1.0016
	C10,C13				6.2526	5.1136	1.1390
	C4,C5	6.2196	5.1137	1.1059	6.2224	5.1063	1.1161
	C11,C12				6.1821	5.1582	1.0239
	H1,H6	0.8425	0.8425		0.8629	0.8629	
	H7,H12				0.8405	0.8405	
	H2,H5	0.8765	0.8765		0.8785	0.8785	
	H8,H11				0.8755	0.8755	
	H3,H4	0.8754	0.8754		0.8802	0.8802	
	H9,H10				0.8642	0.8642	

optimizations.[35] Reference to Table 4 shows clearly that in the D_{2h} structure the unpaired spin density is delocalized in both the rings, but in the C_{2v} structure it is localized essentially in the ring with the larger negative charge.

As for the radical **2**, a comparison of the optimized geometrical parameters between the D_{2h} and C_{2v} structures reveals that in the latter a bond-length alternation is enhanced in one of the rings, but it is relaxed largely in the other ring. The stabilization energy due to the pseudo-JT distortion is calculated to be 8.7 kcal/mol. Inspection of the atomic populations reveals that all the hydrogen atoms are charged positively in both the structures: The magnitude of the positive charges is much larger in the radical **2** than in the radical **1**. It may be said that in spite of being the π-radical system, an electron is removed mostly from the hydrogen atoms when the cation radical **2** is produced from the parent pentafulvalene molecule. It is noted that the larger positive charge (+0.63 e) is located on the ring with the marked double-bond fixation. Taking the atomic

TABLE 3: Total and Partitioned Energies and Their Energy Differences between the Symmetric and Distorted Structures of the Ion Radicals[a]

molecule	component	symmetric (D_{2h})	distorted (C_{2v})	difference[b]
1	E_{total}	−229.196579	−229.218813	−0.022234
	E^{N}	174.416448	173.994285	−0.422163
	$E^{\mathrm{T}}{}_{\sigma}$	221.582262	221.529025	−0.053237
	$E^{\mathrm{V}}{}_{\sigma}$	−803.824916	−802.954929	+0.869987
	$E^{\mathrm{J}}{}_{\sigma}$	219.361107	218.970944	−0.390163
	$E^{\mathrm{T}}{}_{\pi}$	7.566687	7.629458	+0.062771
	$E^{\mathrm{V}}{}_{\pi}$	−87.918348	−87.981237	−0.062889
	$E^{\mathrm{J}}{}_{\pi}$	39.620180	39.593641	−0.026539
2	E_{total}	−383.116981	−383.130817	−0.013836
	E^{N}	443.384074	442.818262	−0.565812
	$E^{\mathrm{T}}{}_{\sigma}$	373.293359	373.264548	−0.028811
	$E^{\mathrm{V}}{}_{\sigma}$	−1613.804990	−1612.743417	+1.061573
	$E^{\mathrm{J}}{}_{\sigma}$	488.267850	487.775381	−0.492469
	$E^{\mathrm{T}}{}_{\pi}$	9.507483	9.548264	+0.040781
	$E^{\mathrm{V}}{}_{\pi}$	−152.551438	−152.535989	+0.015449
	$E^{\mathrm{J}}{}_{\pi}$	68.786680	68.742137	−0.044543
3	E_{total}	−537.058106	−537.074079	−0.015973
	E^{N}	757.927947	755.763432	−2.164515
	$E^{\mathrm{T}}{}_{\sigma}$	521.500201	521.357273	−0.142928
	$E^{\mathrm{V}}{}_{\sigma}$	−2489.177668	−2485.009944	+4.167724
	$E^{\mathrm{J}}{}_{\sigma}$	821.871456	811.035600	−1.835856
	$E^{\mathrm{T}}{}_{\pi}$	15.218714	15.361492	+0.142778
	$E^{\mathrm{V}}{}_{\pi}$	−292.114376	−292.330740	−0.216364
	$E^{\mathrm{J}}{}_{\pi}$	136.715627	136.748809	+0.033182

[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.

