

Investigation of HMO Spectra of Hückel and Möbius Type Cyclacenes

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The Hückel molecular orbital spectra (HMO) of Hückel- and Möbius-type cyclacenes having 3-15 benzenoid rings were investigated and it was found that certain eigenvalues are topologically invariant, whereas others exhibit topological periodicity. For example, Hückel-type cyclacenes having $2r$ ($r: 2,3,4,\dots$) benzenoid rings which possess nonbonding molecular orbitals (NBMO) and are thus expected to be open shell structures.

Introduction

Acenes and cyclacenes are structurally interrelated condensed aromatics¹. The latter compounds (Fig.1) could be considered topologically to be cyclic acenes. Acenes, being cata-condensed aromatics, are characterized by the property that no carbon atom belongs to more than two rings, thus implying that every carbon atom is on the periphery of the conjugated system. In other words, the topology of the cata-condensed hydrocarbons is determined by the requirement that no two rings possess more than one common edge and no three rings possess a common vertex²⁻⁵.

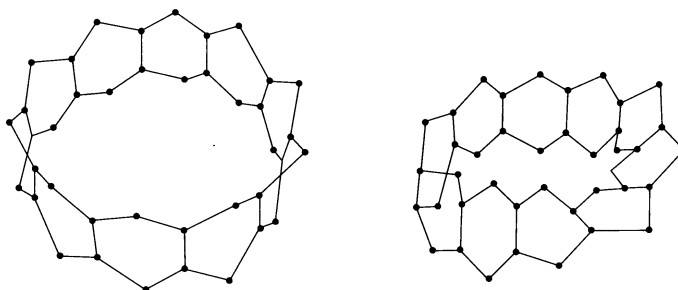


Figure 1. a) Hückel-type cyclacene skeleton, b) Möbius-type cyclacene skeleton.

It is evident that in acenes, one sextet of π -electrons (Clar's sextet¹) is shared among several rings, which must necessarily lead to a gradual loss of benzenoid characteristics in higher acenes, and that with an infinite number of rings, the system becomes a cyclic polyene in which one sextet is not sufficient to give

any degree of stability¹. Hence, acenes are not fully benzenoid compounds; that is, a Clar's formula without double bonds does not exist^{1,6}.

Acenes and Hückel-type cyclacenes are even alternant systems⁷. The main topological difference between them is the cyclic nature of cyclacenes, which is responsible for the existence of two more ring systems, the top and bottom polyene rings (peripheres) present in the cyclacene structure (see Figure 1a).

Because of their cyclic nature, cyclacenes may be considered continuous ring systems. Moreover, the presence of annulenic peripheries implies that cyclacenes possess interesting properties⁸.

Graph theory has been employed as a useful tool for the study of those properties of molecules which depend only upon their topologies. It is known that graph theory, when applied to the investigation of conjugated hydrocarbons, is fully equivalent to a simple HMO treatment^{9,10,11}. In particular, the HMO energies, in units of β , are identical to the eigenvalues of the adjacency matrix of the corresponding graph of the molecule being considered. It is known that, in many cases, the entire spectrum of one graph is contained in the spectrum of another, larger graph¹². In such a case, the larger (composite) graph and the smaller (component) graph are said to be subspectral. Various methods have been reported for the investigation of subspectral graphs¹²⁻¹⁷.

The investigation of subspectral structures embedded in cyclacenes would be interesting because of the remarkable topology of the latter class of compounds.

In the present study, Hückel molecular orbital spectra of various cyclacenes were investigated, and some subspectral structures (components) were identified.

Results and Discussion

Hückel- and Möbius-type cyclacenes are determined by the number of phase dislocations (k). If the number is even, the Hückel-type arises; if not, the Möbius type arises. In the present study, only the systems having $k=0$ and 1 were considered. For the purpose of investigation of HMO eigenvalues of cyclacenes, a computer program written by Lowe¹⁸ was used.

Hückel-Type Cyclacenes

Cyclacenes having R benzenoid rings belong to the D_{2Rh} point group and thus possess various elements of symmetry. In such a symmetrical structure it is possible to identify various embedded component graphs, some acting as repeating units.

Since cyclacenes are even alternant hydrocarbons, their molecular orbital energies (X_i) are symmetrically distributed about the zero level. These energies are for the most part doubly degenerate except in few cases (2.5615 and 1.5615 β). All the molecular orbitals having energies (in β units) $2.5615 > X_i > 1.5615$ have the associated orbitals characterized by X_j such that $X_j = X_i - 1$; thus $1.5615 > X_j > 0$.

