

The Effect of Peripheral Circuits on the Total π -Electron Energies of Cyclacenes

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Within the framework of the Hückel molecular orbital theory, certain linear models are developed to express the contribution of peripheral circuits of cyclacenes into their total π -electron energies, which explain why cyclacenes exhibit the cryptoannulenic behavior as their peripheral circuits which are annulenic in character.

Introduction

Cyclacenes, which can be expressed as continuous ring systems (Fig.1), possess interesting properties. They have long been the subject of experimental and theoretical studies¹⁻¹¹. The Hückel type cyclacenes fall into the class of even alternant hydrocarbons¹², which are characterized by molecular orbital energy levels symmetrically distributed about the zero energy level¹². Recent investigations based on the Hückel molecular orbital approach (HMO), as well as advanced semi-empirical molecular orbital calculations such as AM1 and PM3 have revealed that cyclacenes have many interesting properties, such as cryptoannulenic behavior and variation of latitudinal and longitudinal bond orders depending on whether their peripheral circuits are $4m+2$ or $4m$ type, m being an integer¹³⁻²⁷.

In the present study, within the HMO framework, some linear models have been proposed to express the contribution of some factors into the total π -electron energies (E_{π}) of cyclacenes and to determine the basis of the cryptoannulenic behavior of cyclacenes dictated by their annulenic peripheral circuits.

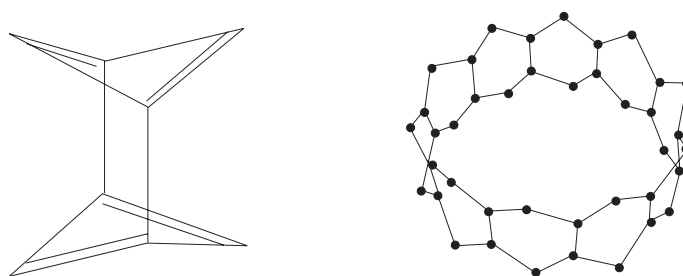


Figure 1. Structures of cyclacene having $R=2$ and $R=10$.

Theory

In HMO treatment, E_π of a conjugated molecule is defined as^{12,27}

$$E_\pi = 2 \sum_{i=1}^n x_i \quad (1)$$

where n and x_i are the number of occupied molecular orbitals and energies of occupied molecular orbitals in β units, respectively. In the case of alternant hydrocarbons, n equals half the number of atoms in the π -conjugation²⁷.

Cryptoannulenic behavior¹³ is simply the structure-dependent fluctuation of the angle of total π -electron energy (Q) defined as

$$Q = \arccos[E_\pi/2(ne)^{1/2}] \quad (2)$$

Let E_j stand for E_π of any conjugated system j possessing e_j π -bonds and $2n_j$ atoms in its π -skeleton (topologically speaking e_j edges and $2n_j$ vertices²⁷). Now, let K_j be defined as

$$K_j = (e_j + n_j - E_j)/(e_j + n_j + E_j) \quad (3)$$

Note that $K_j < 1$. Solve for E_j results

$$E_j = (e_j + n_j)f(K_j) \quad (4)$$

where

$$f(K_j) = (1 - K_j)/(1 + K_j) \quad (5)$$

The function $f(K_j)$ is the compact form of a convergent alternating series²⁸ and obviously $f(K_j) < 1$. Let $j=1$ and $j=2$ stand for a cyclacene system and its peripheral circuit, respectively. Then the following relations hold:

$$e_1 = 2e_2 + R \quad (6)$$

$$R = e_2/2 \quad (7)$$

$$n_1 = 2n_2 \quad (8)$$

where R stands for the number of benzenoid type rings in the cyclacene structure. Inserting eqs. 6-8 into eq. 4, one gets E_π for cyclacenes as

$$E_1 = (5e_2/2 + 2n_2)f(K_1) \quad (9)$$

Since, for annulenes $e_2 = n_2$ then eq. 9 becomes

$$E_1 = 9n_2f(K_1)/2 \quad (10)$$

On the other hand, eq. 9 can be rearranged thus:

$$E_1 = 2(e_2 + n_2)f(K_1) + e_2f(K_1)/2 \quad (11)$$

Note that E_2 in form is $E_2 = (e_2 + n_2)f(K_2)$ (obtained from eq.4 for $j=2$). The model expressed by eq. 9 reproduces E_π of a cyclacene molecule in terms of edges and vertices present in its peripheral circuit which is an annulene. Inserting eq. 4 for $j=2$ into eq.10 one gets

$$E_1 = 2E_2f(K_1)/f(K_2) + e_2f(K_1)/2 \quad (12)$$

If $f(K_1) \cong f(K_2)$ (which requires $K_1 \cong K_2$) then eq.12 becomes $E_1 = E_2 + e_2 f(K_1)/2$. Replacing $f(K_1)$ by $f(K_2)$ and then inserting $f(K_2) = E_2/(e_2 + n_2)$ (from eq.4 for $j=2$) and noting that $e_2 = n_2$ for annulenes, one obtains

$$E_1 = 9E_2/4 \quad (13)$$

Results and Discussion

A computer program written by Lowe²⁹ was used to calculate HMO E_π values. Table 1 tabulates E_π of cyclacenes having $R=2-15$ and their annulenic peripheral circuits.

