

Potential energy profiles along the doubly degenerate vibrational modes in conjugated molecules

II. Application

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On the basis of the general theory put forward in the preceding paper of the same title, we examine the potential energy profiles along the first-order Jahn–Teller active modes or along the doubly degenerate modes through which the second-order vibronic couplings occur in the cyclopropenyl radical, cation, and anion, the cyclopentadienyl radical and anion, the bicyclo[1.1.1]pentane-2,4,5-triyl anion and cation, the ${}^1B_{1u}$ and ${}^3B_{1u}$ excited states of benzene, and the cation and anion radicals of benzene. The geometrical structures of these molecules predicted from the potential energy curves expanded in the power series of the relevant modes, including up to the cubic power are in good agreement with those predicted by using the various MO methods and the available experimental ones.

Key words: Potential energy surfaces—first-order and second-order Jahn–Teller effects—conjugated hydrocarbons

1. Introduction

In the preceding paper of the same title [1], we have examined the potential energy profiles along the first-order Jahn–Teller (FOJT) active modes (Q_1 and Q_2) or the doubly degenerate modes through which the second-order vibronic couplings occur (SO coupling modes, Q'_1 and Q'_2) in conjugated molecules. The characteristic feature of our method is to expand the potential energy in the power series of the relevant mode, including up to the cubic power. It has been shown that although there are cases in which we cannot practically differentiate between the potential energy profiles along Q_1 and Q_2 or Q'_1 and Q'_2 , in so far

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as we can differentiate between them, a potential energy minimum should always be located along Q_1 or Q'_1 that distorts a molecule in a more symmetrical way. Further, on the basis of the perturbation theory, the coefficients of various powers (up to the third power) in the expansion of the electronic part of potential energy in the power series of the relevant mode have been expressed in terms of the zeroth-order wavefunctions and energies (Eqs. (21) and (22) of Ref. [1]).

In this paper, using these equations, we examine the potential energy curves along the FOJT active or SO coupling degenerate modes in individual laterally conjugated molecules and predict their geometrical structures.

2. Estimation of matrix elements

For the conjugated hydrocarbons which we are concerned with in this paper, we invoke the $\sigma - \pi$ separability and express the total energy, E , as the sum of the σ -core energy, E_σ , and the π -electronic energy, E_π . In the Hückel-type one-electron approximation, E_π can be written as

$$E_\pi = N\alpha + \sum_{\mu < \nu} 2p_{\mu\nu}\beta_{\mu\nu} \quad (1)$$

where N , α , $p_{\mu\nu}$ and $\beta_{\mu\nu}$ are the number of π -electrons, the Coulomb integral (for the $2p_z$ AO of the C atom) [2], the bond order and the resonance integral for the $\mu - \nu$ bond, respectively. Since we are concerned only with in-plane deformations in conjugated molecules, excited states appearing in various matrix elements are taken to be π -electronic ones. Thus, the various matrix elements appearing in the expansion of E in power series of Q_i are expressed

$$\left\langle \psi_0 \left| \left(\frac{\partial^2 H}{\partial Q_i^2} \right)_0 \right| \psi_0 \right\rangle = \left(\frac{\partial^2 E_\sigma}{\partial Q_i^2} \right)_0 + 2 \sum_{\mu < \nu} p_{\mu\nu} \beta''_{\mu\nu} \left(\frac{\partial r_{\mu\nu}}{\partial Q_i} \right)_0^2 \quad (2-1)$$

$$\left\langle \psi_0 \left| \left(\frac{\partial^2 H}{\partial Q_i^2} \right)_0 \right| \psi_n^\pi \right\rangle = 2 \sum_{\mu < \nu} p_{\mu\nu}^{0n} \beta''_{\mu\nu} \left(\frac{\partial r_{\mu\nu}}{\partial Q_i} \right)_0^2 \quad (2-2)$$

$$\left\langle \psi_0 \left| \left(\frac{\partial^3 H}{\partial Q_i^3} \right)_0 \right| \psi_0 \right\rangle = \left(\frac{\partial^3 E_\sigma}{\partial Q_i^3} \right)_0 + 2 \sum_{\mu < \nu} p_{\mu\nu} \beta'''_{\mu\nu} \left(\frac{\partial r_{\mu\nu}}{\partial Q_i} \right)_0^3 \quad (2-3)$$

where β'' and β''' are the second and third derivatives of $\beta(r)$ with respect to r . Since for the bond-length variation in question ($1.3 \sim 1.5 \text{ \AA}$) the curvature of $\beta(r)$ would be very small, we may safely assume that $\beta(r)$ varies linearly with r so that β'' and β''' can be neglected. It is noted in this respect that in the Pariser-Parr-Pople SCF MO formalism, $\beta(r)$ can be interpreted as $\tilde{\beta}_{\mu\nu}(r) = (\beta_{\mu\nu}(r) + \beta_{\mu\nu}^F(r))/2$ with $\beta_{\mu\nu}^F(r) = \beta_{\mu\nu}(r) - \frac{1}{2}p_{\mu\nu}\gamma_{\mu\nu}(r)$, where $\gamma_{\mu\nu}(r)$ is the Coulomb repulsion integral, and $\tilde{\beta}_{\mu\nu}''$ and $\tilde{\beta}_{\mu\nu}'''$ are assumed to be neglected, since for the reduced bond-distance interval the curvature of the $\tilde{\beta}(r)$ would also be very small. Further, it is assumed that the nuclear anharmonic term $(1/6)(\partial^3 E_\sigma / \partial Q_i^3)_0 Q_i^3 (Q_i = Q_1 \text{ or } Q'_1)$ can be neglected, since it does not play a decisive role in determining the location of an energy minimum (see Appendix). Under the above assumptions, Eq. (2-1) retains only the first term and Eqs. (2-2) and (2-3) are neglected. The coefficients

