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Energy Component Analysis of the Pseudo-Jahn−Teller Effect in the Ground and Electronically Excited States of the Cyclic Conjugated Hydrocarbons: Cyclobutadiene, Benzene, and Cyclooctatetraene

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To elucidate the nature of the pseudo-Jahn−Teller (JT) effect, an energy component analysis has been carried out for the ground and electronically excited states of the titled cyclic polyenes by using the MCSCF method with 6-31G(d) basis set. Examination of the energy components comprised in the total energy reveals that in the ground state of planar cyclobutadiene and cyclooctatetraene molecules, the stability of a bond-alternated structure is largely attributable to a decrease in the internuclear repulsion energy and the interelectronic repulsion energy due to σ electrons. These observations are consistent with a totally symmetric expansion of the carbon skeleton brought about by the pseudo-JT distortion. Concomitantly, a contraction of the π electron cloud takes place by polarization of the bond charges, and the nuclear−electron attraction energy of π electrons also plays an important role in the pseudo-JT stabilization. Further, the stability of a nonplanar tub structure in cyclooctatetraene results from a lowering of the nuclear−electron attraction energy. In the excited states examined, the situation differs from molecule to molecule. In the lowest excited singlet state of cyclobutadiene, the stability of a rhombic structure originates from the energy lowerings of the nuclear−electron attractive term of σ electrons and the kinetic term of π electrons. While in the lowest excited triplet state of benzene, the stability of a quinoid structure arises from the energy lowerings of the internuclear repulsive term, the interelectronic repulsive term of σ electrons, and the nuclear−electron attractive term of π electrons.

Introduction

The Jahn−Teller (JT) effect is the stabilization that arises from the geometric instability of degenerate electronic states in nonlinear polyatomic molecules.[1−4] Boyd et al.[5,6] have made an energy component analysis of the total energy to elucidate the physical picture of the JT effect in the radical cations of CH_4 and BH_3. In this connection, the pseudo-JT effect is the stabilization which occurs when a certain asymmetric distortion mixes two electronic states which are nearly degenerate in the symmetric nuclear configuration of the ground state or of an electronically excited state.[2] To gain insight into the nature of the pseudo-JT effect, we have carried out the energy component analysis for the typical nonalternant hydrocarbons considered as weakly perturbed cyclic polyenes by using the ab initio RHF method with 6-31G(d) basis set.[7] A characteristic feature inherent in the pentalenoid and heptalenoid systems is that a charge alternation in π electrons appears at the symmetric nuclear configuration. The pseudo-JT effect gives rise to two types of π charge relaxation in the less symmetric nuclear configuration, one corresponding to a contraction of the electron cloud and the other to an expansion of the electron cloud relative to the distribution of π electrons in the symmetric nuclear configuration. The energy component analysis reveals that the pseudo-JT effect in the molecules leads commonly to a decrease in the internuclear repulsion energy and the interelectronic repulsion energy due to σ electrons. Of special interest is the finding that another energy component exists which plays a significant role in the pseudo-JT stabilization. For the typical instances, the stability of a skew C_{2h} structure for pentalene arises from a decrease in the interelectronic repulsion energy due to π electrons, while that for heptalene results from a lowering of the nuclear−electron attraction energy due to π electrons. This marked difference between the two systems has been accounted for in terms of an electrostatic interaction combined with a charge relaxation attributed to migration of π electrons.

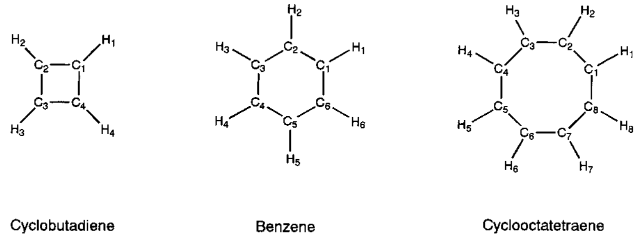

Figure 1. Cyclic conjugated hydrocarbons and numbering of atoms.

