

# Energy Component Analysis of the Pseudo-Jahn–Teller Effect in the Bicyclic Nonalternant Hydrocarbons: The Pentalenoid and Heptalenoid Systems

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To gain insight into the nature of the pseudo-Jahn–Teller (JT) effect, an energy component analysis has been carried out for the bicyclic nonalternant hydrocarbons termed pentalenoid and heptalenoid systems by using the ab initio RHF method with 6-31G(d) basis set. Inspection of the energy component comprised in the total energy reveals that the stability of a less symmetrical nuclear configuration is largely responsible for the decrease in the internuclear repulsion energy and the interelectronic repulsion energy due to  $\sigma$  electrons. These observations are consistent with an expansion of the carbon skeleton brought about by the pseudo-JT distortion. Another energy component also plays an essential role in the pseudo-JT stabilization: For the examples, the preference for the  $C_{2h}$  structure rather than the  $D_{2h}$  one for the pentalene arises from a decrease in the interelectronic repulsion energy due to  $\pi$  electrons, while that for heptalene results from a lowering of the nuclear–electron attraction energy due to  $\pi$  electrons. This sharp distinction between the pentalenoid and heptalenoid systems is accounted for in terms of an electrostatic interaction combined with a charge relaxation attributed to  $\pi$  electrons.

## Introduction

In certain molecules, a nuclear distortion of proper symmetry can mix the ground state and a low-lying electronically excited state and thereby lowers the ground-state energy. Such a distortion is called the pseudo-, or second-order, Jahn–Teller (JT) distortion.<sup>1–4</sup> Pentalene and heptalene (Figure 1), which are considered as the prototypes of the weakly perturbed  $[4n]$ -annulenes, are known to suffer the pseudo-JT distortion both from theoretical<sup>5–16</sup> and experimental<sup>17–25</sup> viewpoints. For instance, taking the pentalene molecule and assuming the symmetrical nuclear arrangement ( $D_{2h}$ ) for the molecule, a semiempirical PPP-type SCF MO CI calculation<sup>26</sup> leads to the prediction that the lowest excited singlet state with  $B_{3g}$  symmetry lies above the ground state only by about 0.35 eV.<sup>11</sup> From symmetry arguments of the two states,<sup>4,11</sup> it is predicted that through the nuclear deformation of bond-length alternation type ( $b_{3g}$ ),<sup>11,13</sup> the  $D_{2h}$  structure of pentalene will tend to distort into a skew  $C_{2h}$  one with alternate short and long bonds in the molecular periphery. It is shown that the bond-alternated  $C_{2h}$  structure is indeed energetically favored over the  $D_{2h}$  one with almost equal CC bond lengths, irrespective of the MO methods used. This is in good agreement with the available experimental facts.<sup>15,19,20</sup>

Thus far the energy partitioning procedures of the total energy have been used to investigate barriers to internal rotation, strengths of chemical bonds, Cope rearrangements, aromaticity, and electronic  $\pi$  delocalization.<sup>27–32</sup> In recent years, Boyd et al.<sup>33</sup> have carried out an energy component analysis of the total energy to elucidate the physical picture of the first-order JT effect by taking the methane cation radical as an example.

Under these circumstances, it is of primary importance to examine the dominant energy components responsible for the pseudo-JT stabilization in understanding the nature of bonding

in the conjugated hydrocarbons.<sup>34</sup> This will provide significant information regarding the physical picture of the pseudo-JT effect in connection with Boyd's study on the first-order JT effect.<sup>33</sup> We thus deal here with such bicyclic nonalternant hydrocarbons as pentalene and heptalene, whose general formula is given by  $C_{4n}H_{4n-2}$  ( $n = 1-4$ ), by means of the ab initio RHF method with 6-31G(d) basis set<sup>35–38</sup> and of the energy partitioning technique.<sup>31</sup> The present energy component analysis reveals that the pseudo-JT effect in these molecules leads commonly to a decrease in the internuclear repulsion energy and the interelectronic repulsion and kinetic energies due to  $\sigma$  electrons. Of interest is the finding that another energy component exists which plays an essential role in the pseudo-JT stabilization. For the typical instances, the energy component responsible for the stability of the  $C_{2h}$  structure for pentalene is the interelectronic repulsion term of  $\pi$  electrons, while that for heptalene is the nuclear–electron attraction term of  $\pi$  electrons. This marked difference is interpreted in terms of an electrostatic interaction combined with a charge relaxation attributed to migration of  $\pi$  electrons.