of the various powers of Q_i in Eq. (21) of Ref. [1] are thus given as follows. In cases in which the ground state is not degenerate, we have

$$\left(\frac{\partial E}{\partial Q_i}\right)_0 = \left\langle \psi_0 \left| \left(\frac{\partial H_\pi}{\partial Q_i} \right)_0 \right| \psi_0 \right\rangle \quad (3-1)$$

$$\frac{1}{2} \left(\frac{\partial^2 E}{\partial Q_i^2} \right)_0 = \frac{1}{2} \left(\frac{\partial^2 E_\sigma}{\partial Q_i^2} \right)_0 - \sum_{n \neq 0} \frac{\left| \left\langle \psi_0 \left| \left(\frac{\partial H_\pi}{\partial Q_i} \right)_0 \right| \psi_n^\pi \right\rangle \right|^2}{E_n^\pi - E_0^\pi} \quad (3-2)$$

$$\frac{1}{6} \left(\frac{\partial^3 E}{\partial Q_i^3} \right)_0 = \sum_{n \neq 0} \sum_{m \neq 0} \frac{\left\langle \psi_0 \left| \left(\frac{\partial H_\pi}{\partial Q_i} \right)_0 \right| \psi_n^\pi \right\rangle \left\langle \psi_n^\pi \left| \left(\frac{\partial H_\pi}{\partial Q_i} \right)_0 \right| \psi_m^\pi \right\rangle \left\langle \psi_m^\pi \left| \left(\frac{\partial H_\pi}{\partial Q_i} \right)_0 \right| \psi_0 \right\rangle}{(E_n^\pi - E_0^\pi)(E_m^\pi - E_0^\pi)} \quad (3-3)$$

Note that in nondegenerate cases we can choose ψ_0 so that $(\partial E/\partial Q_i)_0$ may vanish. In cases in which the ground state is (doubly) degenerate, ψ_0 is replaced by ψ_{01} or ψ_{02} and the extra term A (Eq. (22) of Ref. [1]) should be added to the rhs of Eq. (3-3).

In order to estimate the values of the matrix elements appearing in Eqs. (3-1), (3-2), and (3-3), it is practically useful to introduce the transition density ρ_{nm}^π between ψ_n^π and ψ_m^π , ρ_{nm}^π being the charge density of π -electrons in ψ_n , and write

$$\left\langle \psi_n^\pi \left| \left(\frac{\partial H_\pi}{\partial Q_i} \right)_0 \right| \psi_m^\pi \right\rangle = \int \rho_{nm}^\pi \frac{\partial V_\pi}{\partial Q_i} dv \quad (4)$$

where V_π is the one electron potential energy operator. Since in this paper we are interested mainly in bond distortions in conjugated molecules, we are concerned with the two-center components (between the nearest neighboring atoms) of transition density. The matrix element, Eq. (4), is nonvanishing only when the symmetries of ρ_{nm}^π and Q_i are the same, that is, the distribution of the two-center components of ρ_{nm}^π matches with that of bond distortions in Q_i , the positive two-center component of ρ_{nm}^π corresponding to the bond shortening and the negative one to the bond lengthening. Our approach to the estimation of the values of the coefficients of the second and third powers of Q_i (Eqs. (3-2) and (3-3)) is then simply to examine whether a given molecule has reasonably low excited states that make the matrix elements $\langle \psi_0 | (\partial H_\pi / \partial Q_i)_0 | \psi_n^\pi \rangle$ and $\langle \psi_n^\pi | (\partial H_\pi / \partial Q_i)_0 | \psi_m^\pi \rangle$ nonvanishing.

Since a potential energy minimum should in principle be located along Q_1 or Q'_1 , we examine the potential energy curve along Q_1 or Q'_1 by using Eqs. (3-2) and (3-3) and determine along which of the mutually opposite directions of Q_1 or Q'_1 the energy minimum exists.

3. Applications

3.1. Molecules exhibiting the SOJT effects

We practically treat the molecules in which the ground state is nondegenerate and the lowest excited state is doubly degenerate. As has been shown in Ref. [1],

in these molecules, $(\partial^3 E/\partial Q_1'^3)_0 = (\partial^3 E/\partial Q_2'^3)_0 = 0$ for the modes of Types 2 and 3, Q_1' and Q_2' being the SO coupling modes, and $(\partial^3 E/\partial Q_1'^3)_0 \neq 0$ and $(\partial^3 E/\partial Q_2'^3)_0 = 0$ for the modes of Type 1. $(\partial^2 E/\partial Q_1'^2)_0$ is equal to $(\partial^2 E/\partial Q_2'^2)_0$ for all the modes. The present problem is to estimate the value of $(\partial^3 E/\partial Q_1'^3)_0$ for modes of Type 1 and predict along which of the mutually opposite directions of Q_1' there exists a potential energy minimum.