Table 1. E_π values of certain cyclacenes and their annulenic peripheral circuits.

R	Cyclacene	Annulene
2	10.246	4.000
3	17.190	8.000
4	22.246	9.657
5	28.154	12.944
6	33.612	14.928
7	39.309	17.976
8	44.873	20.109
9	50.511	23.035
10	56.107	25.255
11	61.728	28.106
12	67.334	30.303
13	72.948	33.187
14	78.558	35.501
15	84.170	38.267

E_π in β units

To check the extent of the validity of eq. 13, the following first-order linear model was used^{30,31} where B_0 and B_1 are certain coefficients where Y and X stand for E_1 and E_2 , respectively.

$$Y_0 = B_0 + B_1X \quad (14)$$

The regressed equation^{30,31} has the form of

$$E_1 = 0.609077 + 2.185631E_2 \quad (15)$$

Table 2 tabulates the regression statistics of eq. 15. As can be seen in the table, regression equation 15 is statistically significant, having high $F_{12,1}$ and $t_{12,1}$ with 12 degrees of freedom (DF).^{30,31} The tabulated F - and t -test values for $DF=12$ at the 1% level of significance are 9.33 and 2.681, respectively.

From the regression statistics for eq. 15, it is evident that the peripheral circuits of cyclacenes linearly and highly contribute to the E_π of cyclacenes. Thus, the cryptoannulenic effect of a cyclacene should be dictated by its peripheral circuit, which is an annulenic moiety and itself exhibits the cryptoannulenic effect strongly. Figure 2 shows Q vs. R values of cyclacenes and the corresponding annulenic peripheral circuits (cryptoannulenic effect¹³).

Table 2. Regression statistics of eq. 15.

Coefficient of determination	0.999468
Correlation coefficient	0.999734
F-test	22555.7
t-test	150.186
Unexplained standard deviation	0.565661
Standard error of B_0	0.347746
Standard error of B_1	0.014553

By using eqs. 2 and 15, the angle of total π -electron energy of a cyclacene (Q_1) can be written as

$$Q_1 = \arccos[(0.09/n_1e_1)^{1/2} + 2.18(n_2e_2/n_1e_1)^{1/2} \cos Q_2] \quad (16)$$

where Q_2 stands for the annulenic system. For $R=2$, the first term in the parentheses is 0.04743. Thus, as R increases, it becomes negligible. It can be easily proved that the coefficient of $\cos Q_2$ is 0.97492. Hence, for the first few of the cyclacene family, $Q_1 < Q_2$ because the first term contributes to a certain extent, but as it becomes negligible then $Q_1 > Q_2$ (see Figure 2). The turnover point coincides with the cyclacene having $R=8$.

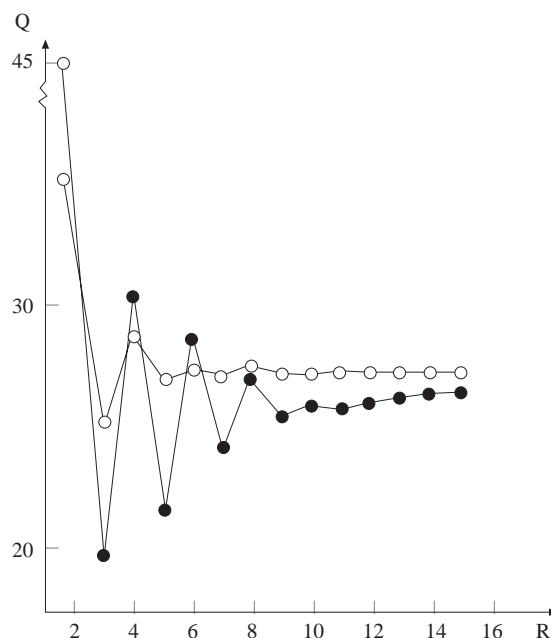


Figure 2. Q values vs. R of cyclacenes and the corresponding annulenic peripheral circuits. ●: annulene, ○: cyclacene.

Conclusion

The present study sheds some light on the cryptoannulenic behavior of cyclacenes via linear models. Eq. 16 explains how closely a cyclacene mimics the angle of the total π -electron energy of its annulenic peripheral circuit. Since E_π correlates with thermal stability of a conjugated system²⁷ the peripheral circuits of a cyclacenes should dictate E_π and thus the stabilities of cyclacenes should exhibit relative fluctuations within the constraints of HMO theory.

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