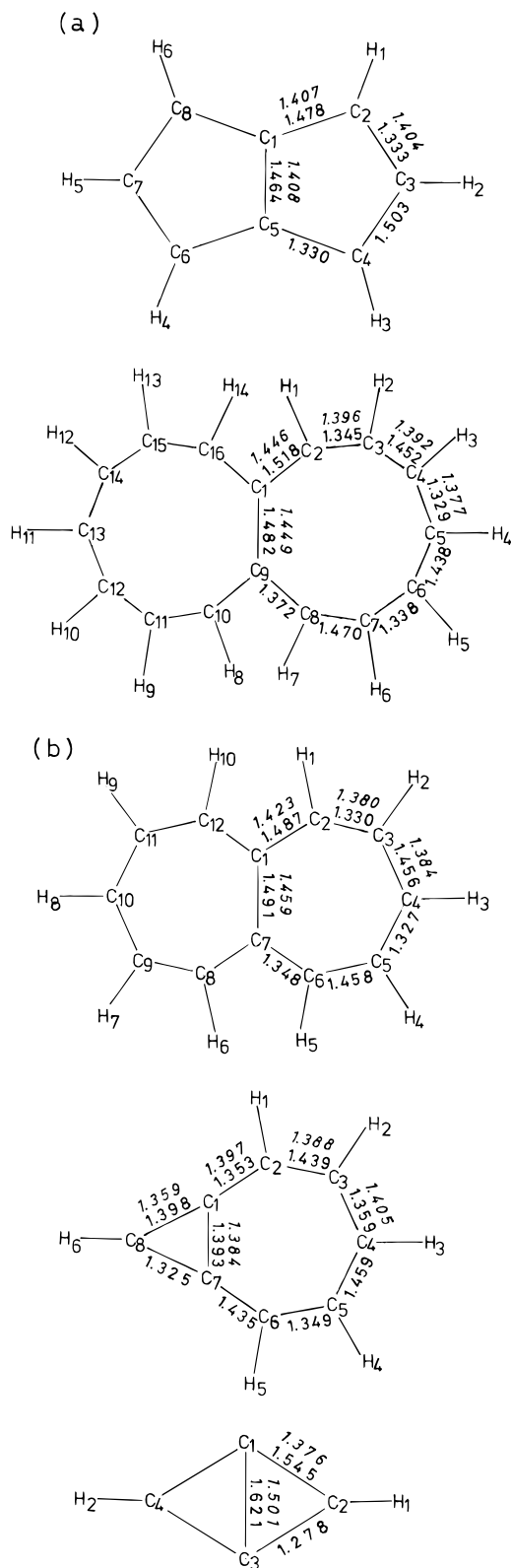
## Energy Partitioning Scheme

Of several types of the energy partitioning reported so far in the articles,<sup>27–33</sup> we employ here the energy partitioning scheme of the total energy presented by Ichikawa.<sup>31</sup> A brief review of the scheme is given below, since the energy components comprised in the total energy are important essentially for discussing the leading terms responsible for the pseudo-JT stabilization in the present molecules.

In HF theory, the total energy of a molecular system is expressed as the sum of the electronic energy ( $E^e$ ) and the internuclear repulsion energy ( $E^N$ ). The  $E^e$  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 ( $E^I$ ):

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**Figure 1.** Optimized CC bond lengths (Å) for the symmetrical and less symmetrical nuclear configurations and numbering of atoms: (a) pentalenoid systems, pentalene and nonalene; (b) heptalenoid systems, heptalene, bicyclo[5.1.0]octatetraene, and propalene, in descending order. The figures in italics are the bond lengths for the symmetrical nuclear configuration.

$$E_{\text{total}} = E^{\text{el}} + E^{\text{N}} \quad \text{and} \quad E^{\text{el}} = E^{\text{T}} + E^{\text{V}} + E^{\text{J}}$$

In the case of a planar conjugated molecule, the  $E^{\text{el}}$  and its partitioned energies can be further partitioned into  $\sigma$ -electron ( $E_{\sigma}$ ) and  $\pi$ -electron ( $E_{\pi}$ ) energies. It is noted that the  $E^{\text{J}}$  term

is formally partitioned into  $E_{\sigma}^{\text{J}}$  and  $E_{\pi}^{\text{J}}$  terms, but the former comprises the two interaction energies arising from between pure  $\sigma$  electrons and between  $\sigma$  and  $\pi$  electrons. Also, the latter comprises the energies arising from between pure  $\pi$  electrons and between  $\pi$  and  $\sigma$  electrons:

$$E^{\text{el}} = E_{\sigma} + E_{\pi} = E_{\sigma}^{\text{T}} + E_{\sigma}^{\text{V}} + E_{\sigma}^{\text{J}} + E_{\pi}^{\text{T}} + E_{\pi}^{\text{V}} + E_{\pi}^{\text{J}}$$

All calculations are carried out by using the quantum chemistry code GAMESS to which new subroutines for the energy component analysis are added. Since our main interest is to obtain a qualitative understanding of the pseudo-JT effect,<sup>33</sup> we use here the RHF MO method with 6-31G(d) basis set<sup>35–38</sup> by assuming the molecule to be planar.<sup>24,25</sup>

## Results and Discussion

**Structural and Concomitant Properties.** Figure 1 and Table 1 present the fully optimized bond lengths and bond angles for the symmetrical and less symmetrical nuclear configurations of the bicyclic nonalternant hydrocarbons. Electron populations on C atoms are obtained at the symmetrical and less symmetrical nuclear configurations by means of Mulliken's population analysis,<sup>39</sup> which are summarized in Table 2 together with  $\sigma$ - and  $\pi$ -electron components. Figure 1 and Table 2 reveal that a symmetrical structure has almost equal CC bond lengths except for the somewhat longer transannular bond but exhibits a marked charge alternation in  $\pi$  electrons along the molecular periphery. A less symmetrical structure, on the other hand, shows a substantial bond-length alternation along the molecular periphery but exhibits a situation of charge relaxation and hence a rather uniform charge distribution. It is readily seen that the charge relaxation is achieved mostly by migration of  $\pi$  electrons, indicating that the distribution of  $\sigma$  electrons is little affected by the pseudo-JT distortion. It is remarked that the charge alternation in  $\pi$  electrons is closely related with the fact that the peripheral carbon skeletons of these molecules correspond to  $[4n]$ annulenes. In the simple Hückel MO picture,  $[4n]$ annulenes possess a degenerate pair of non-bonding orbitals, and the introduction of a transannular bond to form a bicyclic nonalternant hydrocarbon lifts the degeneracy (Figure 2): In molecules such as pentalene, the transannular interaction between two C atoms of like parity lifts the degeneracy into a bonding orbital (HOMO) and a nonbonding orbital (LUMO). Accordingly, in the resultant molecule a charge alternation in  $\pi$  electrons appears in such a fashion that negative charges are located on the C atoms of the transannular bond and the ones with the same parity. In molecules such as heptalene, on the other hand, a similar transannular interaction lifts the degeneracy into a nonbonding orbital (HOMO) and an antibonding orbital (LUMO). This also gives rise to a charge alternation, but positive charges appear on the C atoms of the transannular bond and the ones with the same parity. On the basis of the patterns of orbital splitting, Trost and Bright<sup>40</sup> have termed the former a pentalenoid system and the latter a heptalenoid system. The above orbital splittings are in general small, and the resultant nonalternant hydrocarbons have a very low-lying electronically excited state.<sup>11,41</sup> As a result, of importance is the fact that the pentalenoid systems carry negative  $\pi$  charges on the C atoms of transannular bond, while the heptalenoid systems carry positive  $\pi$  charges on the C atoms of interest. This sharp difference in  $\pi$  charge distribution is shown below to be closely related to the characteristic variations in the partitioned energies with a relaxation of the molecular framework through the pseudo-JT distortion.