In estimating the third derivative of E with respect to Q_i (Eq. (3-3)), we take into account only the lowest degenerate excited state, ψ_{11} and ψ_{12} . We assume that ψ_{11} and ψ_{12} are symmetric and antisymmetric, respectively, with respect to operation σ_v . Consider first the case where ψ_0 is symmetric with respect to σ_v . Since Q_1' has been taken to be symmetric with respect to σ_v , the term $\langle \psi_0 | (\partial H_\pi / \partial Q_1')_0 | \psi_{11} \rangle \langle \psi_{11} | (\partial H_\pi / \partial Q_1')_0 | \psi_{11} \rangle \langle \psi_{11} | (\partial H_\pi / \partial Q_1')_0 | \psi_0 \rangle / (E_1 - E_0)^2$, where suffix π has been omitted, is nonvanishing, while the similar term including ψ_{12} as the excited state is vanishing. The sign of the above product of matrix elements is determined by that of $\langle \psi_{11} | (\partial H_\pi / \partial Q_1')_0 | \psi_{11} \rangle$, and which of the potential energy curves along the positive and negative directions of Q_1' is energetically more favorable is determined by the asymmetric component of the distribution of two-center components of $\rho_{11,11}$. If ψ_0 is antisymmetric with respect to σ_v , it is seen that $\rho_{22,22}$ determines the favorable direction of Q_1' . The above discussions can be applied also to a nondegenerate excited state having nearby higher doubly degenerate excited state with the same spin multiplicity.

3.1.1. Bicyclo[1.1.1]pentane-2,4,5-triyl anion. The geometrical structure with respect to the interatomic separations between the three unsaturated C atoms of this anion is governed mainly by the Möbius-type interaction of three $2p$ AO's, χ_1 , χ_2 and χ_3 (Fig. 1). Therefore, we can apply the general theory for bond distortion, although there is no real bond between unsaturated C atoms. The Möbius-type MO's constructed from the three C $2p$ AO's and the wavefunctions for the ground and lowest excited (singlet) states are presented in Table 1.

A potential energy minimum should be located along mode Q_1' (Fig. 2) if the SOJT distortion is energetically allowed. In fact, the lowest excitation energy,

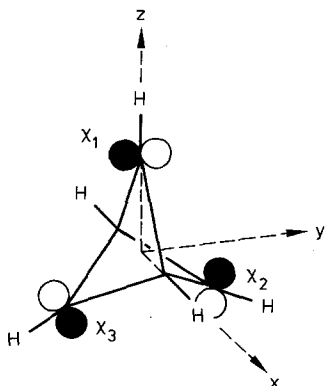


Fig. 1. Carbon $2p$ AO's and the choice of axes in the bicyclo [1.1.1]pentane-2,4,5-triyl anion

Table 1. MO's and wavefunctions for the ground and lower excited (singlet) states of the bicyclo.1.1]pentane-2,4,5-triyl anion

MO's	
$\phi_1(e', +)^a$	$= \frac{1}{\sqrt{2}}(\chi_2 - \chi_3)$
$\phi_2(e', -)$	$= \frac{1}{\sqrt{6}}(2\chi_1 - \chi_2 - \chi_3)$
$\phi_3(a'_2, -)$	$= \frac{1}{\sqrt{3}}(\chi_1 + \chi_2 + \chi_3)$
State wavefunctions	
$\psi_0(A'_1, +)^a$	$= 1\bar{1}2\bar{2}\rangle$
$\psi_{11}(E', +)$	$= \frac{1}{\sqrt{2}}\{ 1\bar{1}2\bar{3}\rangle - 1\bar{1}23\rangle\}$
$\psi_{12}(E', -)$	$= \frac{1}{\sqrt{2}}\{ 2\bar{2}1\bar{3}\rangle - 2\bar{2}13\rangle\}$

^a Irreducible representations in the round brackets are those of the original point group (D_{3h}). MO's or state functions having the positive sign are symmetric with respect to σ_v , and those having the negative sign antisymmetric. The same expression is used in the following Tables

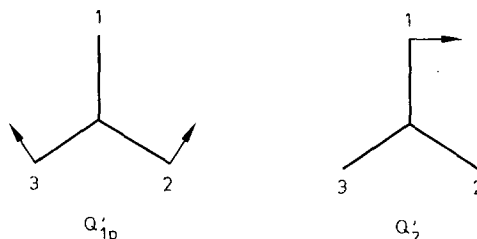


Fig. 2. The SO coupling modes in the bicyclo [1.1.1]pentane-2,4,5-triyl anion

$E_1 - E_0$, of the anion calculated by using the CNDO/S MO method is 1.6 eV, the value being considerably smaller than the critical value (ca. 4 eV) for the occurrence of the SOJT angle bending [3]. Since ψ_0 is symmetric with respect to σ_v , along which of the positive and negative directions of Q'_1 the energy minimum exists is determined by the distributions of two-center components of $\rho_{11,11}$, which is expressed in terms of the MO's as

$$\rho_{11,11} = 2\phi_1^2 + \phi_2^2 + \phi_3^2 \quad (5)$$

The component $\phi_1^2 + \phi_2^2 + \phi_3^2$ of $\rho_{11,11}$ is totally symmetric in the original point group, and the asymmetric component is ϕ_1^2 . The distribution of the signed values of the two-center components of ϕ_1^2 shown in Fig. 3 indicates that the energy minimum should be located along the negative direction of Q'_1 . In view of the smallness of $E_1 - E_0$, the energy lowering along the negative direction of Q'_1 is expected to be fairly large.

