

# Pseudo Jahn-Teller effects and optical activities of negatively curved hydrocarbons

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**Abstract.** As a fundamental study on energetics of negatively curved structures, puckering energetics of  $[n]$ circulene is studied in view of vibronic interactions. In  $[7]$ circulene, the  $D_{7h}$  geometry is subject to pseudo Jahn-Teller effect (PJT) and unstable with respect to the  $E_1''$ ,  $E_2''$ , and  $E_3''$  vibrational modes. It is distorted into  $C_s$  or  $C_2$  geometries to form valleys of the potential surface ca. 9 kcal/mol below the  $D_{7h}$  geometry. The  $C_2$  structure is slightly stable than  $C_s$  one, which is consistent with experiments. The resultant  $C_2$  geometry is optically active, and the CD (circular dichroism) and ORD (optical rotatory dispersion) spectra are well simulated. This type of optical activities is interesting in that they should be proportional to the PJT-distortion. PJT-induced optical activity in  $[2m+1]$ circulenes should be mainly originated from vibronic coupling constants in the initial and final states, which leads to helical rule characteristic of  $C_2$  molecules.

## 1. Introduction

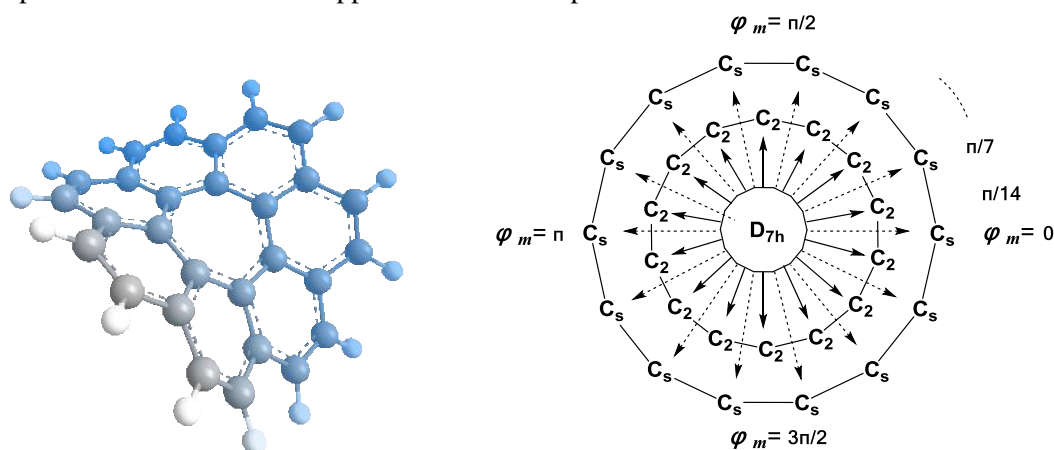
Curved structures are often found in large-size hydrocarbons, fullerenes, nanotubes, and modified graphenes [1, 2]. The Gauss curvatures  $K$  of these materials are classified into three groups: 1) positive curvature ( $K > 0$ ) in bowed structures, 2) zero curvature ( $K = 0$ ) in 'flat' structures, and 3) negative curvature ( $K < 0$ ) in saddled structures. Small circulenes such as  $[5]$ circulene (corannulene) and many fullerenes belong to the first group. Normal nanotubes, graphene sheets belong to the second group, in which the local structures are regarded as 'flat'. Materials classified into the third group are often called negatively curved structures, in which the Gauss curvatures are negative due to the saddle structures. Intuitively, the saddled structures with negative curvatures come from different signs of the curvatures along the principal axes. Large circulenes, some jointed or branched nanotubes, and warped graphenes [2] are classified into the third group. The chemical and physical properties of such negatively curved structures have not been scrutinized yet, because of difficulty in the synthesis and characterization [1].

Of all the negatively curved structures, saddled geometries induced by seven-membered rings are essentially important in that the strain energy is not so large and the conformations are not so complex to grasp the fundamental features of the saddled carbons. In this sense,  $[7]$ circulene (figure 1) is the most important molecule to grasp the theoretical aspects of the puckering energetics and to predict chemical properties characteristic of the distorted geometries.  $[7]$ circulene was first synthesized by Yamamoto et al. in 1983 [3], and the structure at room temperature was characterized by X-ray diffraction. The stable structure was found to have a  $C_2$  geometry, and the geometry was theoretically reproduced by Shen et al., of which stability relative to the  $D_{7h}$  structure was estimated to be ca. 8 kcal/mol [4]. Though their vibration analysis suggested that there were very low-frequency vibration



