

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

M Hatanaka

Graduate School of Engineering, Tokyo Denki University, 5 Senju-Asahi-cho,
Adachi-ku, Tokyo 120-8551, Japan

E-mail: mhatanaka@xug.biglobe.ne.jp

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.

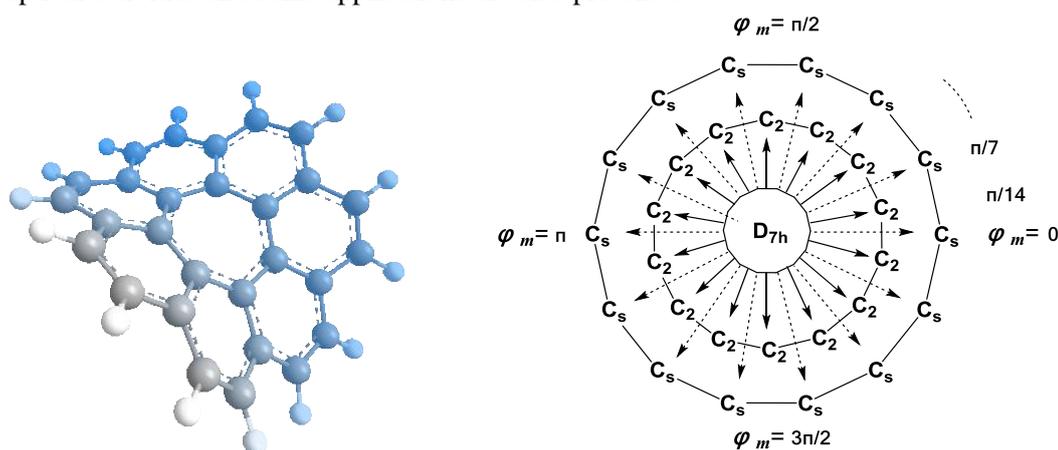


Figure 1. [7]circulene (C_2 geometry) and the pseudo rotation in D_{7h} point group.

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 :

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

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

where H_0 and E_0 correspond to the non-distorted structures, and ψ_0 is the original wavefunction of the high-symmetry geometry. When the state ψ_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]:

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

where 2Δ is energy interval between the ground state Γ and the most active excited state Γ' , $K_0 = \langle \Gamma | (\partial^2 H / \partial Q_i^2)_0 | \Gamma \rangle$, $F = \langle \Gamma | (\partial H / \partial Q_i)_0 | \Gamma' \rangle$. 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:

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

where q_m is amplitude of the m -th puckering normal modes, φ_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 φ_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.

