

Bifurcation Analysis of the Trans \leftrightarrow Cis Rotation of Monorotor Molecules

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The bifurcation analyses of the internal rotation of three different series of monorotor molecules are investigated in this paper. Our results indicate that the types of catastrophe and topological regions are related to the generic form of potential energy function and the critical points. Namely, when the double-barrier energy function is represented as the third-order generic polynomial of the reduced reaction coordinate, the process is isomorphic to the elementary *fold* catastrophe. Similarly, when the triple-barrier energy functions are represented as the fourth-order generic polynomial of the reduced reaction coordinate, the process is isomorphic to the elementary *cusp* catastrophe.

Keywords: Catastrophe theory; Bifurcation; Bithiophene; Bipyrrole; Fold catastrophe; Cusp catastrophe.

1. INTRODUCTION

Gárdenas-Jirón et al.¹ have presented a simple analytic form of the potential energy expressed in terms of linear combinations of local properties of monorotor molecules. The resultant potential energy function can be generated from a small number of calculated energy points. Recently Margalef-Roig et al.² have further presented a theoretical formalism based on simple bifurcation theory to study the trans \leftrightarrow cis rotational isomerization process of (1) glyoxal, (2) Cl-glyoxal, and (3) oxalyl-Cl. They determined a local bifurcation condition on the parameter space of the analytic form of the potential energy presented by Gárdenas-Jirón et al.¹ during the internal rotation processes. They claimed that the behavior of internal rotation process is not isomorphic to any of the elementary catastrophes. Moreover, the Gibbs-like potential mentioned in their work was without any thoughtful analysis.

In the present work, three series of monorotor molecules (a) OXC-CXO, (b) XS-SX (X = H, F, or Cl), and (c) bithiophene and bipyrrole are studied. Clearly, the molecules studied in [2] belong to our category (a). The results will be analyzed by invoking Thom's catastrophe theory.³⁻⁵ The bifurcations during the internal rotation processes will be studied by using the generic polynomials of potential energy. As compared to the previous approaches, the aforementioned problems can be analyzed much more clearly.

2. METHODOLOGY AND THEORY

In order to obtain the generic form of the potential energy for monorotor molecules, we have performed the Hartree-Fock (HF) calculations with the standard 6-31+G* basis set. The energy profiles along the torsional angle θ defined with respect to the central C-C or S-S bond of the molecule are obtained at the optimized geometries along the torsional angle. All calculations are performed using the Gaussian 98 package.⁶

2-1. Double-Barrier Potential Function

Our generic form of potential function representing trans \leftrightarrow cis rotational isomerization processes for monorotor molecules (a) OXC-CXO, and (b) XS-SX along the reduced reaction coordinate ω is written as follows:

$$V[\omega] = a_1 \omega + a_2 \omega^2 + a_3 \omega^3, \quad (1)$$

where $\omega \equiv (1 - \cos \theta)/2$ is the reduced reaction coordinate measuring the reaction process on going from the trans ($\omega = 0$) to the cis ($\omega = 1$) conformations. Eq. 1 comes from a cosine Fourier expansion up to the third term; the coefficients a_1 , a_2 , and a_3 can be accurately found by least-square fitting of the third-order polynomial $V[\omega]$. Notice that the coefficients a_1 , a_2 , and a_3 will be equal to $(A + B)$, $-[A + 3(B - C)]$, and $2(B - C)$,

in theory.² However, the approximation method used in [1] [2] to determine parameters A, B, and C is not as accurate when compared with our approach.