modes, the origin of the puckering energetics was not pursued in detail. Intuitively, degenerate low-frequency vibrations seem to induce shallow valleys in the potential surface through the pseudo rotations around the  $D_{7h}$  geometry. Then, the degenerate puckering vibrational modes cause two principal stable geometries with  $C_2$  and  $C_s$  symmetry. Until now, however, the  $C_s$  geometry of [7]circulene has not been found. Thus, it seems meaningful to scrutinize the puckering energetics of [7]circulene in view of the vibronic interactions, that is, pseudo Jahn-Teller effect (PJT). In particular, specification of the active electronic states and the active vibrational modes are of interest in relation to the resultant geometries. Moreover, chemical properties induced by the PJT is worth analysing for characterization of the molecular structures and for applications. Above all, the optical activities are important, because the  $C_2$  and  $C_s$  geometries are thereby distinguished experimentally. Indeed, di-bromo and di-methyl derivatives of [7]circulene are optically active, and the one of the enantiomers afforded CD (circular dichroism) spectra [3]. The ORD (optical rotatory dispersion) spectra should also be obtained by direct observation or Kramers-Kronig transformation of the CD spectra.

The theoretical calculations of the CD/ORD spectra will serve as a foundation for developing optical active carbons. The simulated spectra are applicable to grasp the optical activities of more extended systems with a few saddle points such as defective graphenes, warped graphenes, and higher circulenes. In this study, geometries and optical activities of higher circulenes are also analysed in view of the amplitude pattern of the orbitals and puckering vibrational modes. General aspects of PJT-induced optical activities and some applications are also presented.



**Figure 1.** [7]circulene ( $C_2$  geometry) and the pseudo rotation in  $D_{7h}$  point group.

## 2. Pseudo Jahn-Teller effect of [7]circulene

The origin of the instability in non-degenerate polyatomic systems is vibronic contribution only [5]. Puckering of planar molecules has also been rationalized to PJT, and the advances in general theory have been reviewed in detail [6]. Recent studies cover not only small molecules but also two-dimensional thin films such as inorganic graphene analogues [7]. Therefore, structural analysis along the PJT scheme is quite reasonable in [7]circulene. The subjects of interest are active vibrational modes, active excitation states, active orbitals (orbital pattern), the stable structure (point group), and energy gaps between the high and low symmetries. In the present case, the resultant chemical properties, e. g., optical activities are also of interest.

The PJT-active vibrational modes are determined by analysing the Hertzberg-Teller expansion of the Hamiltonian  $H$ :

$$H = H_0 + \left( \frac{\partial H}{\partial Q_i} \right)_0 Q_i + \frac{1}{2} \left( \frac{\partial^2 H}{\partial Q_i^2} \right)_0 Q_i^2, \quad (1)$$

$$E(Q_i) \cong E_0 + \langle \psi_0 | \left( \frac{\partial H}{\partial Q_i} \right) | \psi_0 \rangle Q_i + \frac{1}{2} \left\{ \langle \psi_0 | \left( \frac{\partial^2 H}{\partial Q_i^2} \right) | \psi_0 \rangle + 2 \sum_{n \neq 0} \frac{|\langle \psi_n | (\partial H / \partial Q_i)_0 | \psi_0 \rangle|^2}{E_0 - E_n} \right\} Q_i^2, \quad (2)$$

where  $H_0$  and  $E_0$  correspond to the non-distorted structures, and  $\psi_0$  is the original wavefunction of the high-symmetry geometry. When the state  $\psi_0$  is non-degenerate, the second term in Eq. (2) is zero except for the total symmetric modes. Two terms in the curly brackets determine the curvature of the potential surface. They consist of the classical force constant and relaxability. The former is always positive, and the latter is always negative. When the last term is dominant, PJT is induced and the curvature of the potential surface becomes negative. From the non-vanishing condition of the last term, the active vibrational modes and the excited states should belong to the same irreducible representation.

Strictly speaking, the potential curve of the ground-state energy is obtained from a secular equation. In the two-level framework, it becomes [5]:

$$E(Q_i) \cong \frac{1}{2} K_0 Q_i^2 - \sqrt{\Delta^2 + F^2 Q_i^2} + \text{const.}, \quad (3)$$

where  $2\Delta$  is energy interval between the ground state  $\Gamma$  and the most active excited state  $\Gamma'$ ,  $K_0 = \langle \Gamma | (\partial^2 H / \partial Q_i^2)_0 | \Gamma \rangle$ ,  $F = \langle \Gamma | (\partial H / \partial Q_i)_0 | \Gamma' \rangle$ . Of course  $K_0$  is the classical force constant, and  $F$  is the vibronic coupling constant. This expression can be expanded with respect to  $Q_i$ , and the approximate form within the second-order terms is essentially identical to Eq. (2).

