

# A Topological Approach to the Stabilities of Isomeric Hückel and Möbius Type Cyclacenes

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Received 21.2.1997

Within the constraints of Hückel molecular orbital theory, Hückel and Möbius type cyclacenes were investigated in terms of their angle of total  $\pi$ -electron energy,  $O_\pi$ , and  $\cos O_\pi$  to find out how structural changes affect the stabilities. It has been theoretically deduced that as the number of benzenoid rings (R) increases the isomeric Hückel and Möbius type cyclacenes should have comparable stabilities, although for low values of R odd-Hückel type and even-Möbius type are predicted to be more stable.

## Introduction

The  $\pi$ -orbitals are written as a linear combination of atomic p-orbitals of the conjugated carbon atoms. The basis set is normally chosen so that the p-orbitals overlap in phase. However, there are certain situations where this condition cannot be achieved. One such example was proposed by Heilbronner<sup>1,2</sup> who considered the case of a conjugated chain which is twisted through  $180^\circ$  (or in general,  $k\pi$ ) before union at the terminal carbon atoms to form a cyclic conjugated hydrocarbon. The effect is to introduce a “phase dislocation” (or phase disjunction, see Figure 1).

A similar configuration can also arise during the course of a concerted reaction<sup>3,4</sup>.

Möbius systems (anti-Hückel systems) are defined as cyclic arrays of orbitals having an odd number of sign inversions resulting from the negative overlaps between the adjacent  $\pi$ -orbitals of different sign<sup>5</sup>. Some Möbius type compounds are known<sup>6-8</sup>. Recall that the Möbius strip is a one-sided surface topologically<sup>9</sup>.

On the other hand, cyclacenes (Figure 2.) which can be considered as cyclic form of acenes represent a Hückel system and constitute an interesting class of compounds<sup>10-20</sup>. Their counterparts, Möbius type cyclacenes, (Figure 3.) should also possess interesting properties.

In the present study, within the Hückel molecular orbital (HMO) framework<sup>2,5,21,22</sup>, the total  $\pi$ -electron energy<sup>5-21</sup> ( $E_\pi$ ) and the angle of total  $\pi$ -electron energy<sup>23</sup> for Hückel and Möbius type cyclacenes have been considered.

## Theory

### Definition 1.

Odd (even) cyclacenes are cyclacenes having an odd (even) number of benzenoid rings.

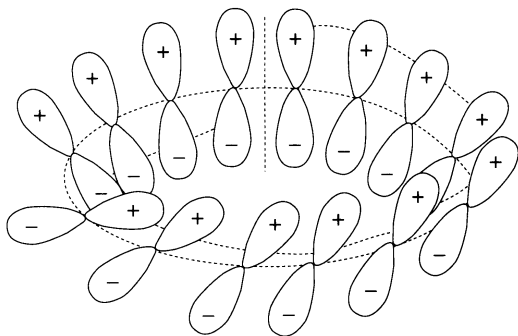


Figure 1. Möbius type  $\pi$  strip.

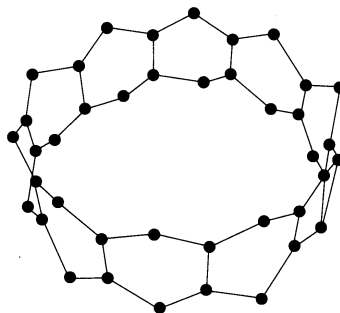


Figure 2. Hückel type cyclacene.

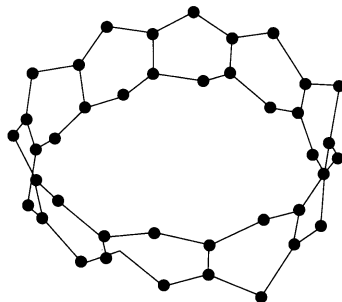


Figure 3. Möbius type cyclacene.

### Definition 2.

A benzenoid strip (or belt) is a strip which contains no other rings except the benzenoid type.