In connection with the above work, of fundamental interest are the conjugated molecules that exhibit virtually no charge polarization in π electrons at the ground state of the symmetric nuclear configuration. This is because the charge distribution seems to be profoundly related to the mechanism of the pseudo-JT distortion.[7,8] In this paper, we thus carry out the energy component analysis of the pseudo-JT effect in the lower three members of cyclic polyenes (Figure 1) by means of the ab initio MO method with 6-31G(d) basis set.[9−13] The electronic states under consideration are the ground and lowest excited singlet states for cyclobutadiene, the lowest excited triplet state for benzene, and the ground state for cyclooctatetraene. It will be shown that the variations of individual energy components on structural changes are explained qualitatively in terms of an

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TABLE 1: Optimized Geometrical Parameters in the Ground and Electronically Excited States of the Cyclic Polyenes Examined

molecule structure	geometrical parameters[a]
	(i) Ground State
cyclobutadiene	
D_{4h} ($^1B_{1g}$)	C1−C2 = 1.4434, C1−H1 = 1.0705, H1−C1−C2 = 135.0
D_{2h} ($^1A_{1g}$)[b]	C1−C2 = 1.5461, C1−C4 = 1.3530, C1−H1 = 1.0715, C2−H2 = 1.0715, H1−C1−C2 = 134.7
cyclooctatetraene	
D_{8h} ($^1B_{1g}$)	C1−C2 = 1.4084, C1−H1 = 1.0768, H1−C1−C2 = 135.0
D_{4h} ($^1A_{1g}$)	C1−C2 = 1.4720, C1−C8 = 1.3514, C1−H1 = 1.0771, C1−C2−C3 = 135.0, C8−C1−C2 = 135.0, H1−C1−C2 = 111.4, C1−C2−H2 = 111.4
D_{2d} ($^1A_1$)[c]	C1−C2 = 1.4795, C1−C8 = 1.3438, C1−H1 = 1.0786, C1−C2−C3 = 127.0, C8−C1−C2 = 127.0, H1−C1−C2 = 115.2, C8−C1−C2−C3 = 55.2, C1−C2−C3−C4 = 0.0, H1−C1−C2−H2 = 47.7, H2−C2−C3−H3 = 0.0
	(ii) Excited State
cyclobutadiene	
D_{4h} ($^1A_{1g}$)	C1−C2 = 1.4464, C1−H1 = 1.0699, H1−C1−C2 = 135.0
D_{2h} ($^1A_{1g}$)[d]	C1−C2 = 1.4364, C1−H1 = 1.0640, C2−H2 = 1.0782, C1−C2−C3 = 84.8, C2−C3−C4 = 95.2, H1−C1−C2 = 137.6, C1−C2−H2 = 132.4
benzene	
D_{6h} ($^3B_{1u}$)	C1−C2 = 1.4303, C1−H1 = 1.0736
D_{2h} ($^3B_{2u}$)[e]	C1−C2 = 1.4679, C1−C6 = 1.3610, C1−H1 = 1.0748, C2−H2 = 1.0719, C1−C2−C3 = 119.0, C6−C1−C2 = 120.5, C1−C2−H2 = 120.5, C2−C1−H1 = 118.8
D_{2h} ($^3B_{2u}$)[f]	C1−C2 = 1.3981, C1−C6 = 1.4989, C1−H1 = 1.0729, C2−H2 = 1.0756, C1−C2−C3 = 120.9, C6−C1−C2 = 119.5, C1−C2−H2 = 119.5, C2−C1−H1 = 121.0

[a] Numbering of atoms is shown in Figure 1. Bond lengths and bond and dihedral angles are in angstroms and degrees. [b] The rectangular structure. [c] The tub structure. [d] The rhombic structure. [e] The quinoid structure. [f] The antiquinoid structure.

expansion or contraction of the carbon skeleton, a contraction of the π electron cloud, and an electrostatic interaction. Moreover, the present analysis reveals clearly what are the dominant factors that contribute to the energetic stability of a less symmetric nuclear configuration. It is remarked that the structural and concomitant properties for such states of the above molecules have been studied extensively from both experimental[14−21] and theoretical[22−48] viewpoints.

Methods of Calculation

Since low-lying electronic states of the present molecules exhibit a situation of open-shell structure at the symmetric nuclear configuration, the traditional restricted Hartree−Fock method is not adequate to describe such electronic states properly. We thus employ here full-optimized reaction space (FORS) multiconfiguration self-consistent field (MCSCF) method with 6-31G(d) basis set.[9−13] It is noted that in our calculations the MCSCF active space includes all inner valence π orbitals and all π electrons for the molecules examined.

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.[49] 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:

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

It is remarked that the $E^J{}_\sigma$ term should comprise two interaction energies arising from between pure σ electrons and between σ and π electrons and the $E^J{}_\pi$ term the energies arising from between pure π electrons and between π and σ electrons. All calculations are carried out by means of the quantum chemistry code GAMESS[9] to which new subroutines for the energy component analysis are added.