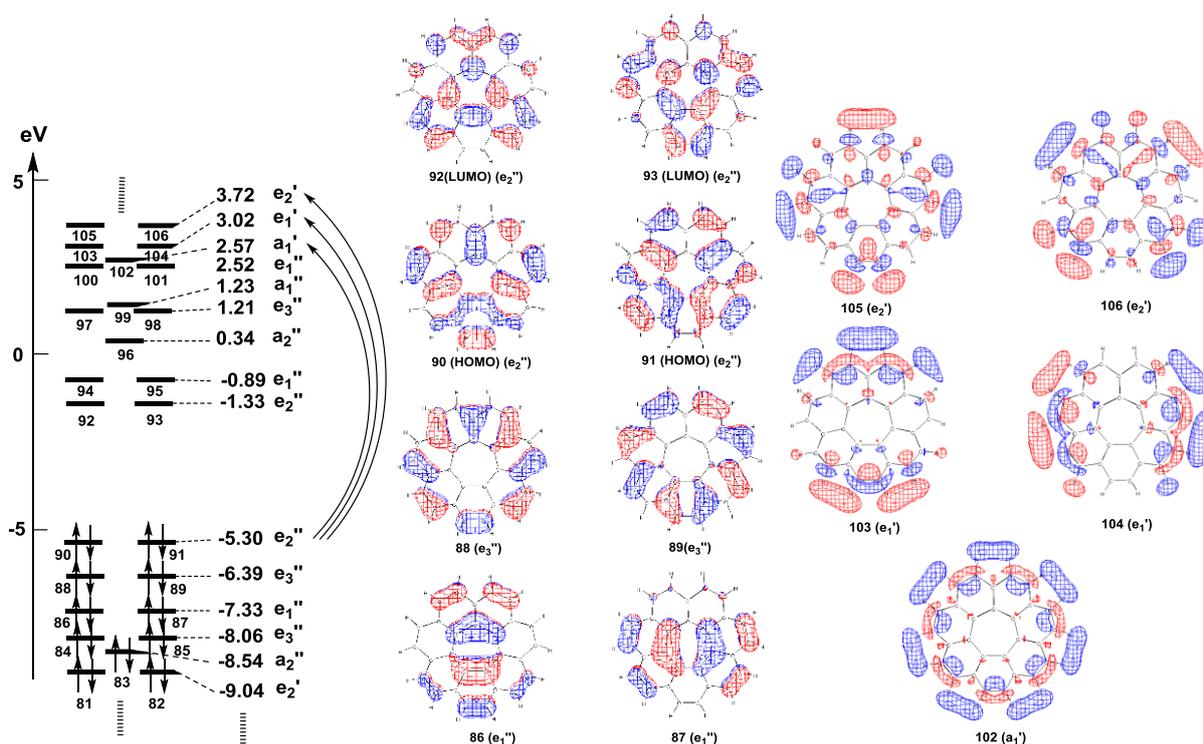


Figure 2. Molecular orbitals of D_{7h} -[7]circulene (B3LYP/3-21G//B3LYP/3-21G). Reprinted with permission from M. Hatanaka, *J. Phys. Chem. A*, **120**, 1074 (2016). Copyright (2016) American Chemical Society.

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 cm^{-1} , but real values below 100 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.

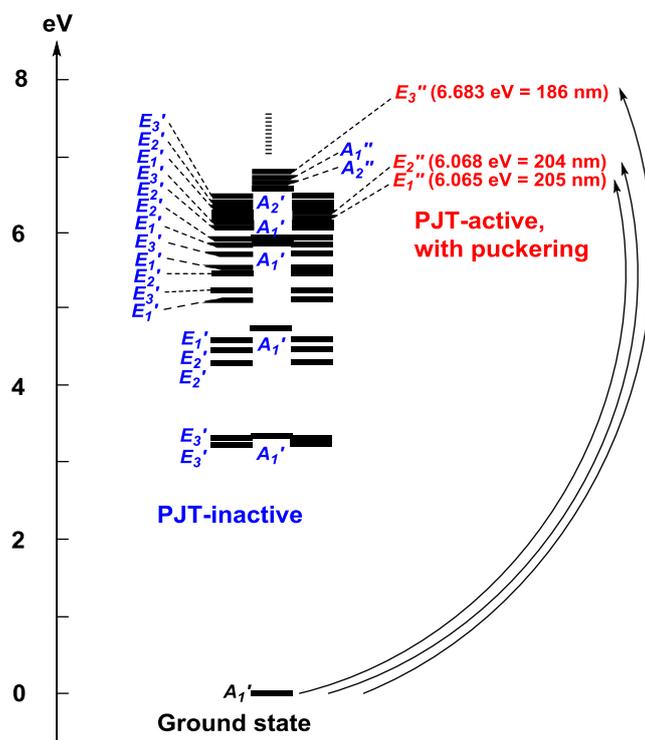


Figure 3. State diagram (CIS(23,7)/PM3//PM3) of D_{7h} -[7]circulene.