TABLE 4: Unpaired Spin Densities on Carbon Atoms of the Ion Radicals at the Symmetric and Distorted Structures

molecule	atom	symmetric (D_{2h}) spin density	distorted (C_{2v}) spin density
1	C1	0.0016	0.0043
	C4		0.0000
	C2,C3	0.2492	0.4977
	C5,C6		0.0001
2	C1	0.0024	0.0000
	C6		0.0045
	C2,C5	0.1795	0.0002
	C7,C10		0.3768
	C3,C4	0.0693	0.0003
	C8,C9		0.1204
3	C1	0.0019	0.0053
	C8		0.0001
	C2,C7	0.1163	0.2673
	C9,C14		0.0012
	C3,C6	0.0297	0.0453
	C10,C13		0.0009
	C4,C5	0.1031	0.1824
	C11,C12		0.0002

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 σ and π electrons. Table 4 shows that the pseudo-JT distortion gives rise to a localization of the unpaired spin density on the ring with the larger positive charge.

For the radical **3**, the optimized D_{2h} structure shows that there exists a moderate double-bond fixation in the seven-membered rings. On the other hand, the optimized C_{2v} structure indicates that a marked double-bond fixation occurs in one of the rings, while the lengths of the CC bonds are considerably equalized in the other ring. Noticeable is the fact that the central cross bond assumes a length of ca. 1.42 Å, which is the most lengthened among the radicals examined. Relative to the D_{2h} structure, a lengthening of the CC bond amounts to ca. 0.03 Å. It may be inferred that this lengthening is largely responsible for the steric repulsion arising from the two pairs of the neighboring hydrogen atoms across the cross bond.[31b] This is because in this radical the nonbonded atomic distance between H1 and H7 is 1.704 Å in the D_{2h} structure while in the radicals **1** and **2** the associated atomic distances are 4.975 and 2.467 Å, respectively. The stabilization energy which favors the distorted C_{2v} structure is calculated to be 10.0 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 σ and π electrons. A larger negative charge is located on the ring with the nearly equal CC bonds in length, showing a contraction of the π-electron cloud on the ring. Concomitantly, it is also observed that the unpaired spin density is localized essentially on the ring with the larger negative charge within the ROHF MO method used here. It should be emphasized that the spin-density distribution thus obtained is indeed in good agreement with the available experimental facts[16] as well as the theoretical results obtained within the semiempirical π-electron approximation.[34]

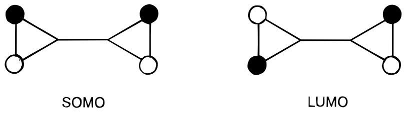

Figure 2. Representation of the Hückel SOMO (b_{1g}) and LUMO (a_u) for the radical **1** at the D_{2h} structure. White and black circles indicate respectively the plus and minus signs of atomic-orbital coefficients, and the values on the atoms C1 and C4 are zero by symmetry.

An explanation about how such a localization in the unpaired spin density (Table 4) should occur in one of the rings at the C_{2v} structure can be given qualitatively from a perturbational MO approach as follows: At the unperturbed D_{2h} nuclear arrangement, the lowest excited doublet state, which is nearly degenerate with the ground state, is represented virtually by one-electron excitation: The excitation corresponds to orbital jump from the singly occupied MO (SOMO) to the LUMO for the radicals **1** and **3** and from the highest doubly occupied MO to the SOMO for the radical **2**. Thus, the vibronic interaction between the ground and lowest excited doublet states through the b_{1u} nuclear deformation Q_{i} can be reduced to the interaction between the SOMO (b_{1g}) and the LUMO (a_u) for the former and between the highest doubly occupied MO (a_u) and the SOMO (b_{1g}) for the latter through the one-electron operator $\partial V/\partial Q_i$, where V represents the operator of nuclear−electron potential energy. After the nuclear deformation Q_{i}, the perturbed SOMO of interest is expressed as a linear combination of the unperturbed SOMO and LUMO for the former and of the unperturbed SOMO and HOMO for the latter. In Figure 2 we represent a distribution of the π atomic orbital coefficients in the unperturbed SOMO and LUMO within the HMO approximation, taking the radical **1** as an example. Their values are just the same in absolute values for the two orbitals. Accordingly, the mixing in of the LUMO into the SOMO leads to the result that the perturbed SOMO is almost confined only to the carbon atoms belonging to one of the rings. This means that in the other ring the atomic-orbital coefficients of the carbon atoms becomes negligibly small, indicating a localization of the perturbed SOMO. With regard to the distribution of the atomic-orbital coefficients in the two orbitals of interest, a quite similar situation can also be observed for the radicals **2** and **3**. As a consequence, it follows that the localization in unpaired spin density takes place in the C_{2v} structure of the radicals.[36]

On the basis of these results, we now discuss the leading factors responsible for the stability of less symmetric nuclear configuration in the radicals **1**−**3**.

