

Some Recursive Relationships Between Acenes and Cyclacenes

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Some structural relationships between acenes and cyclacenes both Hückel- and Möbius-type and within the same class of compounds were demonstrated by the recursive analysis of their E_π and I_π values or the first differences thereof. It was found that the first differences of E_π and I_π tend to have certain limit values as the number of benzenoid rings increases in each class of compounds studied.

Introduction

The question of the dependence of the total π -electron energy (E_π) of conjugated molecules goes back to 1940 and C.A. Coulson, who was the first to address it¹. Thenafter, many attempts have been made²⁻⁹ to investigate the structural factors that contribute to the gross part of E_π . For some macromolecules E_π is known in analytical form, e.g., polyacenes^{10,11} and polymethines¹². It has been established that E_π of benzenoid hydrocarbons is a linear function of the number of Kekule structures^{6,13}. In recent literature, some work on cyclacenes (which may be considered continuous ring systems) have appeared, indicating the possibility of the cryptoannulenic behaviour and superaromatically of Hückel-type cyclacenes^{14,15}. In spite of the fact that Hückel-type cyclacenes are even alternant hydrocarbons, Möbius cyclacenes are nonalternant. Topologically, a cyclacene of the Möbius type is obtained from the corresponding acene by twisting the acene belt through 180 an odd number of times before union at the respective sites (double union). The present study is concerned with the E_π and I_π of cyclacenes of Hückel and Möbius types (Fig. 1) having 3-15 benzenoid rings, in order to unveil certain interrelations existing within the same homologous set of cyclacenes and between different classes of cyclacenes.

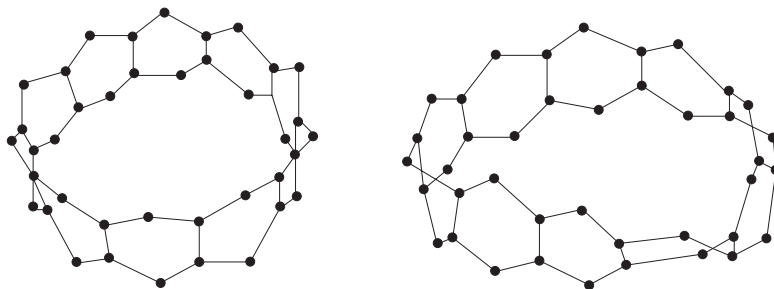


Figure 1. Structures of Hückel- and Möbius-type cyclacene molecules

Theory

The eigenvalues of the Hückel molecular orbitals of the acenes with R-condensed rings are available in analytical form¹⁶. The energies of bonding molecular orbitals can be expressed as

$$\epsilon_j = \alpha + x_j\beta \quad (1)$$

where $x_0 = 1$, $x_j = (r_j + 1)/2$ and $x_j = (r_j - 1)/2$, and α and β are Coulomb and resonance integrals, respectively. The eigenvalue corresponding to the j th molecular orbital is denoted by x_j , whereas r_j is given by¹⁶

$$r_j = (9 + 8 \cos(nj/(R + 1)))^{1/2} \quad (2)$$

where $j = 1, 2, \dots, R$.

On the other hand, the total π -electron energy, E_π , is expressed as

$$E_\pi = 2 \sum_{j=1}^N x_j \quad (3)$$

which becomes

$$E_\pi = 2 + 2 \sum_{j=1}^R (9 + 8 \cos(\pi j/(R + 1)))^{1/2} \quad (4)$$

for acenes by inserting Eqs. 1 and 2 into 3. Note that N is the number of occupied molecular orbitals, and in the case of acenes it is expressed by Eq. 5

$$N = 2R + 1. \quad (5)$$

For cyclacenes of Hückel and Möbius types, there still exists no analytical expression to yield molecular orbital energies; thus, for their E_π values, one has to solve the corresponding secular determinant and the characteristic polynomial. Table 1 tabulates the E_π values of acenes and cyclacenes of Hückel and Möbius types for $R = 3 - 15$. For the evaluation of the total π -electron energies within the framework of Hückel molecular orbital (HMO) theory, a computer program written by Lowe¹⁷ has been employed.

Table 1. Total π -electron energies of various acenes and cyclacenes

R	Acenes	Cyclacenes	
		Hückel type	Möbius type
3	19.3118	17.1905	16.8063
4	24.9308	22.2462	22.4368
5	30.5440	28.1541	28.0539
6	36.1560	33.6127	33.6671
7	41.7675	39.3093	39.2791
8	47.3789	44.8736	44.8906
9	52.9903	50.5117	50.5020
10	58.6017	56.1079	56.1134
11	64.2130	61.7280	61.7248
12	69.8243	67.3342	67.3361
13	75.4357	72.9485	72.9474
14	81.0470	78.5582	78.5588
15	86.6584	84.1705	84.1701

E_π values are in β units.

Calculations of the first differences¹⁸ of $E_\pi, d(a_R)$, expressed as

$$d(a_R) = a_R - a_{R-1} \quad (6)$$

where a_R and a_{R-1} stand for E_π values of cyclacenes having R and $R-1$ benzenoid rings, respectively, for each class of compounds mentioned above reveal that the E_π values of acenes and Möbius-type cyclacenes, particularly for large systems, fit the recurrence relation^{19,20} of

$$a_R - a_{R-1} - d = 0 \quad (7)$$

where $d = 5.611$. The first differences of E_π for Hückel-type cyclacenes oscillate according to the number of benzenoid rings, getting a limit value of 5.61.