**TABLE 1: Bond Lengths (CH) and Bond Angles of the Bicyclic Nonalternant Hydrocarbons Optimized by Means of the RHF/6-31G(d) Method<sup>a</sup>**

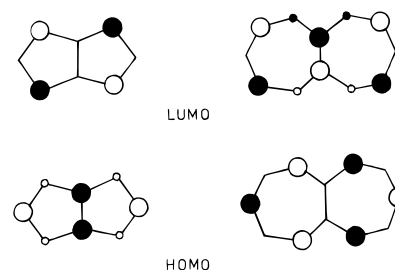
| molecule                    | symmetry | geometrical parameters <sup>b</sup>   |
|-----------------------------|----------|---|
| propylene                   | $D_{2h}$ | $C_2-H_1 = 1.058$ , $C_3-C_1-C_2 = 57.0$ , $C_1-C_2-C_3 = 66.1$ , $C_1-C_2-H_1 = 147.0$   |
|                             | $C_{2h}$ | $C_2-H_1 = 1.059$ , $C_3-C_1-C_2 = 47.5$ , $C_1-C_2-C_3 = 69.4$ , $C_1-C_3-C_2 = 63.1$ , $C_1-C_2-H_1 = 135.2$  |
| pentalene                   | $D_{2h}$ | $C_2-H_1 = 1.075$ , $C_3-H_2 = 1.071$ , $C_5-C_1-C_2 = 107.8$ , $C_1-C_2-C_3 = 108.3$ , $C_2-C_3-C_4 = 107.7$ , $C_1-C_2-H_1 = 126.9$ , $C_2-C_3-H_2 = 126.1$   |
|                             | $C_{2h}$ | $C_2-H_1 = 1.072$ , $C_3-H_2 = 1.073$ , $C_4-H_3 = 1.074$ , $C_5-C_1-C_2 = 106.8$ , $C_1-C_2-C_3 = 106.7$ , $C_2-C_3-C_4 = 110.0$ , $C_1-C_5-C_4 = 108.8$ , $C_5-C_4-C_3 = 107.6$ , $C_1-C_2-H_1 = 126.3$ , $C_2-C_3-H_2 = 126.4$ , $C_5-C_4-H_3 = 128.4$   |
| heptalene                   | $D_{2h}$ | $C_2-H_1 = 1.074$ , $C_3-H_2 = 1.078$ , $C_4-H_3 = 1.074$ , $C_7-C_1-C_2 = 123.4$ , $C_1-C_2-C_3 = 134.1$ , $C_2-C_3-C_4 = 131.2$ , $C_3-C_4-C_5 = 122.6$ , $C_1-C_2-H_1 = 112.9$ , $C_2-C_3-H_2 = 113.4$ , $C_3-C_4-H_3 = 118.7$   |
|                             | $C_{2h}$ | $C_2-H_1 = 1.075$ , $C_3-H_2 = 1.077$ , $C_4-H_3 = 1.076$ , $C_6-H_5 = 1.075$ , $C_5-H_4 = 1.077$ , $C_7-C_1-C_2 = 121.2$ , $C_1-C_2-C_3 = 134.1$ , $C_2-C_3-C_4 = 129.9$ , $C_3-C_4-C_5 = 125.6$ , $C_1-C_7-C_6 = 126.1$ , $C_7-C_6-C_5 = 134.3$ , $C_6-C_5-C_4 = 128.9$ , $C_1-C_2-H_1 = 111.9$ , $C_2-C_3-H_2 = 115.4$ , $C_3-C_4-H_3 = 116.0$ , $C_7-C_6-H_5 = 114.6$ , $C_6-C_5-H_4 = 113.7$   |
| nonalene                    | $D_{2h}$ | $C_2-H_1 = 1.062$ , $C_3-H_2 = 1.076$ , $C_4-H_3 = 1.078$ , $C_5-H_4 = 1.076$ , $C_9-C_1-C_2 = 127.9$ , $C_1-C_2-C_3 = 151.8$ , $C_2-C_3-C_4 = 145.1$ , $C_3-C_4-C_5 = 139.2$ , $C_4-C_5-C_6 = 132.0$ , $C_1-C_2-H_1 = 107.3$ , $C_2-C_3-H_2 = 107.3$ , $C_3-C_4-H_3 = 109.7$ , $C_4-C_5-H_4 = 114.0$   |
|                             | $C_{2h}$ | $C_2-H_1 = 1.064$ , $C_3-H_2 = 1.077$ , $C_4-H_3 = 1.077$ , $C_5-H_4 = 1.076$ , $C_8-H_7 = 1.063$ , $C_7-H_6 = 1.076$ , $C_6-H_5 = 1.077$ , $C_9-C_1-C_2 = 126.8$ , $C_1-C_2-C_3 = 151.5$ , $C_2-C_3-C_4 = 146.3$ , $C_3-C_4-C_5 = 137.6$ , $C_4-C_5-C_6 = 132.9$ , $C_1-C_9-C_8 = 128.2$ , $C_9-C_8-C_7 = 151.9$ , $C_8-C_7-C_6 = 146.4$ , $C_7-C_6-C_5 = 138.5$ , $C_1-C_2-H_1 = 105.3$ , $C_2-C_3-H_2 = 107.8$ , $C_3-C_4-H_3 = 109.5$ , $C_4-C_5-H_4 = 114.7$ , $C_9-C_8-H_7 = 108.7$ , $C_8-C_7-H_6 = 105.1$ , $C_7-C_6-H_5 = 111.0$ |
| bicyclo[5.1.0]-octatetraene | $C_{2v}$ | $C_2-H_1 = 1.072$ , $C_3-H_2 = 1.079$ , $C_4-H_3 = 1.074$ , $C_8-H_6 = 1.067$ , $C_7-C_1-C_2 = 135.4$ , $C_1-C_2-C_3 = 117.2$ , $C_2-C_3-C_4 = 132.5$ , $C_3-C_4-C_5 = 129.7$ , $C_1-C_2-H_1 = 121.9$ , $C_2-C_3-H_2 = 114.2$ , $C_3-C_4-H_3 = 115.1$ , $C_7-C_1-C_8 = 59.4$ , $C_1-C_8-H_6 = 149.4$  |
|                             | $C_s$    | $C_2-H_1 = 1.072$ , $C_3-H_2 = 1.079$ , $C_4-H_3 = 1.075$ , $C_6-H_5 = 1.073$ , $C_5-H_4 = 1.079$ , $C_8-H_6 = 1.067$ , $C_7-C_1-C_2 = 136.8$ , $C_1-C_2-C_3 = 117.2$ , $C_2-C_3-C_4 = 131.7$ , $C_3-C_4-C_5 = 130.5$ , $C_1-C_7-C_6 = 134.2$ , $C_7-C_6-C_5 = 117.6$ , $C_6-C_5-C_4 = 132.1$ , $C_1-C_2-H_1 = 122.9$ , $C_2-C_3-H_2 = 114.2$ , $C_3-C_4-H_3 = 116.1$ , $C_7-C_6-H_5 = 121.0$ , $C_6-C_5-H_4 = 115.0$ , $C_7-C_1-C_8 = 56.7$ , $C_1-C_7-C_8 = 61.9$ , $C_1-C_8-H_6 = 148.8$   |

<sup>a</sup> Numbering of atoms is shown in Figure 1. Bond lengths and bond angles are in angstroms and degrees. <sup>b</sup> CC bond lengths are shown in Figure 1.