The bifurcation (BF) conditions can be obtained by setting both the first and second derivatives of $V[\omega]$ with respect to ω to zero. Thus, $V'[\omega] = V''[\omega] = 0$ occurs at $a_2^2 = 3 a_1 a_3 > 0$. The critical points ω_c can be found by solving the critical condition $V'[\omega] = a_1 + 2a_2 \omega + 3a_3 \omega^2 = 0$. Then,

$$\omega_c = [-a_2 \pm (a_2^2 - 3a_1 a_3)^{1/2}] / (3a_3).$$

Since a_1 , a_2 , and a_3 are real, therefore, for the region (I) $a_2^2 - 3a_1 a_3 > 0$, $\omega_c^I = [-a_2 \pm (a_2^2 - 3a_1 a_3)^{1/2}] / (3a_3)$. The bifurcation (BF) condition $a_2^2 - 3a_1 a_3 = 0$ implies that the root $\omega_c^{BF} = -a_2/3a_3$ represents a two-fold degeneracy. As for the region (II) $a_2^2 - 3a_1 a_3 < 0$, the roots ω_c^{II} are imaginary, hence no real critical points exist. Notice that all the ω_c 's have to be within range $[0, 1]$. Unfortunately, in the Ref. [2], the values ω_c^{II} in region (II) are erroneously claimed to have two nondegenerate critical points.

To analyze the bifurcation condition via Thom's catastrophe theory, the potential function $V[\omega]$ is shifted to a new coordinate ω_h ($\omega_h = \omega - h$) and the following obtained

$$V_n[\omega_h, u] = \omega_h^3 + u \omega_h. \quad (2)$$

Here, $h = -a_2(3a_3)^{-1}$, $u = a_1/a_3 - (a_2/a_3)^2/3$, and $-h \leq \omega_h \leq (1-h)$. The set of critical points of all first derivatives of V_n , called the catastrophe surface, $\{(\omega_h, u): V_n'[\omega_h, u] = 3\omega_h^2 + u = 0\}$ is a parabola in the left half plane as shown in Fig. 1. The BF conditions $V_n'[\omega_h, u] = V_n''[\omega_h, u] = 0$ occur at the origin $(\omega_h, u) = (0, 0)$. Notice that when $u = 0$, we have $a_2^2 = 3 a_1 a_3 > 0$ and $\omega_h = 0$. We obtain the critical point ω_c^{BF} equals to h , i.e. $-a_2(3a_3)^{-1}$.

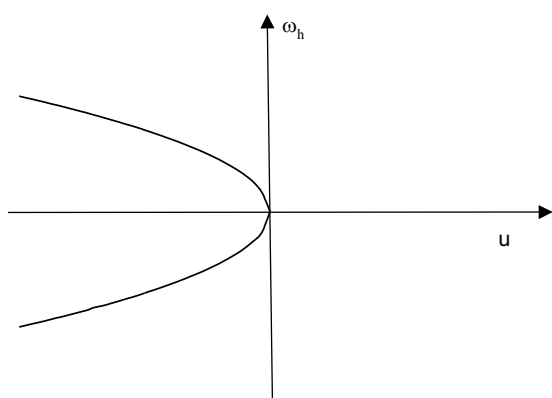


Fig. 1. The catastrophe surface, $\{(\omega_h, u): V_n'[\omega_h, u] = 3\omega_h^2 + u = 0\}$.

In region (I), $u < 0$ i.e., $a_2^2 - 3a_1 a_3 > 0$, there are two critical points, namely, a maximum at $\omega_{h,c}^I = -|u/3|^{1/2}$ and a minimum at $\omega_{h,c}^I = |u/3|^{1/2}$. The BF condition: $u = 0$ or $a_2^2 = 3a_1 a_3$ gives one critical point $\omega_{h,c}^{BF}$ at the origin. In region (II), $u > 0$ i.e., $a_2^2 - 3a_1 a_3 < 0$, there is no real critical point. Notice that all the critical points $\omega_{h,c}$'s have to be within range $[-h, 1-h]$.

2-2. Triple-Barrier Potential Function

The analytic potential function representing trans \leftrightarrow cis rotational isomerization processes for molecules (c) bi-thiophene and bipyrrrole of triple-barrier potential function along the reduced reaction coordinate can be written as follows.

$$V[\omega] = (A - B)\omega - [5A + 8C - 3(B + D)]\omega^2 + [8(A + 2C) - 2(B + D)]\omega^3 - 4(A + 2C)\omega^4. \quad (3)$$

We have the parameters $A \equiv k_t + k_c$, $B \equiv k_t - k_c$, $C \equiv \Delta V_t + \Delta V_c$, and $D \equiv \Delta V_t - \Delta V_c$. Note that this $V[\omega]$ is the same as that in Ref. [7], except that in Ref. [7], the relationships are polynomials in terms of $\cos \theta$.