Let us consider a regular  $j$ -sided polygon and the puckering displacement of the  $j$ -th moiety of the system,  $z_j$ . The displacement  $z_j$  is described by Cremer-Pople coordinate:

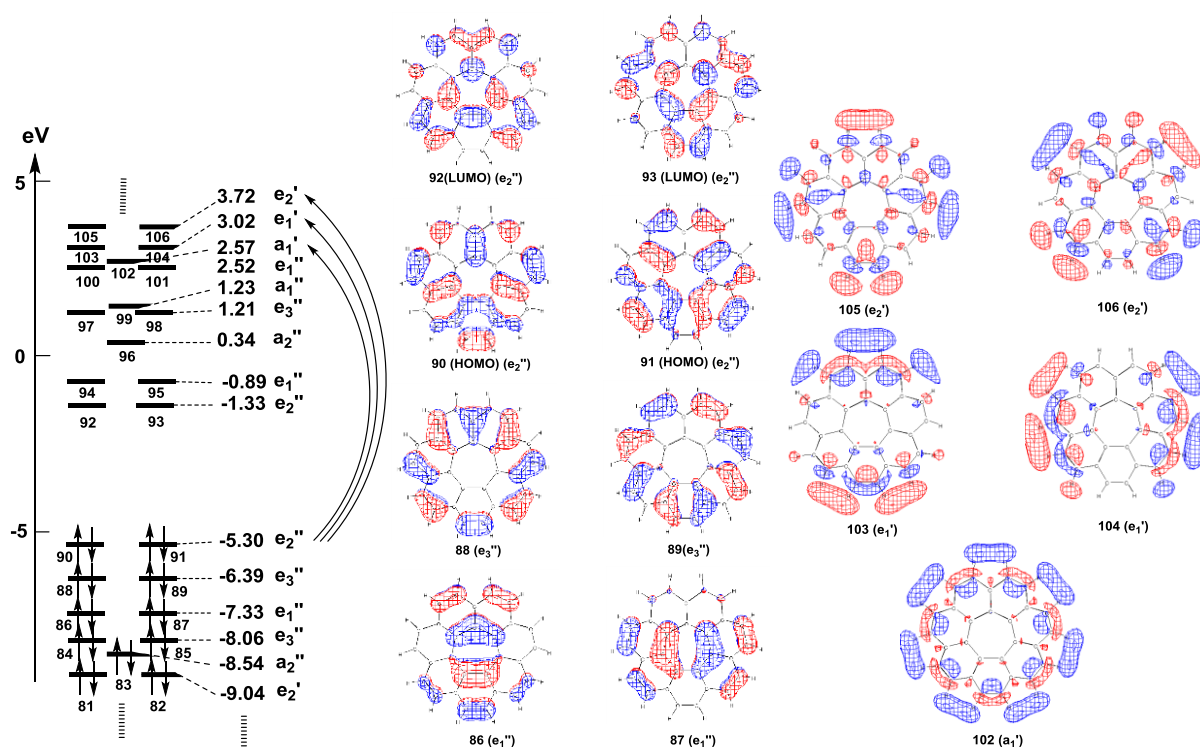
$$z_j = \sqrt{\frac{2}{N}} \cdot \sum_m^{\frac{1}{2}(N-1)} q_m \cos\{\varphi_m + 2\pi m(j-1)/N\} \quad (N = \text{odd number}), \quad (4)$$

where  $q_m$  is amplitude of the  $m$ -th puckering normal modes,  $\varphi_m$  is the phase angle which determines the symmetry of the vibrational modes. In the present case,  $N = 7$ . The larger  $m$  becomes, the more the nodes appears. Thus,  $E_1''$ ,  $E_2''$ , and  $E_3''$  puckering modes in the  $D_{7h}$  point group correspond to  $m = 1, 2$ , and  $3$ , respectively. The pseudo rotation of the present  $D_{7h}$  system is schematically shown in figure 1. A  $D_{7h}$  geometry is distorted into  $C_2$  and  $C_s$  point groups at  $n\pi/14$  ( $n$ ; integer, not the ring size).  $C_2$  and  $C_s$  geometries are alternatively appeared according to the increase of  $\varphi_m$ . Between the  $C_2$  and  $C_s$  points, the geometry belongs to  $C_1$  representation.