Invariant Eigenvalues

The adjacency matrices of all Hückel-type cyclacene molecular graphs are characterized by the property that they possess two common eigenvalues, 2.5615 and 1.5615 ($((17)^{1/2} \pm 1)/2$), which are interrelated by a difference of 1.0000. The first corresponds to the energy (X_1) of the deepest-lying molecular orbital. Topologically, its lowest bound is estimated to be 2.5495 the formula¹⁷

$$X_i^2 \geq \text{mean } d_i^2 \quad (1)$$

where d_i is the degree of vertices in the graph. Note that in the structures of cyclacenes there exist only two kinds of vertices, having degrees of two and three (d_2 and d_3). The number of vertices of each type is given as $2R$, whereas the total number of vertices is expressed as $4R$, where R is the total number of benzenoid rings. The invariant eigenvalues of cyclacenes are nondegenerate.

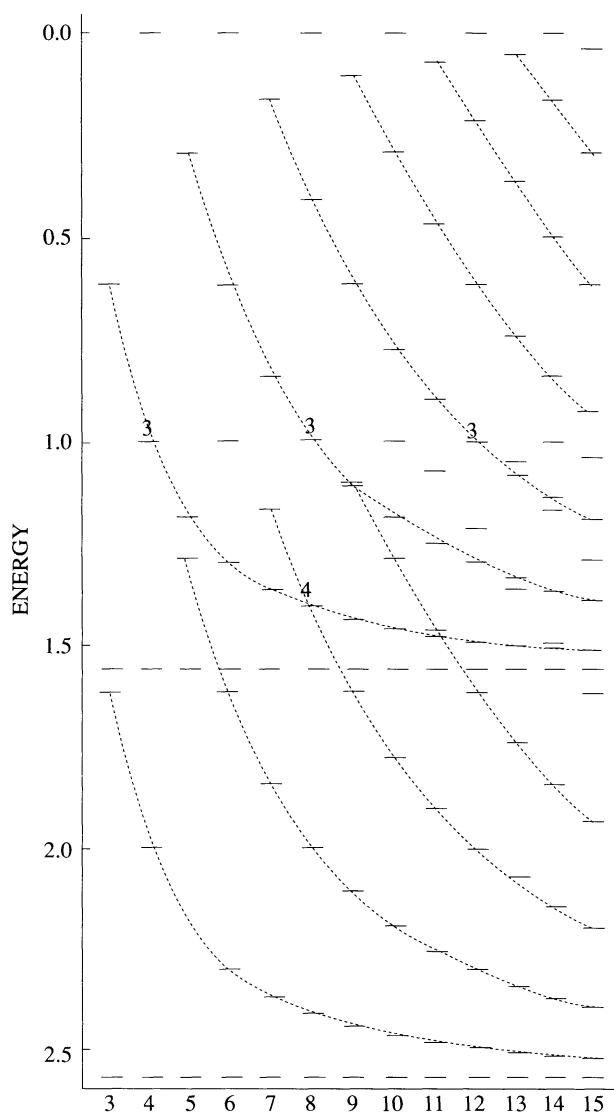


Figure 2. HMO spectra of certain Hückel cyclacenes. Energy levels drawn with thick lines are doubly degenerate, those with thin lines are nondegenerate. Numbers on the lines represent the degeneracy of the corresponding energy level.

Topologically Periodic Eigenvalues

Certain eigenvalues of cyclacenes exhibit periodicity depending on the topology. For instance, in the spectra of cyclacenes $X = 2.000 \beta$ appears whenever the number of benzenoid rings, R , becomes $4, 8, 12, \dots, 4r$ where $r = 1, 2, 3$ etc. (periodicity of 4, see Figure 2.). The corresponding orbitals are doubly degenerate. The occurrence of periodic eigenvalues of cyclacenes can be explained on the basis of the existing two-fold

symmetry element¹². For example, in the case of a cyclacene with $R = 8$, the vertical symmetry plane, σ_v , bisects the molecule into two halves such that anthracene energies are embedded in the spectra, which include $X = 2.000 \beta$ and $X = 1.000 \beta$. The last eigenvalue possesses a periodicity of 2; thus it appears in the spectra of cyclacenes having $R = 4, 6, 8, \dots, 2r$ ($r = 1, 2, 3, \dots$) etc. However, the degeneracy varies alternately. The cyclacenes characterized by $R = 4r$ ($r = 1, 2, 3, \dots$) exhibit triple degeneracy whereas those having $R = 4r + 2$ possess a nondegenerate orbital for $X = 1.000 \beta$.

Similarly, tetracene, pentacene and hexacene energies survive in cyclacenes having $R = 10, 12$ and 14 , respectively.