Results and Discussion

Atomic and Bond Populations. Table 1 presents the fully optimized geometrical parameters for the symmetric and less symmetric nuclear configurations of the cyclic polyenes examined. Atomic and bond populations are obtained at the symmetric and less symmetric nuclear configurations by means of Mulliken's population analysis,[50] which are summarized in Table 2 together with σ- and π-electron components. For the ground state of cyclobutadiene, π atomic charges on the C atoms are unity in both the square D_{4h} and rectangular D_{2h} structures. However, the pseudo-JT effect brings about a significant increase and decrease in the π-bond populations for the CC double and single bonds, respectively. Taking the π-bond populations in the D_{4h} structure as reference values, it is found that the distribution of π electrons in the D_{2h} structure exhibits an appearance of the so-called bond charge alternation along the CC molecular periphery. A similar phenomenon is also observed in the planar bond-alternated D_{4h} structure of cyclooctatetraene. For the electronically excited states of cyclobutadiene and benzene, π atomic charges on the C atoms are unity in the symmetric nuclear configuration. However, in the rhombic D_{2h} structure of cyclobutadiene, a marked atomic charge alternation is observed along the molecular periphery. In the quinoid D_{2h} structure of benzene, a polarization of the π bond charges is observed.

An occurrence of such charge polarizations will be accounted for by invoking the second-order perturbation theory by Bader[51] as follows. Assuming the drastic approximation that the electronic state of question interacts only with the nearest neighbor excited state in the pseudo-JT distortion, it is readily seen that the change of the electron density after a nuclear deformation is proportional to the transition density between the relevant two states.[51−55] In the electronically excited cyclobutadiene molecule, for instance, the transition density

TABLE 2: Atomic and Bond Populations in the Ground and Electronically Excited States of the Cyclic Polyenes Examined

molecule	symmetric structure			distorted structure			
position	total	σ	π	total	σ	π	
				(i) Ground State			
cyclobutadiene							
		D_{4h}			D_{2h}		
C1	6.2031	5.2031	1.0000	6.2008	5.2008	1.0000	
C1−C2	0.9304	0.7928	0.1376	0.7076	0.8150	−0.1074	
C2−C3				1.2318	0.7720	0.4598	
C1−C3	−0.4196	−0.3360	−0.0836	−0.3980	−0.3308	−0.0672	
cyclooctatetraene							
		D_{8h}			D_{4h}		D_{2d}[a]
C1	6.1815	5.1815	1.0000	6.1804	5.1804	1.0000	6.1822
C1−C2	0.9770	0.7736	0.2034	0.7530	0.7388	0.1342	0.7654
C2−C3				1.2358	0.8122	0.4236	1.2542
				(ii) Excited State			
cyclobutadiene							
		D_{4h}			D_{2h}		
C1	6.2092	5.2092	1.0000	6.3849	5.0213	1.3636	
C2				6.0284	5.3919	0.6365	
C1−C2	0.8900	0.7888	0.1012	0.9204	0.7792	0.1412	
C1−C3	−0.4266	−0.3390	−0.0874	−0.4836	−0.2572	−0.2264	
C2−C4				−0.3780	−0.4588	0.0808	
benzene							
		D_{6h}			D_{2h}		
C1	6.1968	5.1968	1.0000	6.1858 (6.2055)[b]	5.1832 (5.2078)	1.0025 (0.9978)	
C2	6.1968	5.1968	1.0000	6.2168 (6.1779)	5.2218 (5.1734)	0.9950 (1.0045)	
C1−C2	0.8932	0.7840	0.1092	0.7600 (1.0252)	0.7712 (0.7945)	−0.0112 (0.2307)	
C1−C6	0.8932	0.7840	0.1092	1.2036 (0.6674)	0.8106 (0.7642)	0.3930 (−0.0968)	

[a] Values refer to the total atomic and bond populations. [b] Values in parentheses refer to those for the antiquinoid structure.

between the lowest excited singlet state ($^1A_{1g}$) and the second excited singlet state ($^1B_{2g}$) in the D_{4h} structure is given by $(\phi_2)^2-(\phi_3)^2$ in terms of relevant MOs. Here ϕ_2 and ϕ_3 represent a pair of degenerate nonbonding MOs, the former being confined to the C1 and C3 atoms and the latter to the C2 and C4 atoms.[32] Inspection of the transition density suggests that relative to the square D_{4h} structure, π charge densities in the rhombic D_{2h} structure should increase on the C_1 and C_3 atoms while those decrease on the C_2 and C_4 atoms. Also in other cases, a direction of such π charge polarizations on structural changes can be accounted for from the above perturbational consideration.