Our generic form corresponding to the above potential function will be

$$V[\omega] = a_1 \omega + a_2 \omega^2 + a_3 \omega^3 + a_4 \omega^4. \quad (4)$$

The normalized potential function takes the following form:

$$V_n[\omega_h, u, v] = \omega_h^4 + u \omega_h^2 + v \omega_h \quad (5)$$

where $h = -a_3(4a_4)^{-1}$, $u = a_2/a_4 - (3/8)(a_3/a_4)^2$, and $v = a_1/a_4 - a_2 a_3 / (2 a_4^2) + (a_3/a_4)^3/8$, respectively. The catastrophe surface, $\{(\omega_h, u, v): V_n'[\omega_h, u] = 4\omega_h^3 + 2u\omega_h + v = 0\}$ is the surface as shown on page 46 of Ref. [3]. Let $\Delta = 8u^3 + 27v^2$, the BF con-

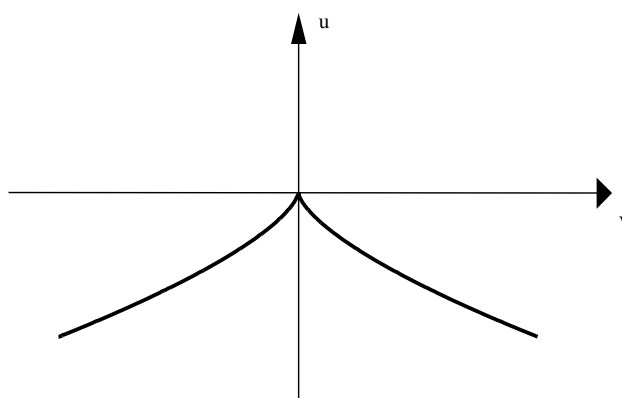
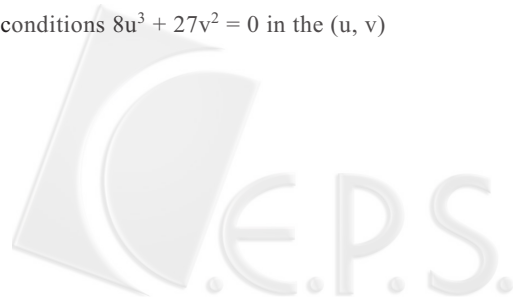


Fig. 2. The BF conditions $8u^3 + 27v^2 = 0$ in the (u, v) plane.



ditions $V_n'[\omega_h, u] = 4\omega_h^3 + 2u\omega_h + v = 0$ and $V_n''[\omega_h, u] = 12\omega_h^2 + 2u = 0$ occur at $\Delta = 0$ as indicated in Fig. 2.

For the critical points, if $\Delta > 0$, there will be one minimum and two conjugate complex roots. When $\Delta = 0$, there will be three real roots of which at least two are equal; if $\Delta < 0$, there will be two minimum and one maximum real and unequal roots. However, the critical points may or may not exist within the ω_h range from $-h$ to $1-h$.

2-3. Gibbs-Like Potential Energy for 2-1 and 2-2

To analyze the Gibbs-like potential $G[\omega] = V[\omega] + \omega \ln \omega + (1 - \omega) \ln(1 - \omega)$ as mentioned in Ref. [2], $G[\omega]$ can be ob-

tained by adding the value $\omega \ln \omega + (1 - \omega) \ln(1 - \omega)$ to our previously calculated HF/6-31+G* potential function $V[\omega]$. The generic form of $G[\omega]$ can be expressed as polynomials of ω as equations (1) or (4).