To grasp the active orbitals for the PJT, orbital diagram of the [7]circulene is shown in figure 2 [8]. For this purpose, very accurate calculations are unnecessary. Instead, qualitative description by Kohn-Sham orbitals at B3LYP/3-21G level of theory is given. There are active  $e''$  ( $e_1''$ ,  $e_2''$ , and  $e_3''$ ) orbitals in the occupied space, and  $e'$  ( $e_1'$ ,  $e_2'$ , and  $e_3'$ ) orbitals in the virtual space. The one-electron excitation (typical examples are shown by arrows) affords the PJT-active electronic states  $E''$  ( $E_1''$ ,  $E_2''$ , and  $E_3''$ ), according to the non-trivial direct products, e. g.:

$$\begin{array}{lll} e_2'' \otimes a_1' = e_2'' & e_3'' \otimes a_1' = e_3'' & e_1'' \otimes a_1' = e_1'' \\ e_2'' \otimes e_1' = e_1'' + e_3'' & e_3'' \otimes e_1' = e_2'' + e_3'' & e_1'' \otimes e_1' = a_1'' + a_2'' + e_1'' \\ e_2'' \otimes e_2' = a_1'' + a_2'' + e_3'' & e_3'' \otimes e_2' = e_1'' + e_2'' & e_1'' \otimes e_2' = e_1'' + e_3'' \end{array}$$

We see that one-electron excitations from  $e''$  to  $e'$  (or  $a_1'$ ) orbitals afford the PJT-active  $E''$  electronic states. Figure 2 shows the amplitude patterns of the active  $e''$  ( $e_1''$ ,  $e_2''$ , and  $e_3''$ ) orbitals. These orbitals are delocalized. In the edge region, the amplitudes are not trivial, and should be coupled with the active puckering modes. HOMO ( $e_2''$ ) is very important for the present PJT distortion. Figure 2 also shows  $e'$  ( $e_1'$ ,  $e_2'$ , and  $e_3'$ ) orbitals. These virtual orbitals are also localized at the edge region. These are coupled with puckering modes including the peripheral C-H bending displacement.

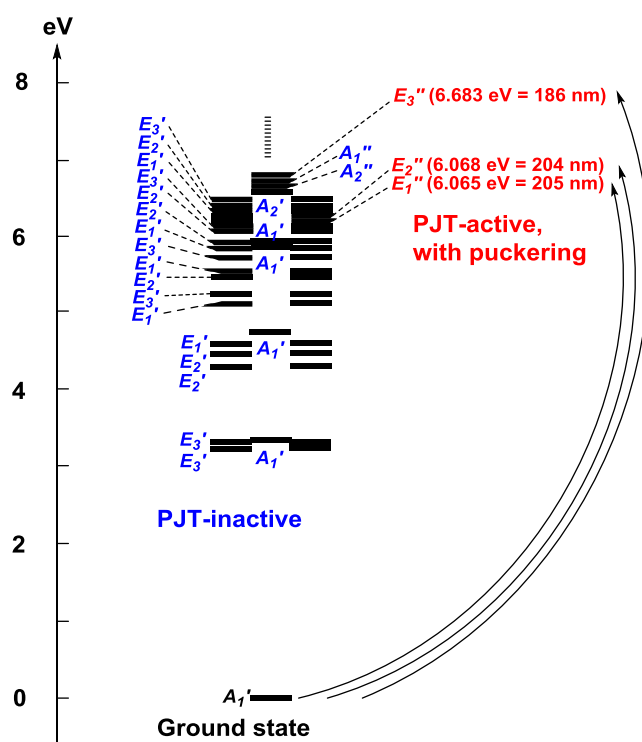


**Figure 2.** Molecular orbitals of  $D_{7h}$ -[7]circulene (B3LYP/3-21G//B3LYP/3-21G). Reprinted with permission from M. Hatanaka, *J. Phys. Chem. A*, **120**, 1074 (2016). Copyright (2016) American Chemical Society.