Total and Partitioned Energies. In Table 3 are listed the total and partitioned energies at the symmetric and less symmetric nuclear configurations for the molecules examined. It is seen that the difference in total energy between the two configurations of the molecule is smaller in comparison with the changes of each energy component comprised in the total energy. For the ground state of cyclobutadiene, the stabilization energy associated with the pseudo-JT effect, i.e., the activation energy of the isodynamical π-bond shift occurring in the interconversion between the two equivalent rectangular structures is calculated to be 6.3 kcal/mol within the MCSCF method including four π orbitals as the active space. For the ground state of cyclooctatetraene, the stabilization energies due to the pseudo-JT effect from D_{8h} to D_{4h} and from D_{4h} to D_{2d} are calculated to be 6.3 and 10.4 kcal/mol, respectively. For the electronically excited molecules, the energy lowering due to the pseudo-JT effect is in the range of ca. 2−5 kcal/mol. A closer inspection of Table 3 reveals that the individual energy components vary largely in energy, indicating that the above stabilization energy is in competition between the two contributions, one arising from energy components which favor the symmetric structure and the other from the ones which favor the less symmetric structure. In other words, the energy terms are highly sensitive to changes in molecular geometry and have mutually opposite signs to the pseudo-JT stabilization. On the basis of these results, we now discuss the dominant energy components responsible for the pseudo-JT effect in the ground and electronically excited states of the cyclic polyenes.[56]

Energy Component Analysis of the Ground States. *(a) Cyclobutadiene.* This molecule undergoes the pseudo-JT distortion from the square D_{4h} to the rectangular D_{2h} structure,[2,3,22−41] and thereby the alternate bond-length changes due to the b_{1g} nuclear deformation amount to 0.097 Å in absolute value along the CC molecular periphery (Table 1). At the same time, all the CC and CH bonds are lengthened respectively by 0.006 and 0.001 Å in a totally symmetric fashion. This indicates that when cyclobutadiene settles at the D_{2h} equilibrium structure the two CC stretching modes of a_{1g} and b_{1g} symmetry take part in. Since the carbon skeleton as well as the CH bonds is expanded in a totally symmetric fashion, the repulsive terms E^N, E^J_σ, and E^J_π should be lowered in energy. As is listed in Table 3, this is actually true for the former two terms. Contrary to the expectation, however, the other repulsive term E^J_π is raised slightly in energy. This energy change seems to be unusual, but it will be explained qualitatively as follows. As noted in the preceding paragraph (Table 2), a bond charge alternation occurs along the CC molecular periphery in the rectangular D_{2h} structure. This phenomenon is equivalent to saying that the π-electron cloud is contracted to the opposite CC double bonds by polarization of the bond charges. In such a case, it is often observed that the interelectronic repulsive interactions between π electrons are enhanced.[7] Hence, it will be presumed that the small energy raising of the repulsive term E^J_π is a result of the competitive behavior between the above two contributions. Numerically, Table 3 reveals that an increase in the repulsion energy due to contraction of the π-electron cloud is somewhat more than a decrease in the repulsion energy due to expansion of the carbon skeleton. Concomitantly, with a contraction of the π-electron cloud the nuclear−electron attractive term E^V_π should be lowered in energy. Further, since the atomic and bond charges of σ electrons exhibit no essential changes, an expansion of the carbon skeleton should raise the nuclear−

TABLE 3: Total and Partitioned Energies and Their Energy Differences between the Symmetric and Distorted Structures in the Ground and Electronically Excited States[a]