3. RESULTS AND DISCUSSIONS

All the numerical analyses of $V[\omega]$, V_n , and $G[\omega]$ are performed by the Matlab software.⁸

Our HF/6-31+G* potential profiles along the torsional angle results are given in Figs. 3a-3c for a series of monorotor

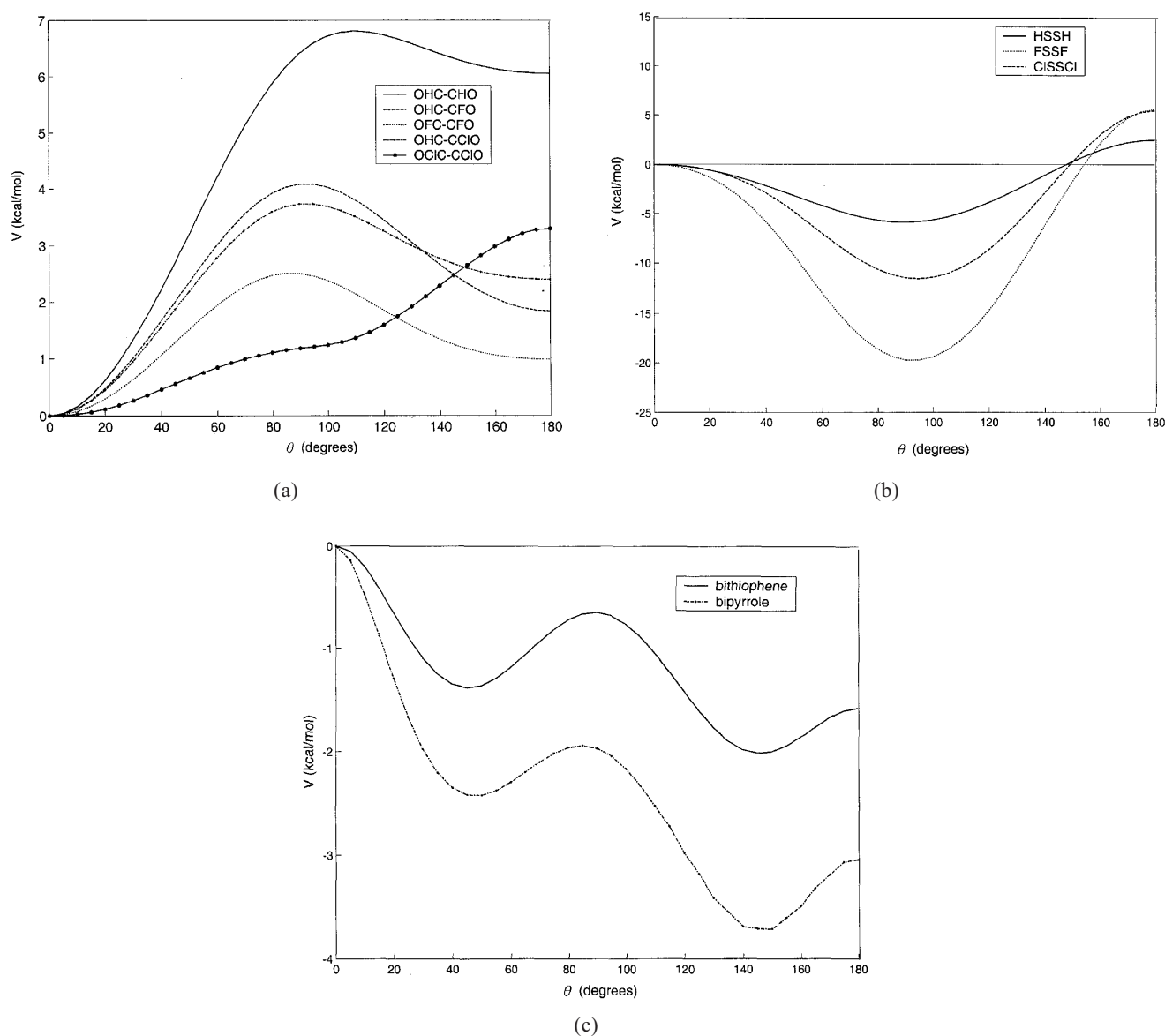


Fig. 3. HF/6-31+G* potential profiles along the torsional angle results for molecules (a) OXC-CXO, (b) XS-SX (X = H, F, or Cl), and (c) bithiophene and bipyrrole, respectively.