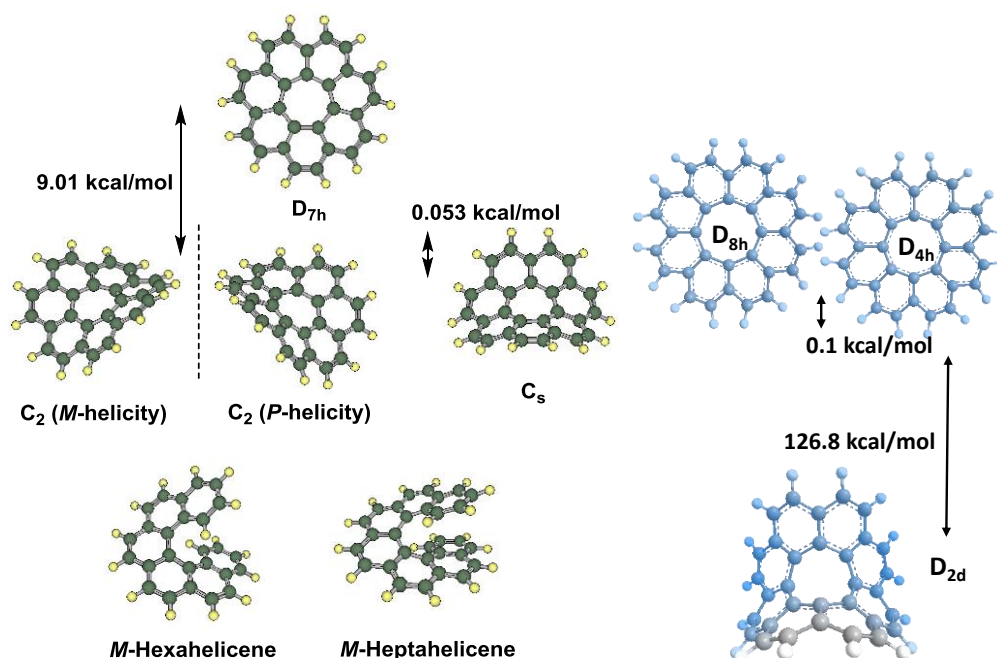
Figure 3 shows the electronic state diagram for  $D_{7h}$ -[7]circulene. The state diagrams including the excited states are obtained by configuration interactions (CI), TDDFT, MCSCF, and other post-Hartree-Fock calculations. Here, the semi-empirical single CI results at CIS(23,7)/PM3//PM3 level is shown, because only qualitative description is needed. The PJT-active states are  $E'$  ( $E_1'$ ,  $E_2'$ , and  $E_3'$ ) states, which lie ca. 6 eV above the ground state.

From the vibration analysis of the  $D_{7h}$ -[7]circulene, it was found that the lowest  $E_2''$  and  $E_3''$  vibrational modes are PJT active, though whether each frequency is real or imaginary depends on the basis sets. The frequencies became imaginary under some basis sets, in which the absolute values are below  $100\text{ cm}^{-1}$ , but real values below  $100\text{ cm}^{-1}$  were also obtained at the other basis sets [8]. The basis-set impact shows that the magnitude of the classical force constant and the relaxability is nearly the same order, and thus, the resultant vibrational frequencies become very small. However, this does not mean that the vibronic interaction itself is trivial. The displacements around the peripheral carbon and hydrogen atoms were significant, which suggests the vibronic interactions occur through interactions between the peripheral amplitudes of the active orbitals and the peripheral displacements of the active vibrational modes.

Energetically, the  $C_2$  geometry was most stable, consistent with the X-ray results [3,8]. The energy difference between  $C_2$  and  $C_s$  geometries was small (ca. 0.05 kcal/mol). The gap between  $D_{7h}$  and  $C_2$  was ca. 9 kcal/mol. We note that  $C_2$  structures are optical active if one of the enantiomers is optically resolved, because there are two asymmetric conformers with  $M$  (minus) and  $P$  (plus) helicities. This formal classification is akin to those of helicenes, which are famous optically active molecules. In particular, hexahelicene and heptahelicene are good comparative examples of the  $C_2$ -[7]circulene. Figure 4 shows the optimized structures of the [7]circulenes, hexahelicene, and heptahelicene. In view of the structural resemblance, optical activities of [7]circulene with  $C_2$  symmetry are worth analysing. Given that the optical activities of  $M$ - and  $P$ -[7]circulene are considered to be induced by vibronic interactions, role of the PJT in the resultant optical rotatory strength is theoretically described later.