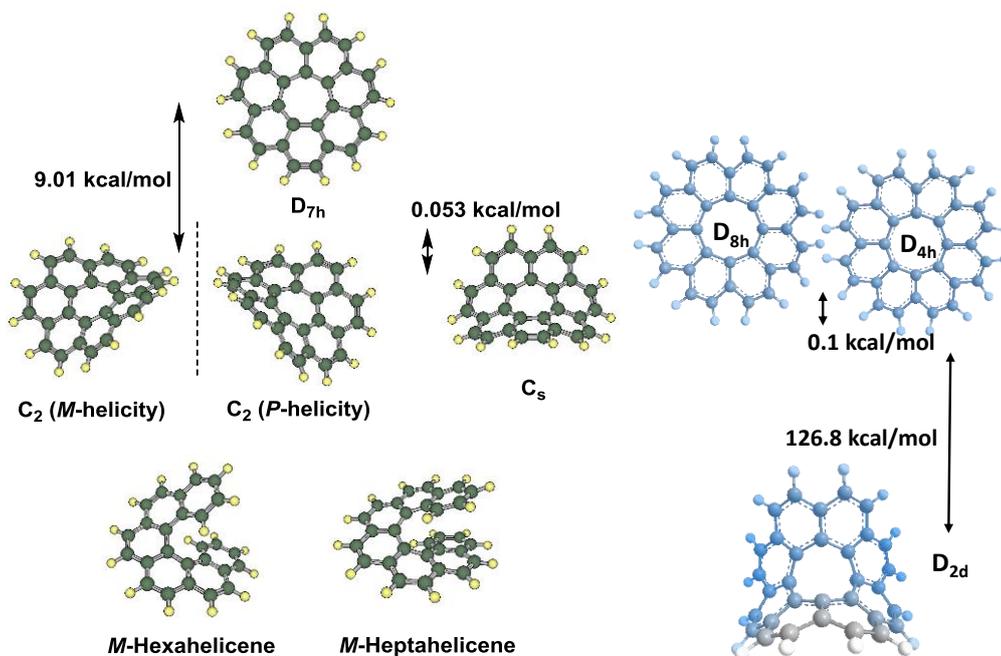


Figure 4. Optimized conformers of [7]circulene and [8]circulene (B3LYP/3-21G//B3LYP/3-21G). The structural resemblance between [7]circulene and helicenes is also shown.

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.

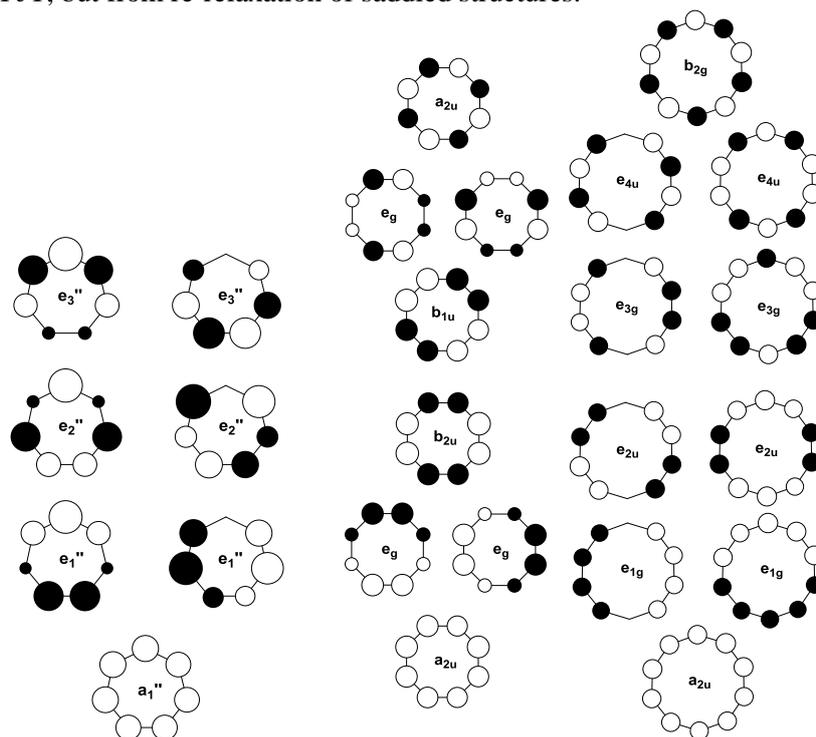


Figure 5. Schematic vibrational modes in 7-, 8-, and 10-membered ring systems.

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;

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

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

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

where I and F mean the initial and final states, $\boldsymbol{\mu}_e$ and $\boldsymbol{\mu}_m$ 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 μ_D and μ_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.