**TABLE 2: Electron Populations on C Atoms at the Symmetric and Distorted Structures of the Bicyclic Nonalternant Hydrocarbons**

| molecule                    | atom           | symmetric structure |       |          | distorted structure |       |          |
|-----------------------------|----------------|---------------------|-------|----------|---------------------|-------|----------|
|                             |                | total               | $\pi$ | $\sigma$ | total               | $\pi$ | $\sigma$ |
| propylene                   | C <sub>1</sub> | 5.837               | 0.551 | 5.286    | 5.950               | 0.698 | 5.252    |
|                             | C <sub>2</sub> | 6.421               | 1.449 | 4.972    | 6.317               | 1.302 | 5.015    |
| pentalene                   | C <sub>1</sub> | 6.128               | 1.220 | 4.908    | 6.013               | 1.015 | 4.997    |
|                             | C <sub>2</sub> | 6.082               | 0.774 | 5.307    | 6.227               | 0.958 | 5.268    |
|                             | C <sub>4</sub> |                     |       |          | 6.149               | 1.007 | 5.142    |
| heptalene                   | C <sub>3</sub> | 6.345               | 1.231 | 5.114    | 6.238               | 1.020 | 5.218    |
|                             | C <sub>1</sub> | 5.835               | 0.788 | 5.047    | 5.906               | 0.949 | 4.957    |
|                             | C <sub>2</sub> | 6.338               | 1.188 | 5.150    | 6.301               | 1.058 | 5.242    |
|                             | C <sub>6</sub> |                     |       |          | 6.201               | 0.995 | 5.206    |
|                             | C <sub>3</sub> | 6.086               | 0.824 | 5.262    | 6.164               | 0.985 | 5.180    |
| nonalene                    | C <sub>5</sub> |                     |       |          | 6.203               | 1.003 | 5.200    |
|                             | C <sub>4</sub> | 6.296               | 1.187 | 5.109    | 6.195               | 1.011 | 5.184    |
|                             | C <sub>1</sub> | 5.915               | 1.134 | 4.781    | 5.874               | 1.027 | 4.847    |
|                             | C <sub>2</sub> | 6.168               | 0.842 | 5.326    | 6.236               | 0.931 | 5.305    |
|                             | C <sub>8</sub> |                     |       |          | 6.200               | 0.963 | 5.238    |
|                             | C <sub>3</sub> | 6.312               | 1.186 | 5.126    | 6.221               | 1.067 | 5.154    |
|                             | C <sub>7</sub> |                     |       |          | 6.261               | 1.082 | 5.179    |
|                             | C <sub>4</sub> | 6.077               | 0.829 | 5.247    | 6.146               | 0.935 | 5.211    |
| bicyclo[5.1.0]-octatetraene | C <sub>6</sub> |                     |       |          | 6.142               | 0.949 | 5.193    |
|                             | C <sub>5</sub> | 6.266               | 1.151 | 5.115    | 6.199               | 1.047 | 5.152    |
|                             | C <sub>1</sub> | 5.822               | 0.730 | 5.092    | 5.852               | 0.771 | 5.082    |
|                             | C <sub>7</sub> |                     |       |          | 5.837               | 0.783 | 5.054    |
|                             | C <sub>2</sub> | 6.376               | 1.325 | 5.050    | 6.299               | 1.211 | 5.088    |
|                             | C <sub>6</sub> |                     |       |          | 6.394               | 1.335 | 5.059    |
|                             | C <sub>3</sub> | 6.049               | 0.743 | 5.307    | 6.084               | 0.788 | 5.296    |
|                             | C <sub>5</sub> |                     |       |          | 6.075               | 0.796 | 5.279    |
|                             | C <sub>4</sub> | 6.360               | 1.314 | 5.046    | 6.322               | 1.250 | 5.072    |
|                             | C <sub>8</sub> | 6.343               | 1.090 | 5.253    | 6.331               | 1.066 | 5.266    |

An explanation about how the  $\pi$  charge alternation is relaxed in the less symmetrical structure can be given qualitatively from a perturbational MO approach as follows: At the unperturbed symmetrical structure of the present molecules examined, the lowest excited singlet state, which is nearly degenerate with the ground state,<sup>41</sup> is represented virtually by one-electron excitation from the HOMO to the LUMO. Thus, the vibronic

**Figure 2.** Representation of the Hückel HOMO and LUMO for pentalene and heptalene. White and black circles indicate the plus and minus signs of atomic-orbital coefficients, respectively.

interaction between the ground and lowest excited singlet states through the nuclear deformation of bond-length alternation type  $Q_i$  can be reduced to the interaction between the HOMO and LUMO through the one-electron operator  $\partial V/\partial Q_i$ , where  $V$  represents the operator of nuclear-electron potential energy. After the nuclear deformation, the perturbed HOMO is expressed as a linear combination of the unperturbed HOMO and LUMO. As a result, the mixing in of the LUMO into the HOMO contributes to a reorganization (or better relaxation) of  $\pi$  charge densities, because in the symmetrical structure the two orbitals (Figure 2) are confined to the sets of C atoms almost different to each other.<sup>42,43</sup>

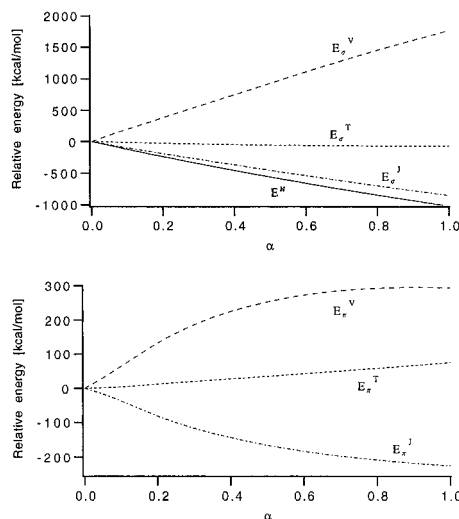
**Total and Partitioned Energies.** In Table 3 are shown the total and partitioned energies at the symmetrical and less symmetrical nuclear configurations of the bicyclic nonalternant hydrocarbons. It seems that the difference in total energy between the two configurations of the molecule, i.e., the stabilization energy associated with the pseudo-JT distortion, is rather small in comparison with the extent of molecular deformation. Especially interesting is the stabilization energy,<sup>15,16</sup> which corresponds to the activation energy of the isodynamical  $\pi$ -bond shift<sup>20,23</sup> occurring in the interconversion between the two equivalent distorted structures obtained above: The activation energy is in the range of ca. 1–17 kcal/