**Figure 3.** State diagram (CIS(23,7)/PM3//PM3) of  $D_{7h}$ -[7]circulene.



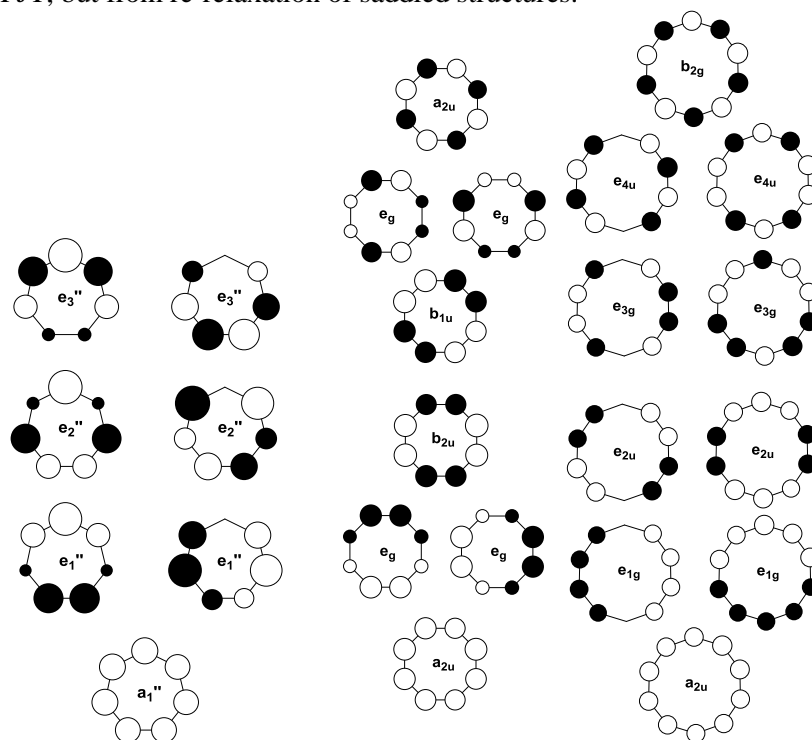
**Figure 4.** Optimized conformers of [7]circulene and [8]circulene (B3LYP/3-21G//B3LYP/3-21G). The structural resemblance between [7]circulene and helicenes is also shown.

### 3. [8], [9], and higher circulenes

[8]circulene derivatives have  $D_{2d}$  skeletons. Possible PJT scheme is considered to be  $D_{8h} \rightarrow D_{4h} \rightarrow D_{2d}$ , similar to cyclooctatetraene (COT). DFT calculations by B3LYP/3-21G//B3LYP/3-21G revealed that the most stable structure has a  $D_{2d}$  geometry, which was 127 kcal/mol below the  $D_{4h}$  structure. The  $D_{8h}$  structure is unstable, of which energy is 0.1 kcal/mol above the  $D_{4h}$  structure. The energetics is schematically shown in figure 4. These are optically inactive. In general,  $[4n]$ circulenes are optically inactive even if they are subject to any PJT. This is easily shown by amplitude pattern of the puckering vibrational modes or orbital pattern in  $D_{8h}$  (or  $D_{4h}$ ) point group, as depicted in figure 5. The ground state of a  $[4n]$ circulene is non-degenerate, and PJT active states are given by one-electron excitation from  $b_{1u}$  (or  $b_{2u}$ ) to  $a_{1g}$  (or  $a_{2g}$ ), in which one of them is vacant. Thus, the PJT active states and puckering vibrational modes belong to  $B_{1u}$  or  $B_{2u}$ , which lead to  $D_{2d}$  geometries.

[9]circulene has not been synthesized yet. However, by the semi-empirical PM3 method, I found  $C_2$  and  $C_s$  geometries below a  $D_{3h}$  geometry. The  $C_2$  and  $C_s$  geometries have almost same energy (the difference is below 0.1 kcal/mol). Though the detail of energetics and vibrational modes are not clear at present, the  $C_2$  geometry is optically active in principle. In general,  $[2m+1]$ circulenes (odd-circulenes) should be optical active due to the  $C_2$ -distorted structures. This is realized through anti-symmetric amplitude pattern of the vibrational modes.

$[4n+2]$ circulenes such as [10]circulene may also be subject to PJT. Though optically active  $C_2$ -distorted structures are possible in principle, they are probably unstable, because the adjacent atomic sites should be twisted. Twisted-saddled structures predicted by Christoph et al. [1] are probably not originated from PJT, but from re-relaxation of saddled structures.