molecule component	symmetric	distorted	difference[b]
(i) Ground State			
cyclobutadiene	D_{4h}	D_{2h}	
E_{total}	−153.699 226	−153.709 278	−0.010 052
E^{N}	99.287 773	99.134 877	−0.152 896
$E^{\mathrm{T}}{}_{\sigma}$	149.158 419	149.184 189	0.025 770
$E^{\mathrm{V}}{}_{\sigma}$	−512.442 456	−512.061 952	0.380 504
$E^{\mathrm{J}}{}_{\sigma}$	130.969 007	130.780 737	−0.188 270
$E^{\mathrm{T}}{}_{\pi}$	4.459 693	4.436 127	−0.021 566
$E^{\mathrm{V}}{}_{\pi}$	−44.162 990	−44.273 115	−0.110 125
$E^{\mathrm{J}}{}_{\pi}$	19.031 328	19.087 845	0.056 517
cyclooctatetraene	D_{8h}	D_{4h}	
E_{total}	−307.609 039	−307.619 145	−0.010 106
E^{N}	316.016 733	315.574 834	−0.441 899
$E^{\mathrm{T}}{}_{\sigma}$	298.844 036	298.843 353	−0.000 683
$E^{\mathrm{V}}{}_{\sigma}$	−1 226.8 79 422	−1 226.0 01 392	0.878 030
$E^{\mathrm{J}}{}_{\sigma}$	362.442 229	362.029 060	−0.413 169
$E^{\mathrm{T}}{}_{\pi}$	8.515 496	8.524 783	0.009 287
$E^{\mathrm{V}}{}_{\pi}$	−121.219 352	−121.269 731	−0.050 379
$E^{\mathrm{J}}{}_{\pi}$	54.671 245	54.679 939	0.008 694
	D_{4h}	D_{2d}	
E_{total}	−307.619 145	−307.635 686	−0.016 541
E^{N}	315.574 834	323.351 614	7.776 780
E^{T}	307.368 136	307.382 783	0.014 647
E^{V}	−1 347.2 71 123	−1 363.100 163	−15.829 040
E^{J}	416.708 999	424.730 081	8.021 082
(ii) Excited State			
cyclobutadiene	D_{4h}	D_{2h}	
E_{total}	−153.613 593	−153.622 689	−0.009 096
E^{N}	99.129 847	99.741 068	0.611 221
$E^{\mathrm{T}}{}_{\sigma}$	149.207 903	149.332 182	0.124 279
$E^{\mathrm{V}}{}_{\sigma}$	−512.358 560	−513.542 286	−1.183 681
$E^{\mathrm{J}}{}_{\sigma}$	130.832 039	131.321 996	0.489 957
$E^{\mathrm{T}}{}_{\pi}$	4.343 162	4.231 981	−0.111 181
$E^{\mathrm{V}}{}_{\pi}$	−43.690 095	−43.686 757	0.003 338
$E^{\mathrm{J}}{}_{\pi}$	18.922 153	18.979 128	0.056 975
benzene	D_{6h}	D_{2h}	
E_{total}	230.640 822	−230.644 747 (−230.643 768)[c]	−0.003 925 (−0.002 946)
E^{N}	199.494 214	199.360 269 (199.414 840)	−0.133 945 (−0.079 374)
$E^{\mathrm{T}}{}_{\sigma}$	223.854 040	223.862 275 (223.866 079)	0.008 235 (0.012 039)
$E^{\mathrm{V}}{}_{\sigma}$	855.711 496	−855.431 044 (−855.542 400)	0.280 452 (0.169 096)
$E^{\mathrm{J}}{}_{\sigma}$	239.842 148	239.707 470 (239.757 135)	−0.134 678 (−0.085 013)
$E^{\mathrm{T}}{}_{\pi}$	6.611 627	6.608 028 (6.603 534)	−0.003 599 (−0.008 093)
$E^{\mathrm{V}}{}_{\pi}$	−80.413 427	−80.447 546 (−80.437 811)	−0.034 119 (−0.024 384)
$E^{\mathrm{J}}{}_{\pi}$	35.682 073	35.695 806 (35.694 855)	0.013 733 (0.012 782)

[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] Values in parentheses refer to those for the antiquinoid structure.

electron attraction energy of σ electrons. This is because a lengthening of the CC bonds corresponds to an expansion of the σ-electron cloud. In addition, the energy changes of the kinetic components $E^{\mathrm{T}}{}_{\sigma}$ and $E^{\mathrm{T}}{}_{\pi}$ are quite small in comparison with those of the other energy terms. As a consequence, it is concluded for cyclobutadiene that the stability of the rectangular D_{2h} structure should benefit from the energy lowerings of the terms E^{N}, $E^{\mathrm{J}}{}_{\sigma}$, $E^{\mathrm{T}}{}_{\pi}$, and $E^{\mathrm{V}}{}_{\pi}$, and all the other energy components change in the opposite direction. The dominant energy components to the stability come from the three terms, $E^{\mathrm{J}}{}_{\sigma}$, E^{N}, and $E^{\mathrm{V}}{}_{\pi}$, in order of importance.