**TABLE 3: Total and Partitioned Energies and Their Energy Differences between the Symmetric and Distorted Structures<sup>a</sup>**

| molecule                        | com-<br>ponent          | symmetric     | distorted     | difference <sup>b</sup> |
|---------------------------------|-------------------------|---------------|---------------|-------------------------|
| propylene                       | $E_{\text{total}}$      | -152.378 959  | -152.387 578  | -0.008 619              |
|                                 | $E^{\text{N}}$          | 89.773 796    | 87.854 195    | -1.919 601              |
|                                 | $E_{\sigma}^{\text{T}}$ | 148.050 379   | 147.989 004   | -0.061 375              |
|                                 | $E_{\sigma}^{\text{V}}$ | -490.570 751  | -487.122 064  | 3.448 687               |
|                                 | $E_{\sigma}^{\text{J}}$ | 120.664 981   | 119.114 696   | -1.550 285              |
|                                 | $E_{\pi}^{\text{T}}$    | 4.287 389     | 4.362 848     | 0.075 459               |
|                                 | $E_{\pi}^{\text{V}}$    | -43.173 413   | -43.090 692   | 0.082 721               |
|                                 | $E_{\pi}^{\text{J}}$    | 18.588 660    | 18.504 435    | -0.084 225              |
| pentalene                       | $E_{\text{total}}$      | -306.320 087  | -306.345 980  | -0.025 893              |
|                                 | $E^{\text{N}}$          | 317.833 648   | 316.215 531   | -1.618 117              |
|                                 | $E_{\sigma}^{\text{T}}$ | 298.110 109   | 298.001 587   | -0.108 522              |
|                                 | $E_{\sigma}^{\text{V}}$ | -1224.620 334 | -1221.797 287 | 2.823 047               |
|                                 | $E_{\sigma}^{\text{J}}$ | 362.195 396   | 360.841 057   | -1.354 339              |
|                                 | $E_{\pi}^{\text{T}}$    | 8.012 828     | 8.133 549     | 0.120 721               |
|                                 | $E_{\pi}^{\text{V}}$    | -124.738 564  | -124.269 639  | 0.468 925               |
|                                 | $E_{\pi}^{\text{J}}$    | 56.886 830    | 56.529 223    | -0.357 607              |
| heptalene                       | $E_{\text{total}}$      | -460.115 172  | -460.142 227  | -0.027 055              |
|                                 | $E^{\text{N}}$          | 608.850 724   | 606.628 787   | -2.221 937              |
|                                 | $E_{\sigma}^{\text{T}}$ | 447.885 614   | 447.708 960   | -0.176 654              |
|                                 | $E_{\sigma}^{\text{V}}$ | -2066.130 373 | -2061.713 870 | 4.416 503               |
|                                 | $E_{\sigma}^{\text{J}}$ | 656.838 382   | 654.897 691   | -1.940 691              |
|                                 | $E_{\pi}^{\text{T}}$    | 11.859 525    | 12.055 287    | 0.195 762               |
|                                 | $E_{\pi}^{\text{V}}$    | -222.377 566  | -222.708 407  | -0.330 841              |
|                                 | $E_{\pi}^{\text{J}}$    | 102.958 521   | 102.989 326   | 0.030 805               |
| nonalene                        | $E_{\text{total}}$      | -613.712 402  | -613.730 228  | -0.017 826              |
|                                 | $E^{\text{N}}$          | 930.498 512   | 926.438 140   | -4.060 372              |
|                                 | $E_{\sigma}^{\text{T}}$ | 597.578 088   | 597.358 916   | -0.219 172              |
|                                 | $E_{\sigma}^{\text{V}}$ | -2959.413 149 | -2952.018 242 | 7.394 907               |
|                                 | $E_{\sigma}^{\text{J}}$ | 977.701 596   | 974.207 528   | -3.494 068              |
|                                 | $E_{\pi}^{\text{T}}$    | 15.684 496    | 15.912 896    | 0.228 400               |
|                                 | $E_{\pi}^{\text{V}}$    | -329.714 018  | -329.106 078  | 0.607 940               |
|                                 | $E_{\pi}^{\text{J}}$    | 153.952 071   | 153.476 611   | -0.475 460              |
| bicyclo[5.1.0]-<br>octatetraene | $E_{\text{total}}$      | -306.283 604  | -306.284 855  | -0.001 251              |
|                                 | $E^{\text{N}}$          | 310.526 519   | 310.017 983   | -0.508 536              |
|                                 | $E_{\sigma}^{\text{T}}$ | 297.993 524   | 297.937 780   | -0.055 744              |
|                                 | $E_{\sigma}^{\text{V}}$ | -1212.053 522 | -1211.000 306 | 1.053 216               |
|                                 | $E_{\sigma}^{\text{J}}$ | 355.678 628   | 355.229 264   | -0.449 364              |
|                                 | $E_{\pi}^{\text{T}}$    | 8.054 963     | 8.109 230     | 0.054 267               |
|                                 | $E_{\pi}^{\text{V}}$    | -121.740 369  | -121.867 512  | -0.127 143              |
|                                 | $E_{\pi}^{\text{J}}$    | 55.256 654    | 55.288 707    | 0.032 053               |

<sup>a</sup> Energies are in hartree. <sup>b</sup> The minus sign means that the energy term is lower in energy for the distorted structure than for the symmetric one.

mol for the present nonalternant hydrocarbons within the RHF/6-31G(d) method. In contrast, 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 symmetrical structure and the other from the ones which favor the less symmetrical structure. For pentalene and heptalene, the variations of all the energy components relative to those of the  $D_{2h}$  structure are shown in Figure 3 and 4, respectively, along a linear synchronous transit between the  $D_{2h}$  and  $C_{2h}$  equilibrium nuclear configurations. The figures show clearly that the energy terms are highly sensitive to changes in molecular geometry and have mutually opposite signs to the pseudo-JT stabilization.