Our conclusion that the stable geometrical structure of the anion is of Y shape is in agreement with the theoretical result by Stohrer and Hoffmann [4], who calculated the potential energy surface for the anion by using the extended Hückel

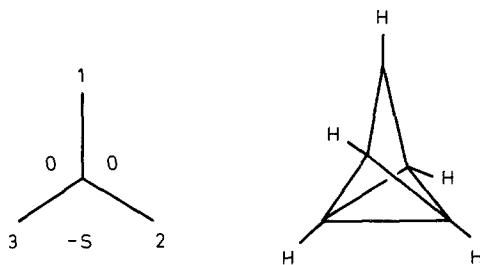


Fig. 3. Two-center components of ϕ_2^2 in the bicyclo[1.1.1]pentane-2,4,5-triyl anion (left) and the tricyclo[2.1.0.0]pentane-5-yl anion (right). S is the overlap density between the neighboring MO's ($S < 0$)

MO method and concluded that the stable structure of the anion is tricyclo^o[2.1.0.0]pentane-5-yl anion shown in Fig. 3.

3.1.2. The ${}^1B_{1u}$ and ${}^3B_{1u}$ excited states of benzene. It is well known [5] that the second excited singlet state, ${}^1\psi_2(B_{1u})$, and the first excited triplet state, ${}^3\psi_1(B_{1u})$, of benzene undergo the SOJT bond distortions by coupling with the third excited singlet state, ${}^1\psi_3(E_{1u})$, and the second excited triplet state, ${}^3\psi_2(E_{1u})$, respectively, through the E_{2g} modes (Q'_1 and Q'_2 , shown in Fig. 2 of Ref. [1]). If we confine ourselves to the singly excited π -electronic states, $\langle \psi(E_{1u}) | (\partial H_\pi / \partial Q'_i)_0 | \psi(E_{1u}) \rangle$ ($\psi(E_{1u}) = {}^1\psi_3(E_{1u})$ or ${}^3\psi_2(E_{1u})$) is vanishing, since the distributions of charge densities of $|{}^1\psi_3(E_{1u})|^2$ and $|{}^3\psi_2(E_{1u})|^2$ are both totally symmetric. In order for the product of matrix elements not to vanish, we have to invoke at least doubly excited π -electronic states, which are very high in energy. Thus, we conclude that the difference in energy between the quinoid and antiquinoid forms should be very small. According to the calculated results by Nakayama et al. [6], who used the Pariser-Parr-Pople type CI MO method with the two sets of empirical parameters, in ${}^1\psi_2(B_{1u})$, the antiquinoid form is lower in energy than the quinoid one by 0.0 and 2.4 kcal mol⁻¹ and in ${}^3\psi_1(B_{1u})$, the quinoid form is lower in energy than the antiquinoid one by 1.8 and 1.9 kcal mol⁻¹.

3.2. Molecules having the degenerate ground state

3.2.1. The cyclopropenyl radical. If the radical is assumed to belong to D_{3h} , the ground states (ψ_{01} and ψ_{02}) belong to E'' of D_{3h} , and the FOJT active modes (Q_1 and Q_2 in Fig. 1 of Ref. [1]) belong to E' and are of Type 1. As has been shown in Ref. [1], a potential energy minimum is found along Q_1 , and its location is governed by the coefficients of the second and third powers of Q_1 . The excited states that are effective for the second-order coupling belong to A''_1 , A''_2 and E'' . Now according to the Pariser-Parr-Pople half-electron SCF MO calculations by Kuhn *et al.* [7], the energy differences between the ground state and the above active states are larger than ca. 8 eV. Therefore, the energy lowering due to Eq. (3-2) for ψ_{01} and ψ_{02} are both very small and almost the same. Since the above excitation energies appear also in Eq. (3-3) as denominators, we conclude that the difference in energy between the two forms, an oblate triangle and a prolate triangle form, due to the second- and third-order effects should be very small. The *ab initio* (STO-3G) optimization of the geometrical structure of the radical

by Davidson and Borden [8] shows that the prolate triangle form is lower in energy than the oblate triangle one only by $1.0 \text{ kcal mol}^{-1}$.

3.2.2. The cyclopentadienyl radical. The FOJT active modes (Q_1 and Q_2) belong to E_2' (Fig. 4) and are of Type 2. It has been shown in Ref. [1] that in the framework of the third-order approximation with respect to the FOJT active modes of Type 2, we cannot differentiate between the potential energies along Q_1 and Q_2 . The *ab initio* (STO-3G) calculation incorporated with the full π -configuration interactions shows that the energy difference between the two forms is actually zero [9].

In the radical under consideration, the second-order vibronic coupling of the ground states with the lowest excited state, $\psi_1(A_2'')$, is possible, the SO coupling modes being belonging to E_1' (Fig. 4). However, according to Kuhn et al. [7] the energy gap $E_1 - E_0$ is calculated to be larger than 3.0 eV , which is considerably larger than the critical energy gap (ca. 1.2 eV) for the occurrence of the SOJT bond distortion [10]. Therefore, the SOJT bond distortion does not occur in this radical.

Our conclusion as for the cyclopentadienyl radical is that the potential energy profiles along Q_1 and Q_2 are quite similar, and the radical is liable to the pseudorotation about the central conical peak of potential energy surface.