(b) Cyclooctatetraene. Upon the pseudo-JT distortion from the planar D_{8h} to the planar D_{4h} structure,[2,22,32,47,48] the alternate bond-length changes due to the b_{1g} nuclear deformation amount to 0.061 Å in absolute value along the CC molecular periphery (Table 1). At the same time, all the CC bonds are lengthened by 0.004 Å in a totally symmetric fashion. Hence, an expansion of the carbon skeleton should be reflected in a decrease in the internuclear and interelectronic repulsion energies. Table 3 shows clearly that the two repulsive terms E^{N} and $E^{\mathrm{J}}{}_{\sigma}$ are actually lowered while the other repulsive term $E^{\mathrm{J}}{}_{\pi}$ is slightly raised in energy. The present energy changes are just the same as those observed in cyclobutadiene. But an increase in the repulsion energy $E^{\mathrm{J}}{}_{\pi}$ is less for cyclooctatetraene by one-seventh of that observed for cyclobutadiene. This will be ascribed to the fact that the change in bond charge is smaller for cyclooctatetraene in magnitude than for cyclobutadiene (Table 2). The contraction of π-electron cloud to the CC double bonds should lead to a lowering of the nuclear−electron attraction energy $E^{\mathrm{V}}{}_{\pi}$. Actually, the nuclear−electron attractive term $E^{\mathrm{V}}{}_{\pi}$ is lowered in energy, but the magnitude is about one-half of the energy lowering observed in cyclobutadiene. This will also be ascribed to the small change of π-bond charges in cyclooctatetraene. Moreover, since the atomic and bond charges of σ electrons show no appreciable changes, an expansion of the carbon skeleton should raise the nuclear−electron attraction energy of σ electrons. It is therefore concluded for cyclooctatetraene that the preference of the bond-alternated D_{4h} structure arises from the energy lowerings of the repulsive terms E^{N} and $E^{\mathrm{J}}{}_{\sigma}$, the kinetic term $E^{\mathrm{T}}{}_{\sigma}$, and the nuclear−electron attractive term $E^{\mathrm{V}}{}_{\pi}$. The leading terms to the stability come from the three terms E^{N}, $E^{\mathrm{J}}{}_{\sigma}$, and $E^{\mathrm{V}}{}_{\pi}$, in order of importance.

Experimentally, cyclooctatetraene is known to be nonplanar.[20,21] It is usually considered that because of angle strain and steric repulsion between vicinal hydrogen atoms, a planar D_{4h} structure is less stable than a nonplanar tub form. We thus examine the origin for the energetic stability of the nonplanar structure below.

The planar bond-alternated structure of cyclooctatetranene suffers the pseudo-JT distortion from D_{4h} to D_{2d} through the out-of-plane nuclear deformation of b_{1u} symmetry. The energy components for the D_{2d} structure are listed in Table 3. A structural analysis reveals that relative to the D_{4h} structure, the double and single bonds in the D_{2d} structure are respectively shortened and lengthened by 0.008 Å in a totally symmetric fashion. At the same time, the out-of-plane nuclear deformation is operative such that the carbon atoms of the ethylenic groups deviate from the molecular plane by 0.387 Å above or below in an alternating fashion. This indicates that the two nuclear deformations of a_{1g} and b_{1u} symmetry take part in the present pseudo-JT distortion. A comparison of the respective energy components between the two structures reveals that the nuclear−electron attractive term E^V contributes to the energetic stability of the nonplanar structure.[47,57] But the other energy terms contribute more or less to the opposite direction to 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 as to how the two repulsive interactions are enhanced to such extents. In the nonplanar tub structure, most nonbonded atomic distances are shortened relative to those in the planar D_{4h} structure, and hence the internuclear repulsive interactions are enhanced. Concomitantly, since the electrons involved in the CC and CH bonds become spatially close together, the interelectronic repulsive interactions should also be enhanced. As a result, the two repulsive terms E^N and E^J are largely raised in energy. Moreover, 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 the nonplanar D_{2d} structure of cyclooctatetraene owes its energetic stability to the energy lowering of the nuclear−electron attractive term E^V.