Energy Component Analysis of the Total Energy in the Ground State. *(a) The Radical **1**.* An analysis with regard to the CC and CH bonds in length between the D_{2h} and C_{2v} structures (Table 1) reveals that in addition to the b_{1u} nuclear deformation of interest, the totally symmetric nuclear deformation is operative to some extent. That is, the molecular skeleton changes its form such that C1−C4 is lengthened by 0.001 Å, C1−C2 is lengthened by 0.008 Å, C2−C3 is shortened by 0.001 Å, and C2−H1 is lengthened by 0.001 Å. At the same time, the b_{1u} nuclear deformation is operative such that C1−C2 is lengthened by 0.026 Å, C2−C3 is shortened by 0.051 Å, and C2−H1 is lengthened by 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. Of course, a displacement vector of the cross bond is zero by symmetry in the b_{1u} nuclear deformation. It is noteworthy that when the radical **1** settles at the C_{2v} equilibrium structure the two stretching modes of a_g and b_{1u} symmetry take part. Since the CC and CH bonds are lengthened in a totally symmetric fashion, the repulsive terms E^N, $E^J{}_\sigma$, and $E^J{}_\pi$ should be lowered in energy. As is listed in Table 3, this is actually true for the three terms. In marked contrast, the expansion of molecular skeleton should generally lead to the energy raising of the nuclear−electron attractive terms. This is because a lengthening of the CC and CH bonds brings about an expansion of the σ-electron and π-electron clouds. As mentioned in the preceding section, however, a contraction of the π-electron cloud takes place 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.[20,21] This suggests that the energy change of interest should depend on a competition between the contributions arising from the two opposing factors. That the term $E^V{}_\pi$ is indeed lowered in energy can thus be attributable to the fact that the contribution from the contraction of π-electron cloud is larger than that from the expansion of molecular skeleton. The energy changes of the kinetic terms due to σ and π electrons are small, the absolute values being almost equal. As a consequence, it can be concluded for the radical **1** that the stability of C_{2v} structure should arise from the energy lowerings of the terms E^N, $E^J{}_\sigma$, $E^V{}_\pi$, $E^T{}_\sigma$, and $E^J{}_\pi$, 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.

*(b) The Radical **2**.* It is found that the present pseudo-JT distortion from D_{2h} to C_{2v} is accompanied by a totally symmetric expansion of the molecular 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 D_{2h} structure: C1−C6 (+0.011 Å), C1−C2 (+0.009 Å), C2−C3 (−0.002 Å), C3−C4 (+0.003 Å), C2−H1 (+0.000_4 Å), and C3−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 (+0.016 Å), C2−C3 (−0.032 Å), C3−C4 (+0.052 Å), C2−H1 (−0.000_4 Å), and C3−H2 (−0.000_1 Å). It is thus expected that an expansion of the carbon skeleton should be reflected in a decrease in the internuclear and interelectronic repulsion energies. Actually, Table 3 shows clearly that all the repulsive terms E^N, $E^J{}_\sigma$, and $E^J{}_\pi$ are 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 terms $E^V{}_\sigma$ and $E^V{}_\pi$. In the present case, however, it seems that a contraction of the π-electron cloud does not contribute to the energy lowering of the term $E^V{}_\pi$. This is probably due to the fact that in the C_{2v} structure the large π-electron densities reside on the atoms forming no CC bond and, accordingly, no strong attractive interactions should occur between the π electrons and nuclei. This feature may be pointed out as being a sharp distinction between the radicals **1** and **2**. As to the kinetic terms due to σ and π electrons, the energy changes are small, the absolute values being almost equal. As a consequence, it can be said for the radical **2** that the preference for the C_{2v} structure should originate from the energy lowering of the terms E^N, $E^J{}_\sigma$, $E^J{}_\pi$, and $E^T{}_\sigma$. The other energy terms contribute to the direction opposite to the stability of distorted structure.