**Figure 3.** Energy variations of individual components for pentalene along the linear synchronous transit from the  $D_{2h}$  ( $\alpha = 0.0$ ) to the  $C_{2h}$  ( $\alpha = 1.0$ ) equilibrium configuration. In the upper half are given the energy terms  $E_{\sigma}^{\text{T}}$ ,  $E_{\sigma}^{\text{V}}$ ,  $E_{\sigma}^{\text{J}}$ , and  $E^{\text{N}}$  and in the lower half are given the energy terms  $E_{\pi}^{\text{T}}$ ,  $E_{\pi}^{\text{V}}$ , and  $E_{\pi}^{\text{J}}$ .

On the basis of these results, we are now concerned with the dominant energy components responsible for the pseudo-JT effect in the pentalenoid and heptalenoid systems.

#### Energy Component Analysis of the Pentalenoid Systems.

(a) *Pentalene*. In the case where the pseudo-JT distortion takes place only through the  $b_{3g}$  nuclear deformation of bond-length alternation type, the transannular bond should remain unchanged and no net changes in bond length should be observed as a whole for the remaining CC bonds of the  $C_{2h}$  structure in comparison with those of the  $D_{2h}$  one. However, the present pseudo-JT distortion leads to the structural changes that, while the average CH bond length is almost equal between the two structures (Table 1), the transannular bond is lengthened and the average CC bond length of the molecular periphery is increased (Figure 1). A simple analysis with regard to the CC bonds in length between the  $D_{2h}$  and  $C_{2h}$  structures reveals that in addition to the  $b_{3g}$  nuclear deformation of interest, the totally symmetric CC breathing deformations are also operative. Namely, the carbon skeleton changes its form such that the transannular bond is lengthened by 0.056 Å, bond 2–3 is lengthened by 0.014 Å, and bond 1–2 is shortened by 0.003 Å. At the same time, the  $b_{3g}$  nuclear deformation is operative such that bond 1–2 is lengthened by 0.074 Å, bond 2–3 is shortened by 0.085 Å, and the successive peripheral CC bonds are alternately lengthened and shortened by lengths that correspond to the changes for the former two bonds. It should be emphasized that when the pentalene molecule will settle at the  $C_{2h}$  equilibrium nuclear configuration, an expansion of the carbon skeleton takes place in a totally symmetric fashion. Hence, it is expected that the repulsion energies  $E^{\text{N}}$ ,  $E_{\sigma}^{\text{J}}$ , and  $E_{\pi}^{\text{J}}$  should be lowered. As is shown in Table 3, this is actually true for pentalene (also see Figure 3). This is further ascribed to the fact that the charge relaxation in pentalene is achieved such that the  $\pi$  electron cloud is spread over the entire carbon skeleton relative to the  $D_{2h}$  structure. Accordingly, this leads to the energy changes that the repulsion energy  $E_{\pi}^{\text{J}}$  is lowered, while the nuclear–electron attraction energy  $E_{\pi}^{\text{V}}$ , which is a negative quantity, is raised. It will be seen that an expansion or a contraction of the  $\pi$  electron cloud arising from the charge relaxation serves as a good guideline to predict qualitatively which sort of the energy component should be lowered or raised in energy. It is often said in this connection that when a charge alternation appears

at the symmetrical nuclear configuration of a conjugated molecule, the charge polarization is relaxed so as to decrease in electron repulsion,<sup>2,44</sup> and thereby the molecule is distorted by a certain nuclear deformation into a less symmetrical configuration with a rather uniform charge distribution. This may be true for such molecules as pentalene, but it is premature to conclude that the appearance of such a charge alternation leads directly to the decrease in electron repulsion. Namely, the above supposition fails for other molecules as will be shown below. This is because whether the relaxation of charge alternation gives rise to a decrease in the electron repulsion energy should depend actually upon the type of charge polarization.

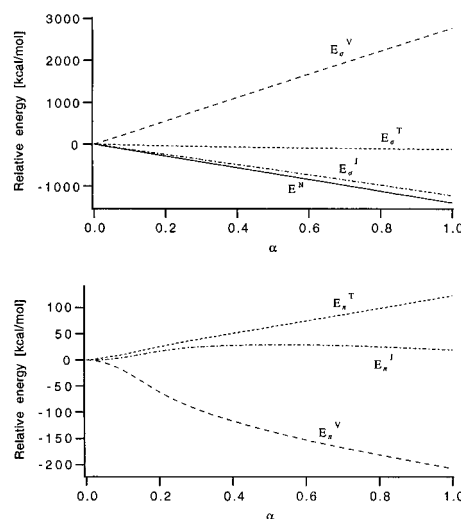
Table 3 also shows that for these nonalternant hydrocarbons the energy changes of the kinetic energy components  $E_\sigma^T$  and  $E_\pi^T$  are rather small, the former being lowered and the latter raised in energy, and that both energy changes are almost equal in absolute value. A plausible explanation for such small energy changes may be given qualitatively by invoking simple one-electron theories, i.e., the free-electron orbital method for an electron in a one-dimensional box of length  $L$  and the Platt perimeter model for an electron in a circle of radius  $L$ .<sup>2,45,46</sup> The theories say that the kinetic energy for the electron is inversely proportional to the second power of the length  $L$ . It is thus expected from the energy dependence that the kinetic energy of question is lowered by the effect due to the CC bond length changes followed by the expansion of the carbon skeleton. At the same time, the kinetic energy is raised by the effect due to the nuclear deformation of bond-length alternation type. This means that the change in kinetic energy due to the pseudo-JT effect is in a delicate balance between the two opposing contributions, one being in the direction toward stability and the other in the opposite direction. For this reason, it is presumed that for all of the present molecules the change in kinetic energy should be rather small, as Table 3 actually shows.

Anyway, it is concluded for pentalene that the energetic stability of the  $C_{2h}$  structure should benefit from the lowerings of the terms  $E^N$ ,  $E_\sigma^J$ ,  $E_\pi^J$ , and  $E_\sigma^T$ , and all the other energy components change in the opposite direction: The dominant energy components to the stability come from the former two terms, in order of importance.