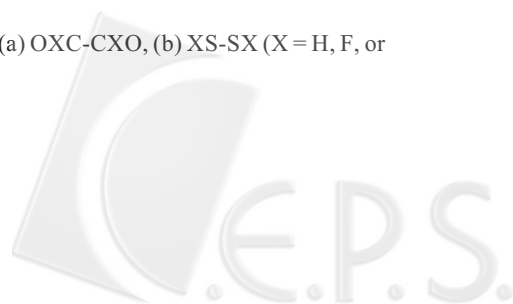


Table 1. The Coefficients a_i ($i = 1-3$) in eq. 1, the Calculated Parameters u , h in eq. 2, and the Critical Points ω_c for Molecules (a) OXC-CXO, and (b) XS-SX ($X = H, F,$ or Cl)

	a_1	a_2	a_3	u	h	ω_c
OHC-CHO	21.67	-20.38	4.71	-1.65	1.44	0.70
OHC-CFO	16.71	-19.63	4.73	-2.20	1.38	0.53
OFC-CFO	11.60	-16.29	5.61	-0.74	0.97	0.47
OHC-CClO	16.04	-21.08	7.41	-0.54	0.95	0.53
OCIC-CClO	5.74	-11.56	9.08	0.09	0.42	
HS-SH	-20.31	11.80	11.06	-2.22	-0.36	0.50
FS-SF	-56.62	8.47	53.88	-1.06	-0.05	0.54
CIS-SCI	-25.89	-18.66	50.09	-0.56	0.12	0.56

molecules (a) OXC-CXO, (b) XS-SX, and (c) bithiophene and bipyrrrole, respectively. For the series of molecules OXC-CXO, and XS-SX, the third-order generic polynomial potential energy function is adequate. Notice that in Fig. 3c, bithiophene and bipyrrrole present triple-well energy profiles; at least a fourth-order generic polynomial is needed to describe the energy profile accurately.

Table 1 gives the fitting coefficients a_i ($i = 1-3$) in eq. 1, the calculated parameters u , h in eq. 2, and the critical points ω_c for molecules OXC-CXO, and XS-SX. Notice that except for oxalyl-Cl, i.e., OCIC-CClO, all the other molecules have the value $u < 0$ and one critical point. This fact indicates that only oxalyl-Cl lies in the right half plane of Fig. 1 and the others are on the left.

Our critical-point results of glyoxal and chlorine derivatives OXC-CXO are different from that of Ref. [2]. There is no critical point obtained for the internal rotation of oxalyl-Cl (OCIC-CClO) in our calculation while Margalef-Roig et al. found two critical points (see eq. (11) of Ref. [2]). This discrepancy is due to their misinterpretation of the two complex roots as two critical points, hence result in the wrong conclusion of not being isomorphic to any elementary catastrophes known.

Similar coefficients such as a_i ($i = 1-4$) in eq. 4, the calculated parameters u , v , h in eq. 4, and the critical points of bithiophene and bipyrrrole are provided in Table 2. Both molecules have three critical points and $\Delta < 0$. Two critical points correspond to minima and one to maximum.

Figs. 4a-4c illustrate different energy profiles along the variable ω for molecules (a) OXC-CXO, (b) XS-SX, and (c) bithiophene and bipyrrrole, respectively. According to Figs. 4a and 4b, the internal rotation processes of glyoxal (OHC-CHO), F-glyoxal (OFC-CHO), Cl-glyoxal (OCIC-CHO), and oxalyl fluoride (OFC-CFO) located in the region (I), all have a maximum critical point corresponding to the transition state (TS). There is no critical point for the process of oxalyl-Cl in region (II). The internal rotation processes of XS-SX located in region (I) all have a minimum critical point that corresponds to a stable conformation. As for the bithiophene and bipyrrrole molecules, Fig. 4c indicates the trans \leftrightarrow cis rotational isomerization processes that have two stable and one unstable conformation.