3.2.3. The cation and anion radicals of benzene. The FOJT active modes in both the radicals belong to E_{2g} and are classified into Type 1. According to the general theory of Ref. [1], a potential energy minimum should lie along Q_1 (Fig. 2 of Ref. [1]). The bond distortion along the positive direction of Q_1 leads to an antiquinoid form and that along the reverse direction to a quinoid form. In order to energetically differentiate between the two forms, we now examine the third-order term (Eq. (3-3)). In the cation radical, in order that the third-order effect may be operative, the matrix element $\langle \psi_0(E_{1g}) | (\partial H_\pi / \partial Q_i)_0 | \psi_n(\Gamma_{\psi_n}) \rangle$, ψ_0 and Q_i being ψ_{01} or ψ_{02} and Q_1 or Q_2 , respectively, must not vanish. Γ_{ψ_n} 's that satisfy the above

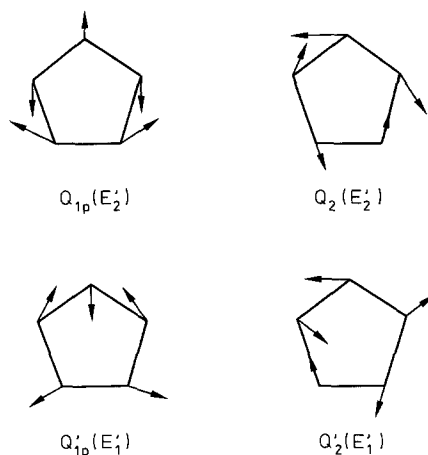


Fig. 4. The FOJT active modes, Q_1 and Q_2 , and SO coupling modes, Q'_1 and Q'_2 , of the cyclopentadienyl radical

condition are B_{1g} , B_{2g} , and E_{1g} . On the other hand, according to the MO calculations by Kuhn *et al.* [7] and Nakayama and I'Haya [11], all the excited states belonging to these representations are higher in energy than the ground state by more than 7 eV. Furthermore, in the anion radical, all the relevant excited states (belonging to A_{1u} , A_{2u} , and E_{2u}) are higher than the ground state by almost the same amount [7, 12]. We thus conclude that in both the radicals, the difference in energy between the two forms is very small. This is in agreement with the theoretical results obtained by using the semiempirical SCF CI MO method by Nakayama and I'Haya that in the cation radical, the quinoid form is lower in energy than the antiquinoid form only by $0.2 \text{ kcal mol}^{-1}$ [11], and in the anion radical, the two forms have almost the same energy [12]. The recent *ab initio* (STO-3G) calculation by Hinde *et al.* [13] shows that in the anion radical the difference in energy between the two forms is only $0.1 \text{ kcal mol}^{-1}$. Using *ab initio* (6-31G) MO method, together with the configuration interactions including the single and double excitations constructed from π -MO's, Raghavachari *et al.* [14] have recently shown that in the cation radical, the two forms have almost the same energy.

3.3. Molecules having the electronic configuration ... (e)² [15]

If we assume a molecule having the above electronic configuration to have the most symmetrical molecular geometry belonging to the highest point group, the ground state is a triplet and the next higher states are doubly degenerate singlets except for molecules of a certain type such as cyclobutadiene in which Hund's rule is violated [16]. Here we do not treat such unusual molecules (note that molecules belonging to D_{4nh} ($n \geq 1$) are excluded from our treatment for other reasons [1]). We are concerned only with the potential energy curves of the singlet states, the energetical differentiation between the undistorted triplet and a distorted singlet being out of our question.

3.3.1. Bicyclo[1.1.1]pentane-2,4,5-triyl cation. Using the MO's shown in Table 1 and taking into account configuration interactions, we can construct wavefunctions for the lower excited singlet states as shown in Table 2. The lowest degenerate singlet states undergo the FOJT distortion only after the configuration interaction. Therefore, it is concluded that the FOJT effect is very small.

The FOJT active modes, Q_1 and Q_2 , corresponding to Q'_1 and Q'_2 , respectively, shown in Fig. 2 belong to E' and are classified in Type 1. As has been shown in Ref. [1], an energy minimum should be found along Q_1 , and by taking into account the second-order terms with respect to Q_1 , we can determine along which of the mutually opposite directions of Q_1 the energy minimum is located. Now, it is shown that the distribution of the two-center components of $\rho_{01,01}$ (nontotally symmetric) $= -2cc'\phi_1\phi_3 + c'^2\phi_1^2$ matches the angle distortions along the positive direction of Q_1 , Q_{1p} , and that of $\rho_{02,02}$ (nontotally symmetric) $= 2cc'\phi_1\phi_3 + c'^2\phi_2^2$ matches the angle distortions along the negative direction of Q_1 , Q_{1n} . The most dominant second-order terms with respect to Q_1 are due to the couplings of $\psi_{01}(E')$ and $\psi_{02}(E')$ with $\psi_1(A'_1)$. It is shown that the distribution of two-center

Table 2. Wavefunctions for the ground and lower excited (singlet) states of the bicyclo[1.1.1]pentane-2,4,5-triyl cation

Without configuration interactions including	
$\psi'_{01}(E', +) = \frac{1}{\sqrt{2}}\{ 1\bar{1}\rangle - 2\bar{2}\rangle\}$	
$\psi'_{02}(E', -) = \frac{1}{\sqrt{2}}\{ 1\bar{2}\rangle - \bar{1}2\rangle\}$	
$\psi'_1(A'_1, +) = \frac{1}{\sqrt{2}}\{ 1\bar{1}\rangle + 2\bar{2}\rangle\}$	
$\psi'_{21}(E', +) = \frac{1}{\sqrt{2}}\{ 1\bar{3}\rangle - \bar{1}3\rangle\}$	
$\psi'_{22}(E', -) = \frac{1}{\sqrt{2}}\{ 2\bar{3}\rangle - \bar{2}3\rangle\}$	