**Figure 5.** Schematic vibrational modes in 7-, 8-, and 10-membered ring systems.

### 3. PJT-induced optical activities

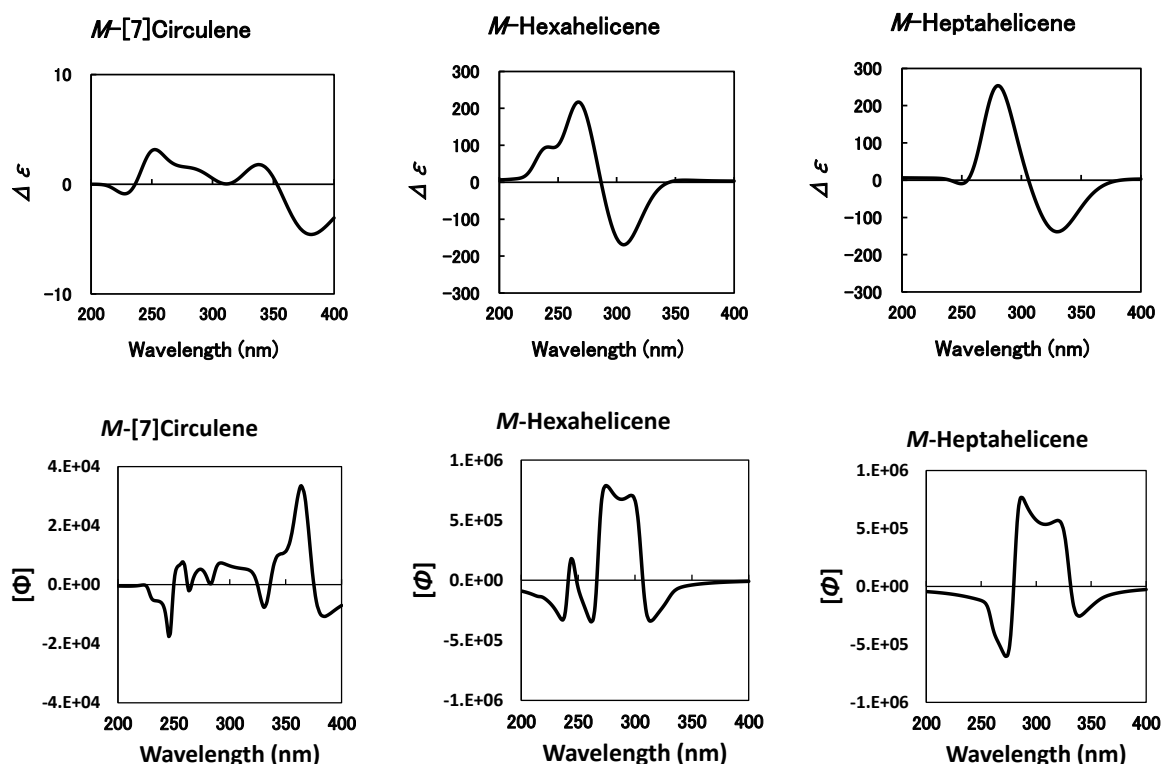
While the  $C_s$  conformers are optically inactive,  $C_2$  conformers are optically active. How strong the intensity is, compared with helicenes? Does the so-called helical rule of Cotton effect hold? Optical rotatory strength  $R_{LF}$  is calculated based on Rosenfeld formula;

$$R_{I-F} = \text{Im} \left\{ \langle I | \sum_n \mu_e(n) | F \rangle \cdot \langle F | \sum_{n'} \mu_m(n') | I \rangle \right\}, \quad (5)$$

$$[R_{I-F}] = \frac{100 R_{I-F}}{\mu_D \mu_B} = 1.08 \times 10^{40} R_{I-F} (\text{cgs}), \quad (6)$$

$$[R_{\phi_G - \phi_E}] \cong -\frac{7313}{E_E - E_G} \sum_{a,r} \sum_{b,s} c_a^r c_b^s \{ \langle a | \nabla | r \rangle \cdot \langle s | \mathbf{r} \times \nabla | b \rangle \}, \quad (7)$$

where  $I$  and  $F$  mean the initial and final states,  $\mu_e$  and  $\mu_m$  are electronic and magnetic transition moment operators, and the sum in Eq. (5) is taken for all the electrons.  $R_{I-F}$  is often reduced to the second formula, in which  $\mu_D$  and  $\mu_B$  are Debye unit and Bohr magneton, respectively. The third formula is the extended formula for the configuration interactions (CI), in which the energy and coordinates are in units of eV and Å. We calculated  $[R_{I-F}]$  by this expression by using PM3-CASCI wavefunctions [8]. The simulated CD/ORD spectra are shown in figure 6. In the long-wavelength region, minus-sign Cotton effects are seen in all cases due to anti-symmetric B excited state, which indicates the helical rule. The intensity of spectra in [7]circulene is much smaller than that in helicenes, because of the nearly degenerate electronic states.