According to our study, the behavior of internal rotation process for molecules (a) OXC-CXO and (b) XS-SX are isomorphic to the elementary *fold* catastrophe that has no critical point in region (II); a maximum at $\omega_{h,c}^I = -|u/3|^{1/2} < 0$ and/or a minimum at $\omega_{h,c}^I = |u/3|^{1/2} > 0$ in region (I). The behavior of internal rotation process for molecules (c) bithiophene and bipyrrrole is isomorphic to the elementary *cusp* catastrophe that has two stable critical points for the region $\Delta < 0$.

The analyses of the Gibbs-like potentials $G[\omega]$ are exactly the same as that of the potential function $V[\omega]$. Figs. 5a-5c give different Gibbs-like potential profiles along the variables ω for molecules (a) OXC-CXO, (b) XS-SX, and (c) bithiophene and bipyrrrole, respectively. The same results for $G[\omega]$ are obtained as that of $V[\omega]$. The behavior of Gibbs-like potential profiles along the reaction coordinate for molecules (a) OXC-CXO and (b) XS-SX are isomorphic to the elementary *fold* catastrophe, and the molecules (c) bithiophene and bipyrrrole are isomorphic to the *cusp* catastrophe.

Table 2. The Coefficients a_i ($i = 1-4$) in eq. 4, the Calculated Parameters u , v , h in eq. 4, and the Critical Points of Bithiophene and Bipyrrrole

	a_1	a_2	a_3	a_4	u	v	h	ω_c
bithiophene	-19.69	85.15	-131.36	62.31	-0.27	-0.01	0.53	0.17 0.50 0.90
bipyrrrole	-32.05	129.43	-189.90	89.48	-0.24	-0.02	0.53	0.20 0.49 0.90



4. CONCLUSIONS

Our bifurcation analyses of the rotational isomerization processes of mono-rotor molecules along the reduced reaction coordinate give us the bifurcation conditions on the reaction pathway space. Results have indicated that if the energy functions can be represented as the third-order generic polynomial of the reduced reaction coordinate, the process is isomorphic to the elementary *fold* catastrophe. The parameter space u is one-dimensional and the BF condition is only at one point $(0,0)$ which separates two different topological re-

gions $u < 0$ or $u > 0$ depending on the types and numbers of critical points. Similarly, if the energy functions with triple-barrier rotational potential can be represented as the fourth-order generic polynomial of the reduced reaction coordinate, the process is isomorphic to the elementary *cusp* catastrophe. The parameter space (u, v) is two-dimensional and the BF condition is the *Neil parabola* as indicated in Fig. 2 of the bifurcation set. This *Neil parabola* separates the u - v plane into two different topological regions, either $\Delta < 0$ or $\Delta > 0$, depending on the types and numbers of critical points.