With the (singly excited) configuration interactions including	
$\psi_{01}(E', +) = c\psi'_{01} - c'\psi'_{21} = \frac{c}{\sqrt{2}}\{ 1\bar{1}\rangle - 2\bar{2}\rangle\} - \frac{c'}{\sqrt{2}}\{ 1\bar{3}\rangle - \bar{1}3\rangle\}$	
$\psi_{02}(E', -) = c\psi'_{02} + c'\psi'_{22} = \frac{c}{\sqrt{2}}\{ 1\bar{2}\rangle - \bar{1}2\rangle\} + \frac{c'}{\sqrt{2}}\{ 2\bar{3}\rangle - \bar{2}3\rangle\}$	
$\psi_1(A'_1, +) = \psi'_1$	
$\psi_{21}(E', +) = c'\psi'_{01} + c\psi'_{21} = \frac{c'}{\sqrt{2}}\{ 1\bar{1}\rangle - 2\bar{2}\rangle\} + \frac{c}{\sqrt{2}}\{ 1\bar{3}\rangle - \bar{1}3\rangle\}$	
$\psi_{22}(E', -) = c'\psi'_{02} - c\psi'_{22} = \frac{c'}{\sqrt{2}}\{ 1\bar{2}\rangle - \bar{1}2\rangle\} - \frac{c}{\sqrt{2}}\{ 2\bar{3}\rangle - \bar{2}3\rangle\}$	
c and $c' > 0$ and $c^2 + c'^2 = 1$.	

components of $\rho_{01,1}$ (nontotally symmetric) = $c(\phi_1^2 - \phi_2^2) - c'\phi_1\phi_3$ matches the angle distortions along Q_1 , and that of $\rho_{02,1}$ (nontotally symmetric) = $2c\phi_1\phi_2 + c'\phi_2\phi_3$ matches the angle distortions along Q_2 . Thus, it is revealed that the second-order terms energetically favor the distortion along Q_{1p} and, consequently, a T -type form. The energetically most dominant third-order term with respect to Q_1 is $\langle \psi_{01} | (\partial H_\pi / \partial Q_1)_0 | \psi_1 \rangle \langle \psi_1 | (\partial H_\pi / \partial Q_1)_0 | \psi_{21} \rangle \langle \psi_{21} | (\partial H_\pi / \partial Q_1)_0 | \psi_{01} \rangle Q_1^3 / (E_1 - E_0)(E_2 - E_0)$. The examination of the distribution of two-center components of $\rho_{01,1}\rho_{1,21}\rho_{21,01}$ reveals that the T -type form would further be stabilized by the above term. However, the actual energy lowering due to the third-order term should be quite small on account of the large value of $E_2 - E_0$ (ca. 10 eV). Further, term A can be neglected because of the smallness of the FOJT effect. All the MO calculations of the geometrical structure of the cation so far made [4, 17, 18] show that the T -form (the pyramidal form (C_{4v})) is lower in energy than the Y -form. However, all these calculations are insufficient in the sense that the

configuration interactions are not taken into account. Further, in these calculations a comparison between the energies of the *T*-form singlet and the triangular triplet has not been made. Finally, it is remarked that in the cation under consideration, the potential energy profiles along Q_{1p} and Q_{1n} can be differentiated by the terms up to the second-order, which is due to the fact that the most important second-order active excited state is nondegenerate and it couples only with one of the ground states, ψ_{01} .

In addition, it is interesting to mention the geometrical structures of the cyclopropenyl anion and the triaziridenyl dication. The electronic features of the various states of these molecules are quite similar to those of the cation discussed just above, particularly in the sense that the second-order active excited state is nondegenerate, the other states being very high in energy. It is therefore expected that in both molecules an oblate triangle form corresponding to the *T*-form of the above cation is more stable than a prolate triangle form. Davidson and Borden [8, 19, 20] have analyzed the potential energy profiles along the FOJT active modes (Fig. 1 of Ref. [1]) of the anion and the dication on the basis of the perturbation theory and reached the same conclusion. Further, *ab initio* calculations show that an oblate triangle form is lower in energy than a prolate triangle one by 7.3 kcal mol⁻¹ for the anion [8] and by 8.6 kcal mol⁻¹ for the dication [20].

3.3.2. The cyclopentadienyl cation. Unlike in the molecules treated above, the FOJT active and SO coupling modes in this cation belong to the different irreducible representations, i.e. E'_1 and E'_2 , respectively (Fig. 4). The state functions including π -configuration interactions (π -CI's) and π -MO's are presented in Table 3. The FOJT effect should be very small since it becomes operative only if the π -CI's are taken into account. On the other hand, a strong SOJT effect is expected since the most important SOJT active state is the nondegenerate lowest excited state, $\psi_1(A'_1)$. According to the general theory of Ref. [1], the SOJT energy lowering along Q'_1 is larger than that along Q'_2 . We then consider the third-order terms with respect to Q'_1 . In order to use the lowest excited state $\psi_1(A'_1)$ as an effective excited state in the third-order terms, a relevant excited state $\psi_n(\Gamma_{\psi_n})$ higher in energy than ψ_1 must satisfy the following conditions: $A'_1 \times \Gamma_{\psi_n} \supseteq E'_2$ and $E'_2 \times \Gamma_{\psi_n} \supseteq E'_2$. However, there is no irreducible representation that satisfies the above conditions in D_{5h} . Moreover, since $E'_2 \times E'_2 = A'_1 + A'_2 + E'_1$, excited states belonging to E'_2 do not contribute to the third-order terms. Finally, it is shown that the product of matrix elements $\langle \psi_{01}(E'_2) | (\partial H_\pi / \partial Q'_1)_0 | \psi_n(E'_1) \rangle \times \langle \psi_n(E'_1) | (\partial H_\pi / \partial Q'_1)_0 | \psi_n(E'_1) \rangle \langle \psi_n(E'_1) | (\partial H_\pi / \partial Q'_1)_0 | \psi_{01}(E'_2) \rangle$, ψ_n being ψ_{21} or ψ_{41} , is group theoretically nonvanishing but very small: if the state functions without configuration interactions are used, $\rho_{01,21}$ and $\rho_{41,41}$ belong to E'_1 and A'_1 , respectively, so that the matrix elements including these terms are vanishing. The third-order terms with respect to Q'_1 are thus all very small, and we conclude that we cannot actually differentiate between the potential energy profiles along Q'_{1p} and Q'_{1n} . Borden and Davidson [9, 19] have optimized the geometrical structure of the cation by using *ab initio* (STO-3G) full π -CI MO method. According to their results, the local energy minima are found along the positive