As the cyclacene structure increases in size, some other systems, such as those with $R = 13, 15$ which do not fit the $4r$ or $4r + 2$ type exhibit some roots nearly equal to the above-mentioned eigenvalues (1.000 and 2.000) (see Figure 2), implying that the regular periodicity of certain eigenvalues should virtually appear to be changed such that $R > 15$.

Perhaps the most interesting feature of cyclacenes lies in the existence of degenerate NBMOs in certain members of the family ($R = 4, 6, 8, \dots, 2r$; $r = 2, 3, 4, \dots$). The occurrence of NBMOs in those systems cannot be due to certain embedded structures interrelated to the composite molecular graph through a symmetry operation involving σ_v (vertical plane of symmetry). On the other hand, σ_h (horizontal plane of symmetry) produces two ring systems (peripheries), which are actually polyene rings (see Figure 3).

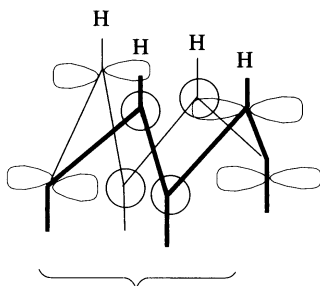


Figure 3. Periphery of a cyclacene molecule

When $R = 4, 6, 8, \dots, 2r$, each of the peripheries of the corresponding cyclacenes possess $8, 12, 16, \dots, 4m$ carbon atoms, respectively. The peripheries of cyclacenes may be considered to be special types of the corresponding annulenes. It is known that although $4m$ annulenes are even alternant hydrocarbons, they are characterized by the existence of supernumerary nonbonding molecular orbitals¹⁹. It is clear that these cyclacenes are expected to be open shell structures within the constraints of HMO theory.

Some other periodic roots of the adjacency matrices of cyclacenes exist. Of these, butadiene energies (1.618 and $.618 \beta$) survive in structures having $R = 3, 6, 9, \dots, 3r$. Naphthalene and cyclacenes with $R = 6, 12, \dots, 6r$ are subspectral systems. note that naphthalene and structure I (Fig. 4) are subspectral systems (structure possesses doubly degenerate NBMOs).

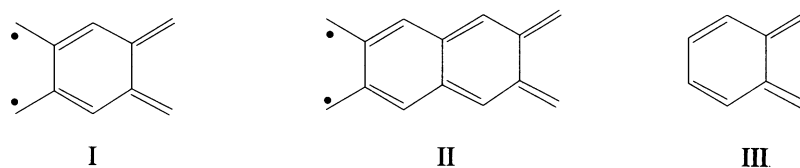


Figure 4. Some subgraphs embedded in cyclacenes.

Although allyl energies (1.414β and 0.000β) are readily detected in the spectrum of cyclooctacene ($R = 8$), a careful analysis reveals that the allyl system (or Dewar benzene) is subspectral with structure

II (Fig. 4) which has energies of 2.4142, 2.0000, 1.4142, 1.0000, 0.4142, 0.0000, and 0.0000 in units of β . Structure II subspectral with cyclooctacene.

For cyclacenes having $R = 5, 10, 15, \dots, 5r$ ($r = 1, 2, 3, \dots$), ortho-quinodimethane energies (2.193, 1.294, 1.193 and 0.294 β) were found to exist (structure III, Fig. 4).

Möbius-Type Cyclacenes

Möbius-type cyclacenes are nonalternant systems; hence, in contrast to the Hückel-type, they do not possess symmetrical spectra. Inspection of the spectra of these systems reveals that the topology invariant roots of the Hückel type, that is, the eigenvalues of 2.5615 and 1.5615, now do not occur simultaneously in the occupied and unoccupied parts of the spectra, but the latter one represents an unoccupied molecular orbital, by reversal of the sign (see Figure 5).