The obtained conclusions on types of catastrophe are

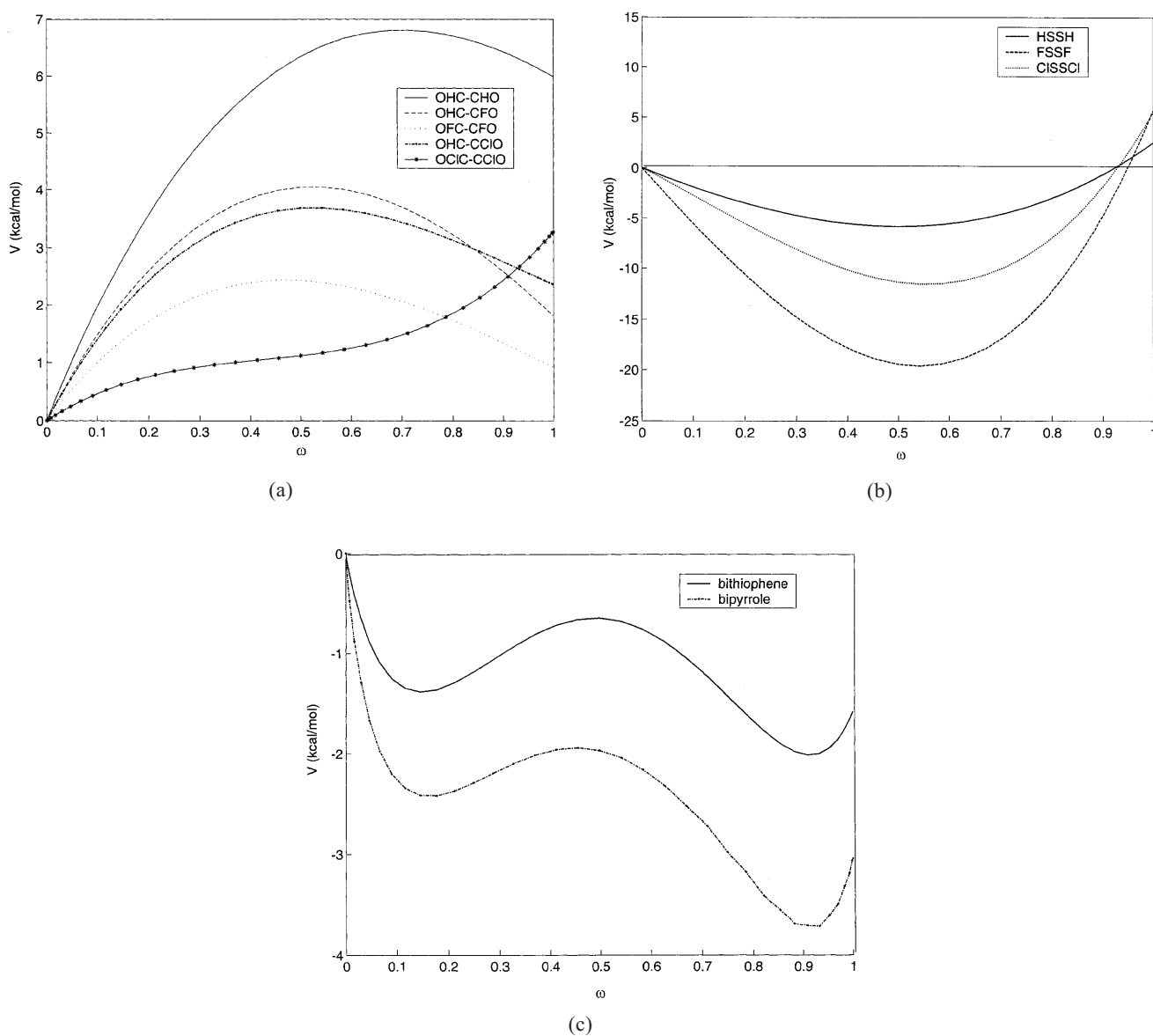


Fig. 4. The energy profiles along the variables ω for molecules (a) OXC-CXO, (b) XS-SX ($X = H, F, \text{ or } Cl$), and (c) bithiophene and bipyrrrole, respectively.