Table 3. π MO's and wavefunctions after configuration interaction for the ground and lower excited (singlet) states of the cyclopentadienyl cation

π MO's
$\phi_1(a_2'', +) = \frac{1}{\sqrt{5}}(\chi_1 + \chi_2 + \chi_3 + \chi_4 + \chi_5)$
$\phi_2(e_1'', +) = \sqrt{\frac{2}{5}}(\chi_1 + a\chi_2 + b\chi_3 + b\chi_4 + a\chi_5)$
$\phi_3(e_1'', -) = \sqrt{\frac{2}{5}}(c\chi_2 + d\chi_3 - d\chi_4 - c\chi_5)$
$\phi_4(e_2'', -) = \sqrt{\frac{2}{5}}(d\chi_2 - c\chi_3 + c\chi_5 - d\chi_5)$
$\phi_5(e_2'', +) = \sqrt{\frac{2}{5}}(\chi_1 + b\chi_2 + a\chi_3 + a\chi_4 + b\chi_5)$
$a = \cos \frac{2}{3}\pi, b = \cos \frac{4}{3}\pi, c = \sin \frac{2}{3}\pi, \text{ and } d = \sin \frac{4}{3}\pi$

State wavefunctions
$\psi_{01}(E'_2, +) = \frac{c}{\sqrt{2}}\{ 1\bar{1}2\bar{2}\rangle - 1\bar{1}3\bar{3}\rangle\} - \frac{c'}{2}\{ 1\bar{1}2\bar{5}\rangle - 1\bar{1}2\bar{5}\rangle - 1\bar{1}3\bar{4}\rangle + 1\bar{1}3\bar{4}\rangle\}$
$\psi_{02}(E'_2, -) = \frac{c}{\sqrt{2}}\{ 1\bar{1}2\bar{3}\rangle - 1\bar{1}2\bar{3}\rangle\} + \frac{c'}{2}\{ 1\bar{1}2\bar{4}\rangle - 1\bar{1}2\bar{4}\rangle + 1\bar{1}3\bar{5}\rangle - 1\bar{1}3\bar{5}\rangle\}$
$\psi_1(A'_1, +) = \frac{1}{\sqrt{2}}\{ 1\bar{1}2\bar{2}\rangle + 1\bar{1}3\bar{3}\rangle\}$
$\psi_{21}(E'_1, +) = \frac{d}{\sqrt{2}}\{ 1\bar{2}3\bar{3}\rangle - \bar{1}23\bar{3}\rangle\} - \frac{d'}{2}\{ 1\bar{1}2\bar{5}\rangle - 1\bar{1}2\bar{5}\rangle + 1\bar{1}3\bar{4}\rangle - 1\bar{1}3\bar{4}\rangle\}$
$\psi_{22}(E'_1, -) = \frac{d}{\sqrt{2}}\{ 1\bar{3}2\bar{2}\rangle - \bar{1}32\bar{2}\rangle\} - \frac{d'}{2}\{ 1\bar{1}2\bar{4}\rangle - 1\bar{1}2\bar{4}\rangle - 1\bar{1}3\bar{5}\rangle + 1\bar{1}3\bar{5}\rangle\}$
$\psi_{31}(E'_2, +) = \frac{c'}{\sqrt{2}}\{ 1\bar{1}2\bar{2}\rangle - 1\bar{1}3\bar{3}\rangle\} + \frac{c}{2}\{ 1\bar{1}2\bar{5}\rangle - 1\bar{1}2\bar{5}\rangle - 1\bar{1}3\bar{4}\rangle + 1\bar{1}3\bar{4}\rangle\}$
$\psi_{32}(E'_2, -) = -\frac{c'}{\sqrt{2}}\{ 1\bar{1}2\bar{3}\rangle - 1\bar{1}2\bar{3}\rangle\} + \frac{c}{2}\{ 1\bar{1}2\bar{4}\rangle - 1\bar{1}2\bar{4}\rangle + 1\bar{1}3\bar{5}\rangle - 1\bar{1}3\bar{5}\rangle\}$
$\psi_{41}(E'_1, +) = \frac{d'}{\sqrt{2}}\{ 1\bar{2}3\bar{3}\rangle - \bar{1}23\bar{3}\rangle\} + \frac{d}{2}\{ 1\bar{1}2\bar{5}\rangle - 1\bar{1}2\bar{5}\rangle + 1\bar{1}3\bar{4}\rangle - 1\bar{1}3\bar{4}\rangle\}$
$\psi_{42}(E'_1, -) = \frac{d'}{\sqrt{2}}\{ 1\bar{3}2\bar{2}\rangle - \bar{1}32\bar{2}\rangle\} + \frac{d}{2}\{ 1\bar{1}2\bar{4}\rangle - 1\bar{1}2\bar{4}\rangle - 1\bar{1}3\bar{5}\rangle + 1\bar{1}3\bar{5}\rangle\}$
$c \text{ and } c' > 0 \text{ and } c^2 + c'^2 = 1.$
$d \text{ and } d' > 0 \text{ and } d^2 + d'^2 = 1.$