(b) *Nonalene*. A quite similar situation is observed in nonalene. This molecule undergoes the pseudo-JT distortion from  $D_{2h}$  to  $C_{2h}$ , and thereby the carbon skeleton is expanded in a totally symmetric fashion. The associated changes in bond length are given as follows, where the signs + and - denote respectively a lengthening and a shortening of the CC bonds relative to the  $D_{2h}$  structure: transannular bond (+0.032 Å), bond 1-2 (-0.001 Å), bond 2-3 (+0.012 Å), and bond 4-5 (+0.007 Å). Besides, the alternate bond-length changes due to the  $b_{3g}$  nuclear deformation amount to ca. 0.05-0.07 Å in absolute value along the molecular periphery, while the average CH bond length is almost equal between the two structures. As a consequence, the expansion of carbon skeleton should be reflected in a decrease in the internuclear and interelectronic repulsion energies. Actually, Table 3 shows that the repulsion energies  $E^N$ ,  $E_\sigma^J$ , and  $E_\pi^J$  are lowered as is the case observed for pentalene. It is thus concluded that the  $C_{2h}$  structure of nonalene owes its energetic stability to the lowerings of the terms  $E^N$ ,  $E_\sigma^J$ ,  $E_\pi^J$ , and  $E_\sigma^T$  and the large contributions come from the former two energy terms, in order of importance.

#### Energy Component Analysis of the Heptalenoid Systems.

(a) *Heptalene*. With regard to the structural changes due to the pseudo-JT effect, a very similar situation is observed in heptalene as that in the pentalenoid systems. A structural



**Figure 4.** Energy variations of individual components for heptalene along the linear synchronous transit from the  $D_{2h}$  ( $\alpha = 0.0$ ) to the  $C_{2h}$  ( $\alpha = 1.0$ ) equilibrium configuration. In the upper half are given the energy terms  $E_\sigma^T$ ,  $E_\sigma^V$ ,  $E_\pi^J$ , and  $E^N$  and in the lower half are given the energy terms  $E_\pi^T$ ,  $E_\pi^V$ , and  $E_\pi^J$ .

analysis shows that relative to the  $D_{2h}$  structure, the carbon skeleton of the  $C_{2h}$  structure is expanded in a totally symmetric fashion and the associated changes in bond length are given as follows: transannular bond (+0.032 Å), bond 1-2 (-0.006 Å), bond 2-3 (+0.014 Å), and bond 3-4 (+0.008 Å). At the same time, the alternate bond-length changes by the  $b_{3g}$  nuclear deformation amount to ca. 0.06-0.07 Å in absolute value along the molecular periphery. Accordingly, these bond-length changes suggest that the repulsion energies  $E^N$ ,  $E_\sigma^J$ , and  $E_\pi^J$  should be lowered. Table 3 shows that the former two terms are largely lowered but the latter term is somewhat raised in energy. It is also seen that the nuclear-electron attraction energy  $E_\pi^V$  is appreciably lowered. It can thus be pointed out that these energy changes differ from those in pentalene in the following respects: For pentalene the term  $E_\sigma^V$  is lowered and the term  $E_\pi^V$  is raised while for heptalene the reverse is observed for the corresponding two energy terms (Figures 3 and 4). An explanation about how such unusual energy changes should take place in heptalene can be offered in terms of electrostatic interactions combined with the charge relaxation attributed to the  $\pi$  electrons. As described above, the charge relaxation in the present molecules takes place for the most part by migration of  $\pi$  electrons. For heptalene, the positive charges on the C atoms of the transannular bond and the ones with the same parity are neutralized by migration of  $\pi$  charge densities from the other C atoms with the different parity. This is equivalent to saying that the charge alternation in  $\pi$  electrons is relaxed such that the  $\pi$  electron cloud is contracted toward the central moiety of the molecular skeleton relative to the  $D_{2h}$  structure. It is therefore expected that this behavior should enhance the interelectronic repulsive interactions between  $\pi$  electrons, even though the carbon skeleton is expanded to such extents as described above. On the contrary, the attractive interactions between nuclei and  $\pi$  electrons, especially between nucleus  $C_1(C_7)$  and the  $\pi$  electrons distributed around atom  $C_7(C_1)$ , should increase because an appreciable quantity of the  $\pi$  electron densities is transferred to around atoms  $C_1$  and  $C_7$  with the relaxation of the molecular framework through the pseudo-JT distortion (Table 3). Accordingly, it is expected that the lowering of the attractive term  $E_\pi^V$  should generally occur in the heptalenoid systems, provided that the expansion of the molecular framework, especially the elongation of the transan-

nular bond, due to the pseudo-JT effect is not so great as to cause the electrostatic attractive interactions to be less effective. A part of the stabilization for the  $C_{2h}$  structure of heptalene arises from the energy lowering of the nuclear–electron attractive term  $E_{\pi}^V$ , but the magnitude of the energy lowering is at best one-sixth of those of the repulsive terms  $E^N$  and  $E_{\sigma}^J$ . It can thus be said for heptalene that the preference for the bond-alternated  $C_{2h}$  structure should originate from the lowerings of the repulsive terms  $E^N$  and  $E_{\sigma}^J$ , the nuclear–electron attractive term  $E_{\pi}^V$ , and the kinetic energy term  $E_{\sigma}^T$ . The leading energy components correspond to the former two terms, in order of importance.

(b) *Bicyclo[5.1.0]octatetraene*. This molecule is a valence isomer of pentalene, but it belongs to the heptalenoid systems. In this molecule, the pseudo-JT distortion from  $C_{2v}$  to  $C_s$  gives rise to such structural changes that, relative to the  $C_{2v}$  structure, the carbon skeleton of the  $C_s$  structure is expanded in a totally symmetric fashion as follows: transannular bond (+0.003 Å), bond 1–7 (–0.009 Å), bond 1–2 (–0.003 Å), bond 2–3 (+0.006 Å), and bond 3–4 (+0.004 Å). The alternate bond-length changes due to the  $b_2$  nuclear deformation amount to ca. 0.04–0.05 Å in absolute value along the molecular periphery, while the average CH bond length is the same between the two structures. It is thus expected that the expansion of the carbon skeleton should be reflected by a decrease in the internuclear and interelectronic repulsion energies. Table 3 indicates that the repulsion energies of the terms  $E^N$  and  $E_{\sigma}^J$  are lowered but that of the term  $E_{\pi}^J$  is raised and that the nuclear–electron attraction energy  $E_{\pi}^V$  is lowered in energy. Needless to say, these energy changes are just the same as those in heptalene. It is remarked, however, that the energy lowerings of the terms  $E^N$  and  $E_{\sigma}^J$  are less for bicyclo[5.1.0]octatetraene than those for pentalene by about one-fourth and one-third, respectively. This is easily ascribed to the fact that the expansion of the carbon skeleton is smaller in magnitude for bicyclo[5.1.0]octatetraene than for pentalene. It is thus concluded for bicyclo[5.1.0]octatetraene that the energetic stability of the  $C_s$  structure results from the lowerings of the terms  $E_{\pi}^V$ ,  $E_{\sigma}^J$ ,  $E^N$ , and  $E_{\sigma}^T$ . The large contributions come from the former three terms, their magnitudes being almost equal.