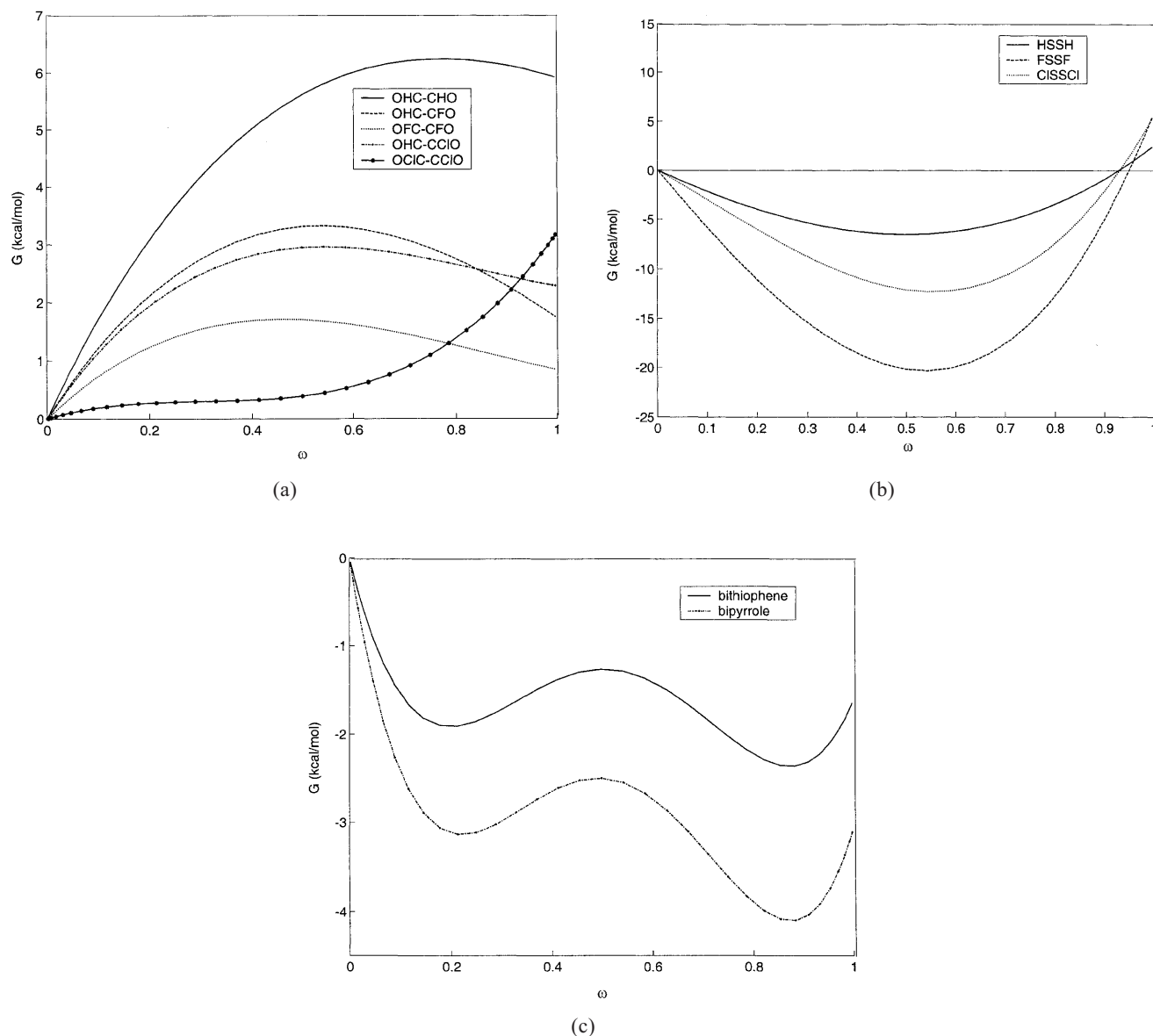


Fig. 5. The Gibbs-like energy profiles along the variables ω for molecules (a) OXC-CXO, (b) XS-SX (X = H, F, or Cl), and (c) bithiophene and bipyrrrole, respectively.

different from that of Margalef-Roig et al. Our explanations for these discrepancies are twofold. First, they have not used the correct range for ω_c . Secondly, they have misinterpreted the two complex roots as two real critical points.

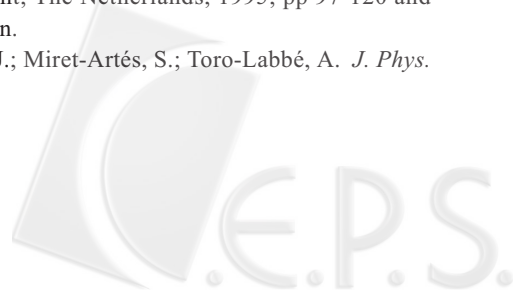
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