Energy Component Analysis of the Electronically Excited States. *(a) Cyclobutadiene.* In the lowest excited singlet state ($^1A_{1g}$), the pseudo-JT distortion from the square D_{4h} to the rhombic D_{2h} structure takes place through the b_{2g} nuclear deformation.[38] Relative to the D_{4h} structure (Table 1), all the CH bonds in the D_{2h} structure are lengthened in a totally symmetric fashion by 0.001 Å. Of special interest is the finding that all the CC bonds are shortened in a totally symmetric fashion by 0.010 Å. At the same time, the changes of bond angles $\angle$C−C−C due to the b_{2g} nuclear deformation amount to about 5.2° in absolute value, i.e., $\angle C_2-C_1-C_4 = 84.8°$ and $\angle C_1-C_2-C_3 = 95.2°$. Besides, the CH bonds are alternatively lengthened and shortened by 0.007 Å. Because the carbon skeleton is contracted symmetrically to such an extent, the repulsive interactions in the D_{2h} structure should be enhanced significantly. Table 3 shows clearly that all the repulsive terms E^N, $E^J{}_\sigma$, and $E^J{}_\pi$ are actually raised in energy. In contrast, the attractive interactions between the nuclei and electrons should be enhanced with a contraction of the carbon skeleton. As is expected, the attractive term $E^V{}_\sigma$ is largely lowered in energy. However, the other attractive term $E^V{}_\pi$ remains almost unchanged in energy. This behavior may probably be ascribed to the fact that the present pseudo-JT distortion gives rise to a large negative two-center π-electron population between the C1 and C3 atoms (Table 2). Obviously, the energetic contribution arising from this π-electron population through the electrostatic interaction is in the opposite direction toward stability. Because of the above two opposing contributions, the nuclear−electron attraction energy E^V should be invariant during the structural changes. Noticeable is the following finding that the changes in kinetic energy due to σ and π electrons are considerably large in comparison with those observed in the ground state of cyclobutadiene. More specifically, the π kinetic energy is lowered and the σ kinetic energy is raised in energy, the absolute value of the energy changes being almost the same. A plausible explanation for such energy changes may be given qualitatively by invoking the free-electron orbital method for an electron in a one-dimensional box of length L.[2,58,59] The b_{2g} nuclear deformation gives rise to such structural changes that relative to the D_{4h} structure, the atomic distance between the C1 and C3 atoms is lengthened by 0.076 Å while that between the C2 and C4 atoms is shortened by 0.109 Å in the D_{2h} structure. Concomitantly, the atomic populations of π electrons are increased on the C1 and C3 atoms by 0.3636 and those of σ electrons are increased on the C2 and C4 atoms by 0.1827 (Table 2). These variations should be reflected in both the energy changes as follows. Since the so-called box length L is increased along the long axis (x) of the rhombic cyclobutadiene molecule, the x component of kinetic energy due to π electrons should be lowered in energy. This energy change may be interpreted as the effect due to a lowering (or release) of the so-called kinetic energy pressure[60−64] of π electrons. On the other hand, the box length L is shortened along the short axis (y) of the molecule, so that the y component of kinetic energy due to σ electrons should be raised in energy. In this case, the energy change may be said to result from a raising of the kinetic energy pressure due to σ electrons. It can be concluded for the lowest excited singlet state of cyclobutadiene that the energetic stability of the rhombic D_{2h} structure results from the lowerings of the nuclear−electron attraction energy of σ electrons and the kinetic energy of π electrons, the other energy terms being in the opposite direction to the stability.

(b) Benzene. In the lowest excited triplet state ($^3B_{1u}$), the pseudo-JT distortion from D_{6h} to D_{2h} occurs through the CC stretching mode of e_{2g} symmetry.[2,42−46] The pair of displacements S_a and S_b given below is the two components of the e_{2g} symmetry coordinate for the CC bond stretching:[2]

$$S_a = 12^{-1/2}(r_{12} - 2r_{23} + r_{34} + r_{45} - 2r_{56} + r_{61})$$

$$S_b = {}^{1}/_{2}(r_{12} - r_{34} + r_{45} - r_{61})$$

Since the S_a nuclear deformation is actually active, two nonequivalent D_{2h} nuclear configurations are obtained in the lowest excited triplet state: one is a quinoid structure and the other an antiquinoid structure (Table 1), the former being lower in energy than the latter by 0.7 kcal/mol.