and negative directions of Q'_1 and the two minima have almost the same energy. The true energy minimum corresponds to the triplet state belonging to D_{5h} , and they have concluded that the pseudorotation about the D_{5h} energy minimum should be essentially free. The pseudorotation is essentially free if the potential energy curves along Q'_1 and Q'_2 are almost the same, that is, if the numerical coefficient b'_2 of the second-order term with respect to Q'_1 in Eq. (15) of Ref. [1] is accidentally very small.

The cyclopentadienyl cation is one of the typical examples in which the SOJT effect predominates over the FOJT effect.

4. Concluding remarks

The molecular symmetries and shapes of the conjugated molecules predicted by examining the potential energy curves expanded in the power series of the relevant modes, including up to the cubic power are in good qualitative agreement with those predicted by using the various MO methods and available experimental ones.

The most critical assumption we have made is the neglect of the matrix elements including $\beta''(r)$ and $\beta'''(r)$ (Eqs. (2.1), (2.2), and (2.3)). In fact, $\beta''(r)$ and $\beta'''(r)$ are not necessarily negligibly small, even though $\beta(r)$ can safely be approximated to be a linear function of r . The error in energy due to the neglect of $\beta''(r)$ and $\beta'''(r)$ may amount to the ca. 2 kcal mol⁻¹ in some cases (the $^1B_{1u}$ and $^3B_{1u}$ excited states of benzene and the cyclopropenyl radical). Our method should be accepted within the limit of this error.

Appendix. Estimation of the values of the nuclear anharmonic terms for bond distortions in conjugated hydrocarbons

We first assume for a conjugated hydrocarbon the σ - π separability. The value of the anharmonic term of the σ -core energy, E_σ , $(1/6)(\partial^3 E_\sigma / \partial Q_1^3)_0 Q_1^3$, for bond distortion can be estimated as follows. The bond order-bond length relationship including up to the third-order anharmonic term can be written as

$$r = r_0 - \frac{k_2}{k_3} - \left[\left(\frac{k_2}{k_3} \right)^2 - \frac{4\beta'}{k_3} p \right]^{1/2} \quad (\text{A1})$$

where $k_2 = (\partial^2 E_\sigma / \partial r^2)_0$, $k_3 = (\partial^3 E_\sigma / \partial r^3)_0$, p is the bond order, β' is the first derivative of the resonance integral β , and r_0 is the bond length of the single bond between the approximately sp^2 hybridized carbon atoms. Substituting the bond orders and observed bond lengths of ethylene, benzene, and graphite into Eq. (A1), we can determine the values of r_0 and k_2/k_3 . In order to determine the value of k_3 , we use the equilibrium condition $(\partial E / \partial Q_b)_{r=1.397} = 0$, where Q_b is the breathing mode for benzene and the force constant $k_b = (\partial^2 E / \partial Q_b^2)_{r=1.397}$. The total energy E is taken to be the sum of E_σ and E_π :

$$E_\sigma(r) = E_\sigma^0 + 3k_2(r - r_0)^2 + k_3(r - r_0)^3 \quad (\text{A2})$$

$$E_{\pi}(r) = 6\alpha + 8\beta + \frac{3}{2}\gamma_{11} - \frac{19}{6}\gamma_{14} \quad (\text{A3})$$

The functional form of β is assumed to be $\beta(r) = -2.38 \exp(-a(r-1.397))$ eV and that of the electron repulsion integral, γ , to take Mataga-Mishimoto's formula [21]. We thus determine the value of k_3 to be $-85.50 \text{ eV } \text{\AA}^{-3}$. For a triangular conjugated hydrocarbon belonging to D_{3h} , $Q_1 = (1/\sqrt{6})(2\Delta r_1 - \Delta r_2 - \Delta r_3)$ and the anharmonic term is written as

$$\frac{1}{6} \left(\frac{\partial^3 E_{\sigma}}{\partial Q_1^3} \right)_0 Q_1^3 = \frac{k_3}{6} \sum_{i=1}^3 \left(\frac{\partial(r_i - r_e)}{\partial Q_1} \right)_0^3 Q_1^3 = -\frac{85.50}{6\sqrt{6}} Q_1^3 \text{ eV} \quad (\text{A4})$$

where r_e is the equilibrium bond length. If we assume a rather large value of 0.1 \AA for Q_1 we obtain

$$\frac{1}{6} \left(\frac{\partial^3 E_{\sigma}}{\partial Q_1^3} \right)_0 Q_1^3 = -5.82 \times 10^{-3} \text{ eV} = -0.13 \text{ kcal mol}^{-1}. \quad (\text{A5})$$

For larger molecules, the anharmonic term should be smaller on account of a smaller normalization constant in $Q_1(r_1, \dots, r_b, \dots)$. Obviously, for Q_2 the third-order nuclear anharmonic term is vanishing.

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