On the other hand, for all types of compounds studied ($R = 3 - 15$), it has been found that the recursion formula (8) generally holds for E_π .

$$a_R - 2a_{R-1} + a_{R-2} = 0 \quad (8)$$

where a_R, a_{R-1} and a_{R-2} stand for the E_π of cyclacenes having $R-i$ ($i = 0, 1, 2$) benzenoid rings, respectively. Equation 8, when applied for E_π enables one to evaluate the E_π of any cyclacene molecule in terms of the corresponding values of the lower members of the family having $R-1$ and $R-2$ benzenoid rings, respectively.

Recurrence relations (7) and (8) are linear relations with constant coefficients, and Eq. 8 is a second-order homogeneous recurrence relation. Its solution is readily available by considering its characteristic equation^{19,21},

$$x^2 - 2x + 1 = 0 \quad (9)$$

which possesses multiple roots and yields a basic solution¹⁹ with respect to $x = 1$.

$$a_R = A + BR \quad (10)$$

where A and B are certain constants.

It is known that for alternant hydrocarbons², Eq. 11 holds,

$$E_\pi \leq 2(en)^{1/2} = E_{\max} \quad (11)$$

where n and e stand for half the number of carbon atoms and the number of carbon-carbon bonds, respectively.

Now, let

$$I_\pi = E_{\max} - E_\pi = 2(ne)^{1/2} - E_\pi \quad (12)$$

Table 2 shows the first difference, b_R , of I_π values of various acenes and cyclacenes.

Furthermore, it is easily shown that the first differences of I_π values (b_R, b_{R-1} and b_{R-2}) for a set of cyclacenes (having members consisting of $R, R-1$ and $R-2$ benzenoid rings, respectively) conform to Eq. 13

$$b_R - 2b_{R-1} + b_{R-2} = 0. \quad (13)$$

However, in practice (within the constraints of HMO theory and the range of compounds studied) they also fit generally the recursion formula

$$2b_R - b_{R-1} - b_{R-2} = 0 \quad (14)$$

because the first differences for these compounds possess the property that $b_R = b_{R-1}$.

Table 2. The first difference, b_R , of I_π values of various acenes and cyclacenes

R	Acenes	Cyclacenes	
		Hückel type	Möbius type
4	.7104	1.2688	.6940
5	.7144	.4166	.7074
6	.7146	.8659	.7113
7	.7145	.6279	.7125
8	.7143	.7602	.7131
9	.7140	.6864	.7131
10	.7138	.7283	.7131
11	.7138	.7044	.7131
12	.7137	.7183	.7132
13	.7135	.7102	.7132
14	.7136	.7148	.7131
15	.7134	.7122	.7132

Difference are in β units.

Results and Discussion

Inspection of Table 1 reveals that E_π values of acenes are always greater than the corresponding values of Hückel- and Möbius-type cyclacenes, whereas the latter possess comparable E_π values. The first differences of Hückel-type cyclacenes are affected by the number of benzenoid rings. Whenever R is odd, $d(a_R) > d(a_{R-1})$. It is obvious then that $d^2(a_R)$ is an oscillatory and damped in behavior¹⁸. A similar characteristic was observed in the I_π values of Hückel-type cyclacenes (Table 2). For acenes and Möbius-type cyclacenes, some fluctuations in the first differences of E_π and I_π occur but not in a regular fashion. However, in every case the first differences of E_π and I_π tend to approach a limit value of 5.61 and 0.71, respectively. Hence, they appear as certain characteristic constants for the above-mentioned compounds. On the other hand, inspection of Table 2 reveals that Möbius-type cyclacenes mimic acenes closely, whereas only large members of Hückel cyclacenes are comparable to acenes in terms of the property under consideration in the present study.

On the other hand, the recursion formula (10) can be used to estimate the E_π and I_π values of the above-mentioned compounds by setting the initial conditions or by means of regression analysis. For example, the regression analyses of E_π of the Hückel and Möbius types were determined to be, respectively,

$$E_\pi = 0.0865402 + 5.60359R \quad (15)$$

$$E_\pi = -0.014183 + 5.61257R \quad (16)$$

The regression statistics^{22,23} of Eqs. 15 and 16 are tabulated in Table 3. As seen in the table, the regressed equations are statistically significant. As the coefficients in Eqs. 15 and 16 were obtained by regression analysis, they must maintain five decimal places for ideal conformity; however, the resultant E_π values should be rounded to four decimal points.

Table 3. The regression statistics for E_π values of Hückel- (Eq. 15) and Möbius- (Eq. 16) type cyclacenes.*

	Hückel type	Möbius type
The coefficient of determination	1	1
Correlation coefficient	.999986	1
Unexplained standard deviation	.122805	$5.57367 \cdot 10^{-3}$
Unbiased estimate of the variance of the regression coefficient	$9.10293 \cdot 10^{-3}$	$4.13148 \cdot 10^{-4}$
F-test	$3.78941 \cdot 10^5$	$1.84599 \cdot 10^8$
t-test	$6.15582 \cdot 10^2$	$1.35849 \cdot 10^4$

* For compounds having 3-15 benzenoid rings. The tabular value²³ of F at the 1% level of significance with degree of freedom 1 and 11 is 9.65.

The tabular value²³ of t at the 1% level of significance with degree of freedom 11 \equiv 2.718.

Conclusion

The treatise presented above unveils some hidden structural behavior or relationships between acenes and cyclacenes or within the same set of compounds. Topologically, it is interesting that the double union of an acene molecule with itself to yield the corresponding Hückel-type cyclacene introduces a characteristic property to the latter class of compounds that is the alternating behavior of the first differences of E_π and I_π values with the increasing number of benzenoid rings. This property is lost by the presence of a single phase dislocation; hence, Möbius cyclacenes resemble the corresponding acenes. Therefore, this subject is open to further investigation.

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