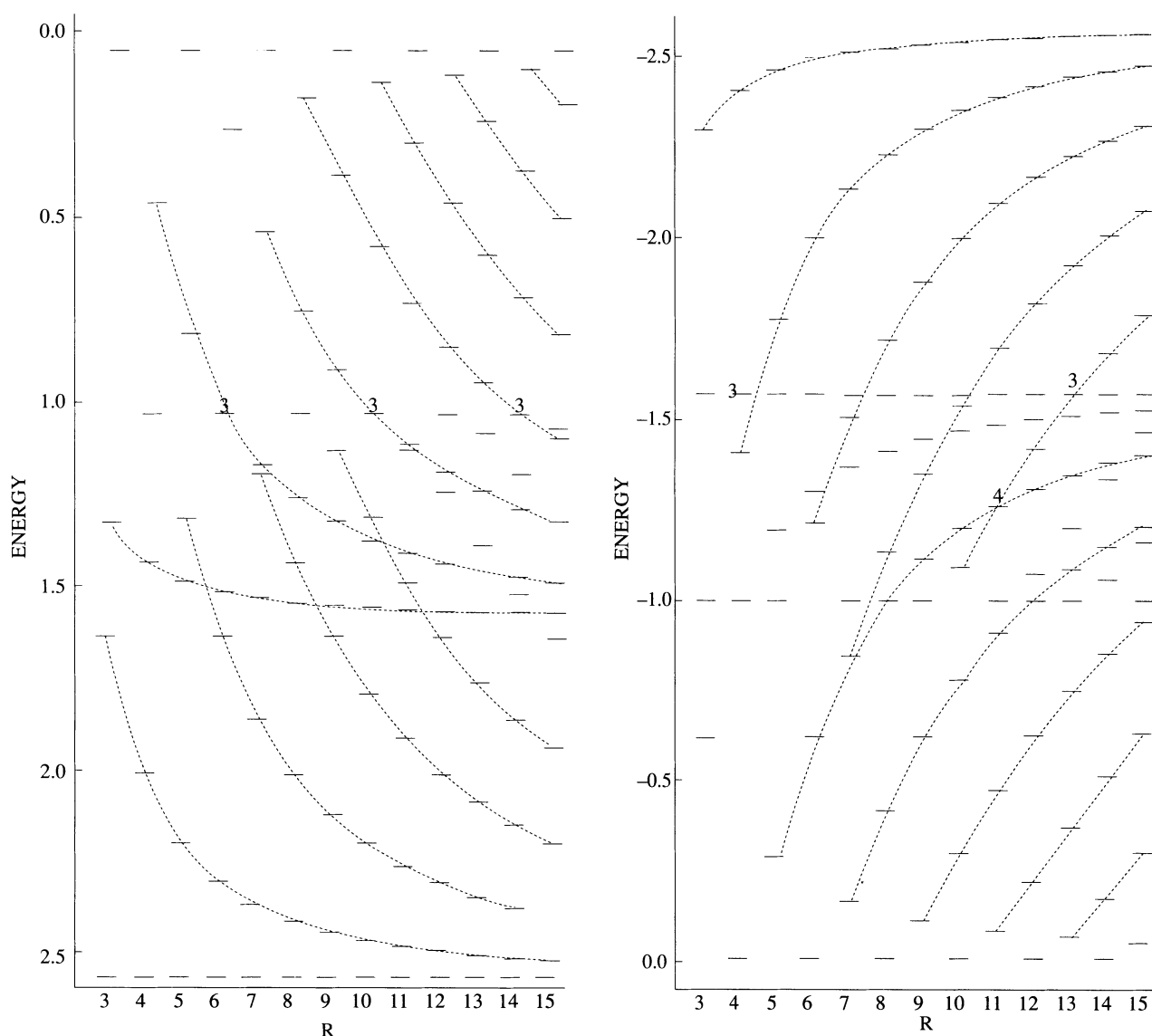


Figure 5. HMO spectra of certain Möbius-type cyclacenes. a) Occupied b) Unoccupied. Refer to Figure 2 for details of the figure.

The NMBO situation in this case is interesting. Whenever R is odd, they are occupied (HOMO), but for even values of R they stand for the LUMO of the system. The eigenvalue 1.618 is periodic and emerges for

$R = 3, 6, 9$, etc. Another periodic eigenvalue is 1.000, which occurs for $R = 4, 6, 8$ etc. Thus, the occupied orbitals, except the above-mentioned four different periodic eigenvalues, possess structure-dependent original roots in the range of $R = 3-15$.

In the case of unoccupied orbitals, there exist three other periodic eigenvalues: $-0.618, -1.000$ and -1.561 . Of these, the last is common in every cyclacene. The first is periodic for systems having $R = 3, 6, 9$, etc. The eigenvalue -1.000 occurs for $R = 3, 5, 7, 9$, etc. However, it also occurs for other systems nonperiodically.

Conclusion

The high symmetry existing in cyclacene structures causes the emergence of interesting HMO spectra having certain regularities and periodicity. Topology invariant roots such as annulenes are common in some other systems. In light of the above investigation it is evident that peripheries of cyclacenes have certain effects on HMO spectra. Therefore, those vertices of cyclacenes characterized by degree 3 are actually shared not by two, but by three rings. Furthermore, the two existing common edges shared by the periphery and the benzenoid ring present in the structures of cyclacenes definitely excludes cyclacenes from being cata-condensed systems although their parent compounds, acenes, are cata-condensed aromatics.

Another interesting feature of these rather strained molecules is the existence of NBMOs which lead to open shell structures in certain cyclacenes.

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