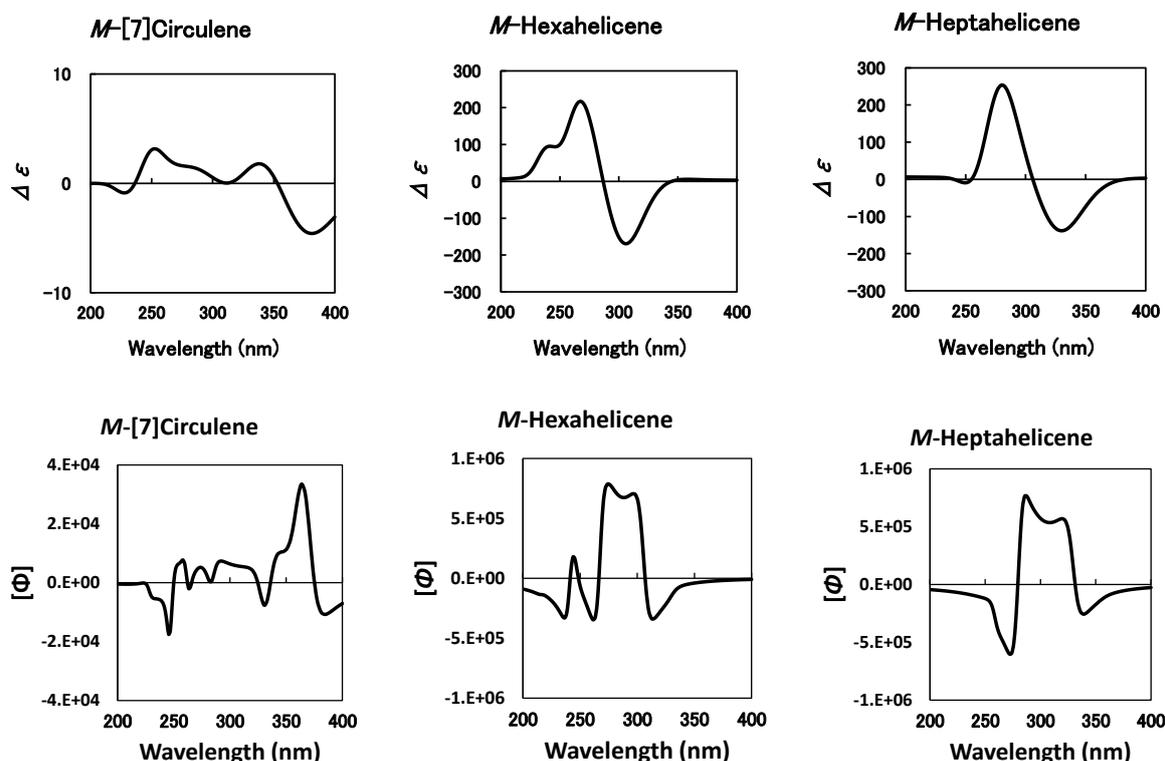


Figure 6. CD (circular dichroism) and ORD (optical rotatory dispersion) spectra of [7]circulene, hexahelicene, and heptahelicene simulated by PM3-CASCI level. Reprinted with permission from M. Hatanaka, *J. Phys. Chem. A*, **120**, 1074 (2016). Copyright (2016) American Chemical Society.

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 $\Delta E (= 2A)$ 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 not 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.

Acknowledgments

Thanks are due to ACS publications for permission to reprint the part of figures.

References

- [1] Christoph H, Grunenberg J, Hopf H, Dix I, Jones P G, Scholtissek M, Maier G 2008 *Chem. Eur. J.* **14** 5604
- [2] Kawasumi K, Zhang Q, Segawa Y, Scott L T, Itami K 2013 *Nature Chemistry*, 5 739
- [3] Yamamoto K, Harada T, Nakazaki M, Naka T, Kai Y, Harada S, Kasai N 1983 *J. Am. Chem. Soc.* **105** 7171; Yamamoto K, Harada T, Okamoto Y, Chikamatsu H, Nakazaki M, Kai Y, Nakao T, Tanaka M, Harada S, Kasai N 1988 *J. Am. Chem. Soc.* **110** 3578
- [4] Shen M, Ignatyev I S, Xie Y, Schaefer III H F 1993 *J. Phys. Chem.* **97** 3212
- [5] Bersuker I B 2013 *Chem. Rev.* **113** 1351
- [6] Bersuker I B 2001 *Chem. Rev.* **101** 1067
- [7] Jose D, Datta, A 2014 *Acc. Chem. Res.* **47** 593
- [8] Hatanaka M 2016 *J. Phys. Chem. A* **120** 1074