**Figure 6.** CD (circular dichroism) and ORD (optical rotatory dispersion) spectra of [7]circulene, hexahelicene, and heptahelicene simulated by PM3-CASCI level. Reprinted with permission from M. Hatanaka, *J. Phys. Chem. A*, **120**, 1074 (2016). Copyright (2016) American Chemical Society.

The optical rotatory strength induced by the PJT is estimated by perturbation theory. When change in the magnetic transition moment is neglected, the first-order approximation affords;

$$R_{I-F} \cong \text{Im} \left\{ \begin{aligned} & \sum_{M_0 \neq I_0} \frac{\langle I_0 | \left( \frac{\partial H}{\partial Q_i} \right)_0 | M_0 \rangle}{E_{I_0} - E_{M_0}} Q_i \langle M_0 | \sum_n \mu_e(n) | F_0 \rangle \cdot \langle F_0 | \sum_{n'} \mu_m(n') | I_0 \rangle \\ & + \sum_{N_0 \neq F_0} \frac{\langle N_0 | \left( \frac{\partial H}{\partial Q_i} \right)_0 | F_0 \rangle}{E_{F_0} - E_{N_0}} Q_i \langle I_0 | \sum_n \mu_e(n) | N_0 \rangle \cdot \langle F_0 | \sum_{n'} \mu_m(n') | I_0 \rangle \end{aligned} \right\}, \quad (8)$$

where the subscript 0 means the  $D_{7h}$  geometry, index  $M_0$  and  $N_0$  run ground and excited states except for  $I_0$  and  $F_0$ . The integrals  $\langle I_0 | (\partial H / \partial Q_i)_0 | M_0 \rangle$ , etc., are vibronic coupling constants between  $I_0$  and  $M_0$ , etc. The direct product between  $I_0$  and  $M_0$  should be identical to the representation of  $(\partial H / \partial Q_i)_0$ . In the present case, for the excitation from the ground state ( $I_0$  is  $A_1'$  state),  $M_0$  should be  $E''$  ( $E_1''$  or  $E_2''$  or  $E_3''$ ) states in the first term. Similarly,  $N_0$  in the second term should also be limited so that the direct product between  $F_0$  and  $N_0$  contains one of the  $E''$  states. Anyway, only low-lying excited states contribute to the optical rotatory strength. Then,  $R_{I-F}$  is approximately proportional to the displacement  $Q_i$ , and is an odd function of  $Q_i$ . This situation corresponds to the minus and plus sign of  $R_{I-F}$ . It goes without saying that the higher-order terms should be the third-order, fifth-order, and so on. Though the precise estimation of  $R_{I-F}$  is complex, it is notable that this formalism is akin to charge transfer model of the so-called octant rule, and leads to the conventional helical rule for  $C_2$ -symmetry molecules.

Roughly estimating, magnitude of  $R_{I-F}$  is approximately proportional to  $(\text{relaxability}/\Delta E)^{0.5}$  of the initial and final states, where  $\Delta E$  ( $= 2\Delta$ ) is the energy gap to the lowest PJT active state. Given that relaxability is related to strain energy and the strain is determined nearby the irregular polygons only, optical activities of higher circulenes probably increase with the ring size. As applications to extended systems, optical activities of the heptagon-embedded graphenes are probably no so different from that of [7]circulene. Furthermore, in warped graphenes, contribution of the each heptagon to  $R_{I-F}$  is probably additive.

#### 4. Concluding remarks

Puckering energetics of [n]circulene was analysed in view of vibronic interactions. It was shown that the origin of the  $C_2$  and  $C_s$  geometries of [7]circulene is attributed to pseudo Jahn-Teller effect (PJT), and modern DFT calculations supported the experimental results. The optical activities in such  $C_2$  geometries were deduced by perturbation theory. While in  $[2m+1]$ circulenes PJT-induced optical activities are possible, in  $[4n]$  and  $[4n+2]$ circulenes, any PJT does not induce optical activities ( $[4n]$ ) or results in unstable twisted geometries ( $[4n+2]$ ). PJT-induced optical activities will be useful for fundamental analyses of CD/ORD spectra in negatively curved structures.

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