A simple analysis of the CC and CH bond lengths between the D_{6h} and quinoid D_{2h} structures reveals that a pair of the opposite CC bonds is shortened by 0.071 Å and the remaining four CC ones lengthened by 0.036 Å along the positive direction of S_a nuclear deformation. At the same time, a totally symmetric nuclear deformation is operative such that all the CC bonds are lengthened by 0.002 Å. Since the carbon skeleton is expanded symmetrically, the internuclear and interelectronic repulsive terms should be lowered in energy. As is expected, the internuclear repulsive term and the interelectronic repulsive term of σ electrons are actually lowered in energy. But the interelectronic repulsive term of π electrons is slightly raised in energy. This will be ascribed to the fact that the net change in interelectronic repulsion energy due to π electrons exhibits a competitive behavior between the two contributions arising from the expansion of carbon skeleton and the contraction of π-electron cloud by polarization of the bond charges. Numerically, Table 3 reveals that the latter is slightly more than the former. On the contrary, a contraction of the π-electron cloud should lower the nuclear−electron attraction energy of π electrons. It is noticeable, however, that the nuclear−electron attractive term of σ electrons is definitely raised in energy, reflecting the effect brought about by an expansion of the carbon skeleton. It is concluded for the lowest excited triplet state of benzene that the quinoid D_{2h} structure owes its stability to the energy lowerings of the terms E^{N}, $E^{\mathrm{J}}{}_{\sigma}$, $E^{\mathrm{V}}{}_{\pi}$, and $E^{\mathrm{T}}{}_{\pi}$. The large contributions to the stability come from the former two terms, the contributions from the latter terms being rather small.

For the antiquinoid D_{2h} structure, a quite similar situation is observed. The carbon skeleton is expanded in a totally symmetric fashion such that all the CC bonds are lengthened by 0.002 Å (Table 1). At the same time, a pair of the opposite CC bonds is lengthened by 0.067 Å and the remaining four CC ones shortened by 0.034 Å along the negative direction of S_{a} nuclear deformation. The energy component analysis reveals that the dominant terms to the stability of the antiquinoid structure are identical with those observed for the quinoid structure. It is noted, however, that according to the vibrational analysis by Osamura,[46] the antiquinoid structure has one imaginary frequency and hence corresponds to a transition state for the pseudorotation of the benzene ring.

Conclusions

The present study indicates that the energy component analysis is informative to elucidate what happens inside the molecule when it is subject to the pseudo-JT distortion. In the ground state of cyclobutadiene, it is shown that in addition to the $\mathrm{b}_{1\mathrm{g}}$ nuclear deformation of bond-length alternation type, an expansion of the carbon skeleton takes place in a totally symmetric fashion. Hence, a reduction of the internuclear repulsion energy and the interelectronic repulsion energy due to σ electrons contributes to the stability of the rectangular D_{2h} structure. Concurrently, the nuclear−electron attraction energy of π electrons plays a key role in the stability of the D_{2h} structure. This is ascribed to the behavior that the π-electron cloud is contracted to the opposing CC bonds by polarization of the bond charges. A quite similar situation is observed when cyclooctatetraene suffers the bond distortion from the planar D_{8h} to the planar D_{4h} structure. Subsequently, when the planar D_{4h} structure undergoes the out-of-plane distortion, the resulting nonplanar D_{2d} structure owes its stability to the energy lowering of the nuclear−electron attractive term. This reasoning is given such that relative to the D_{4h} structure, most distances between the nuclei and electrons (or better electron clouds) become close together in the D_{2d} structure and, hence, the nuclear−electron attractive interactions are enhanced. As for the electronically excited state of cyclobutadiene, the situation differs from that in the ground state. The analysis reveals that in addition to the bond angle changes by the $\mathrm{b}_{2\mathrm{g}}$ nuclear deformation, a contraction of the carbon skeleton takes place in a totally symmetric fashion. It thus follows that the energy lowering of the nuclear−electron attractive term of σ electrons contributes to the stability of the rhombic D_{2h} structure. The other contributor to the pseudo-JT stabilization is the kinetic energy term of π electrons. This energy lowering is accounted for in terms of a release of the kinetic energy pressure of π electrons, because the region of π-electron movement is elongated along the long molecular axis. In the case where the lowest excited triplet state of benzene is distorted into the quinoid D_{2h} structure, an expansion of the carbon skeleton and a contraction of the π-electron cloud take place. Accordingly, the dominant contributors to the stability arise from the lowerings of the internuclear repulsion energy, the interelectronic repulsion energy of the σ electrons, and the nuclear−electron attraction energy of π electrons. It is thus confirmed that an expansion or contraction of the carbon skeleton and a charge polarization play a dominant role in the stability of a less symmetric structure. In short, the present pseudo-JT stabilization can be said to stem mostly from the combined effects due to a structural change and a redistribution of the π-electron density through electrostatic interactions.

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