*(c) The Radical **3**.* Relative to the D_{2h} structure, most parts of the molecular skeleton in the C_{2v} structure are expanded in a totally symmetric fashion, and the associated changes in bond length are given as follows: C1−C8 (+0.028 Å), C1−C2 (−0.008 Å), C2−C3 (+0.006 Å), C3−C4 (−0.004 Å), C4−C5 (+0.016 Å), C2−H1 (+0.002 Å), C3−H2 (+0.000_2 Å), and C4−H3 (+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 (−0.012 Å), C2−C3 (+0.024 Å), C3−C4 (−0.046 Å), C4−C5 (+0.049 Å), C2−H1 (−0.001 Å), C3−H2 (+0.001 Å), and C4−H3 (−0.000_4 Å). Since the carbon skeleton is stretched in a totally symmetric fashion, the repulsive interactions are expected to be reduced in the C_{2v} structure. Table 3 shows that the two repulsive terms E^N and $E^J{}_\sigma$ are actually lowered in energy, but another repulsive term $E^J{}_\pi$ is raised in energy. On the contrary, the expansion of molecular skeleton should lead to an energy raising of the nuclear−electron attractive terms. This is true for the attractive term $E^V{}_\sigma$, but another attractive term $E^V{}_\pi$ is indeed lowered in energy. This behavior in energy may be ascribed to the fact that a contraction of the π-electron cloud takes place on the atoms forming the C4−C5 bond. Concomitantly, the energy raising of repulsive term $E^J{}_\pi$ can be attributable to the contribution arising from the contraction of π-electron cloud, instead of the one arising from the expansion of carbon skeleton. It is remarked that the energy changes of the kinetic terms due to σ and π electrons are rather large, the former being lowered and the latter being raised in energy. As a result, it can be concluded for the radical **3** that the energetic stability of the C_{2v} structure should result from the energy lowering of the terms E^N, $E^J{}_\sigma$, $E^T{}_\sigma$, and $E^V{}_\pi$. The large contributions come from the former two terms, in order of importance.

Conclusion

Characteristic electronic features inherent in the present radicals are that as a result of the pseudo-JT effect, a charge alternation in π electrons appears at the C_{2v} nuclear configuration and, concomitantly, a localization of the unpaired spin density takes place essentially on one of the rings. It is further revealed that when the present radicals undergo the pseudo-JT distortion, an expansion of the carbon skeleton takes place in a totally symmetric fashion, in addition to the b_{1u} nuclear deformation. Hence, it is revealed that a reduction of the internuclear repulsion energy and the interelectronic repulsion energy due to σ electrons contributes commonly to the stability of the C_{2v} structure. Concurrently, in the radicals **1** and **3** the nuclear−electron attraction energy of π electrons plays a role in the stability of the C_{2v} structure. This is ascribed to the behavior that the π-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 can thus be confirmed that an expansion of the carbon skeleton and a charge polarization play dominant roles in the stability of a less symmetric structure. It is thus apparent that the energy component analysis is informative to elucidate what happens inside the molecule when it is subject to the pseudo-JT distortion. In conclusion, the present pseudo-JT stabilization can be said to arise mostly from the combined effects due to a structural change and a redistribution of the electron density through electrostatic interactions.

In connection with this work, it would be pertinent to refer to the results for the methane and borane radical cations by Boyd et al.[37,38] In both the cations, the first-order JT effect is found to lead to a contraction of the molecular framework. It seems that no essential difference should exist between the first-order JT and pseudo-JT effects at least in the sense that the former deals with the geometric instability of degenerate electronic states and the latter merely with that of nearly degenerate electronic states. From this point of view, it is worthy to note that the results for the methane and borane radical cations differ markedly from those for the present ion radicals in structural changes of the molecular framework.

Further, it should be mentioned for the radical **3** that the nonbonded atomic distance between H1 and H7 is 1.740 Å even in the distorted C_{2v} structure. Clearly, the atomic distance is still shorter than the sum of their van der Waals radii, ca. 2.0−2.4 Å.[39−41] For the ground state of the parent heptafulvalene molecule, Scott et al.[31b] have recently shown theoretically that the relevant atomic distance is 1.724 Å at the conventional D_{2h} nuclear arrangement and, as a result, the ground-state nuclear arrangement undergoes a pseudo-JT distortion from the planar D_{2h} to the nonplanar C_{2h} structure. With reference to their results, there is every reason to believe that the radical **3** should further undergo a pseudo-JT distortion from the planar C_{2v} to a nonplanar C_s structure. In this context, we are now much interested in the subject of nonplanarity especially in conjugated molecules,[42] and the results will be reported in detail in the near future together with the result for the radical **3**.

Finally, we must note that it is much desirable to use more flexible basis set than 6-31G(d) basis set for properly representing electronic structures of the present ion radicals. In this study, however, since the differences of total energy and its components between the symmetric and less symmetric structures are mainly considered, we conjecture that the likely correlation effects on the energy terms at the different structures should be virtually canceled when estimating the relevant energy differences.[37,38,43] We thus hope that the essence of the present basis conclusions would remain almost the same even if more flexible basis sets larger than 6-31G(d) basis set are used in the MCSCF calculations for the ion radicals **1**−**3**.

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