(c) *Propalene*. In this molecule, the pseudo-JT distortion gives rise to great structural changes. Relative to the  $D_{2h}$  structure, the carbon skeleton of the  $C_{2h}$  structure is expanded symmetrically such that the transannular bond and bond 1–2 are lengthened by 0.120 and 0.036 Å, respectively. The alternate bond-length changes due to the  $b_{3g}$  nuclear deformation amount to 0.134 Å in absolute value along the molecular periphery, and the CH bond length is increased by 0.001 Å. A similar consideration based on the structural changes accompanied by the charge relaxation leads to the prediction that in propalene the repulsion energies  $E^N$  and  $E_{\sigma}^J$  should be reduced and the nuclear–electron attraction energy  $E_{\pi}^V$  should be lowered just as in heptalene. Table 3 indicates, however, that this is not the case for propalene. Instead, the reverse is found to occur for the energy terms  $E_{\pi}^J$  and  $E_{\pi}^V$ , and this behavior is the same as that seen in the pentalenoid systems. The anomaly in energy change in propalene can be interpreted as follows. Since the transannular bond is substantially lengthened, it may be expected that the attractive interactions between nuclei and  $\pi$  electrons, especially between nucleus  $C_1(C_3)$  and the  $\pi$  electrons distributed around atom  $C_3(C_1)$ , do not become large such that the nuclear–electron attraction energy  $E_{\pi}^V$  is lower for the  $C_{2h}$  structure than for the  $D_{2h}$  one. This situation can be seen numerically from the energy change

of the term  $E_{\pi}^V$  in Table 3. The attraction energy  $E_{\pi}^V$  is raised, but the amount of energy raising is quite small in comparison with that in pentalene. In addition, the energy reduction of the term  $E_{\pi}^J$  is less than one-fourth of that observed in pentalene. Obviously, such small energy changes are attributable to the fact that the  $\pi$  electron cloud is contracted toward the central C atoms with the charge relaxation. Despite the fact that propalene belongs to the heptalenoid systems, it is concluded that the energetic stability of the  $C_{2h}$  structure should arise from a reduction of the repulsion energies  $E^N$ ,  $E_{\sigma}^J$ , and  $E_{\pi}^J$  and a lowering of the kinetic energy  $E_{\sigma}^T$ . The dominant energy components correspond to the former two terms, the contributions from the latter two terms being rather small.

**The First-Order JT and Pseudo-JT Effects.** In connection with this study, it will be pertinent to express our view briefly to the following question put forth by Boyd et al. on the basis of the result of the methane cation radical:<sup>33,47</sup> Is it generally true that the first-order JT effect leads to a contraction of the electron cloud and to a concomitant decrease in the nuclear–electron attraction energy and to an increase in the interelectronic and internuclear repulsion energies? Our results reveal that the pseudo-JT effect leads to expansion of the electron cloud for pentalene and nonalene. 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, there is every reason to believe that the first-order JT effect leads to expansion of the electron cloud as well. As has been pointed out by Boyd et al., further detailed studies will be required to answer this question. Especially, it will be most essential to make an energy component analysis of the first-order JT effect in the neutral and negatively charged species. Along this line, we are undertaking an investigation by dealing with charged species that undergo the pseudo-JT distortion.

## Conclusions

A characteristic electronic feature inherent in these nonalternant hydrocarbons is that a charge alternation in  $\pi$  electrons appears at the symmetrical nuclear configuration. It is observed that the pseudo-JT effect gives rise to two types of  $\pi$  charge relaxation in the less symmetrical nuclear configuration, one corresponding to the contraction of the electron cloud and the other to the expansion of the electron cloud relative to the distribution of  $\pi$  electrons in the symmetrical nuclear configuration. Moreover, the observation that the kinetic energy is almost constant under the nuclear deformation of bond-length alternation type coupled with the totally symmetric nuclear deformation is also a characteristic feature common to these nonalternant hydrocarbons. These phenomena are shown to provide an important clue for us to grasp the nature of interactions involved in the pseudo-JT effect. The present energy component analyses reveal that the primary contributions to the energetic stability of the distorted structure arise commonly from the lowering of the internuclear and interelectronic repulsion terms,  $E^N$  and  $E_{\sigma}^J$ . This is attributable to the structural changes that the pseudo-JT distortion gives rise to more or less the totally symmetric expansion of the molecular framework and hence leads to a reduction of the repulsion energies. In addition, another energy component plays an important role in the pseudo-JT stabilization: In the pentalenoid systems the energy component is the interelectronic repulsion term  $E_{\pi}^J$ , while in the heptalenoid systems it is the nuclear–electron attraction term  $E_{\pi}^V$ . This marked difference is interpreted in terms of the charge relaxation accompanied by the

contraction or expansion of the  $\pi$  electron cloud. It is thus confirmed that the charge relaxation also plays a key role in lowering the molecular symmetry group at least in these nonalternant hydrocarbons.<sup>48</sup> In summary, the physical background of the present pseudo-JT effect can be taken as the combined effects due to the expansion of the carbon skeleton and the relaxation of charge polarization through Coulombic interactions.

In connection with this work, of interest is the conjugated molecules that exhibit essentially no charge polarization in  $\pi$  electrons at the symmetrical nuclear configuration. As a part of this work, further studies on the most fundamental conjugated molecules such as cyclobutadiene are now under consideration. Our preliminary analysis<sup>34,49</sup> within the semiempirical PPP-type  $\pi$ -electron approximation reveals that the energy component responsible for the pseudo-JT stabilization in cyclobutadiene is the nuclear-electron attraction term  $E_{\pi}^V$  instead of the inter-electronic repulsion term  $E_{\pi}^J$ . The results obtained by means of the MCSCF method with the 6-31G(d) basis set will be discussed elsewhere in the near future.

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