The total  $\pi$ -electron energy is expressed<sup>2</sup> as

$$E_{\pi} = 2 \sum^{OCC} x_i, \quad (1)$$

where  $x_i$  stands for the  $i^{th}$  molecular orbital energy. For alternant hydrocarbons it was proved<sup>23</sup> that

$$E_n = 2(ne)^{1/2} \cos O_{\pi} \quad (2)$$

where half the number of vertices (carbon atoms), number of bonds (carbon-carbon) and the angle of total  $\pi$ -electron energy are represented by  $\pi$ ,  $e$  and  $O_{\pi}$ , respectively. The angle is the one existing between vectors,

$$A(1, \cdot, 1) \quad \text{and} \quad B(x_1, \cdot, x_n)$$

in  $n$ -dimensional Euclidean linear space<sup>24</sup>. In the case of nonalternant hydrocarbons, Eq. (2) becomes.

$$E = 2 \left( \sum^{OCC} x_i^2 \right)^{1/2} (n)^{1/2} \cos O_{\pi} \quad (3)$$

because  $\sum^{OCC} x_i^2$  is no longer equal to  $e$ . As it is seen from Eq.(2) and (3),  $E_\pi$  actually consists of two functions,  $F(x_i, n)$  and  $\cos O_\pi$ . The first one is an increasing function as the system becomes larger and larger, whereas the subtle topological variations are dictated by the function of  $\cos O_\pi$ . For certain sets of compounds e.g., annulenes,  $\cos O_\pi$  for homologous members exhibits a fluctuating character depending on the size of the system (eg.  $4m+2$  or  $4m$  type annulene). In form this behavior is analogous to damped oscillations in physics<sup>25-26</sup>. A similar behavior exists for Hückel and Möbius type cyclacenes and it is the subject of the present study.

## Results and Discussion

A simple topological survey reveals maybe the most striking difference between the Hückel and Möbius type cyclacenes. Although, the former class of systems is an example of alternant hydrocarbons, the latter group of systems are nonalternant. It should be mentioned that even annulenes, irrespective of Hückel or Möbius type, are alternant hydrocarbons. However in the case of cyclacenes, which possess annulenic peripheral circuits, this property is the function of number ( $k$ ) of phase-dislocations along the benzenoid strip. Whenever  $k$  is an even number, alternancy of the sites occurs resulting in an alternant system but for odd values of  $k$ , a nonalternant system arises (Möbius type). Note that in the present study, the strip considered (Hückel or Möbius type) is the strip of benzenoid rings. Figure 4. depicts the open projected formulas of those types of cyclacenes originating from pentacene. In the present study, otherwise stated,  $k$  is taken as one for Möbius and zero for Hückel cyclacenes. Note that as the  $\pi$ -circuit along the periphery is considered, the number of phase-dislocations is  $2k$ .

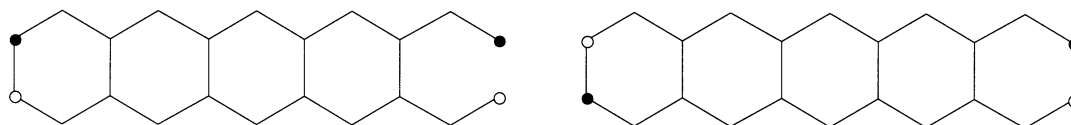


Figure 4. Open projected formulas for Hückel and Möbius type cyclacenes.

The present treatise reveals that within the homologous series of Möbius type cyclacenes, the existing single nonbonding molecular orbital plays the role of HOMO or LUMO orbital-depending on the number of benzenoid rings present. Moreover, the symmetrically distributed molecular orbital energies of a Hückel type cyclacene are reshuffled through the process of twisting the benzenoid belt through  $180^\circ C$  to produce the corresponding Möbius type cyclacene. Note that when a Möbius type cyclacene is dissected along the benzenoid strip a continuous ring of  $2n$ -atoms is produced where  $2n$  is the number of carbon atoms. Whereas the same operation on Hückel type cyclacenes results in two rings of  $n$ -atoms only. Structurally, in these systems  $2n = 8, 12, 16, \dots, 4m$ ,  $m$  being an integer.

In the present study HMO calculations were carried out by using a computer program originally written by Lowe<sup>22</sup>.

Table 1. Tabulates  $E_\pi$  and  $\cos O_\pi$  values of Hückel and Möbius type cyclacenes and Figure 5. depicts  $O_\pi$  vs.  $R$  (the number of benzenoid rings) graphs of these systems. As it is shown in Table I, an odd-Hückel cyclacene is more stable than its isomeric Möbius system, and an even-Möbius cyclacene is more stable than its isomeric Hückel cyclacene. The above conclusion holds true for small sized system. As  $R$  increases  $E_\pi$  tends to be the same for the isomeric cyclacenes. In each case, the angle of total  $\pi$ -electron energy exhibits the characteristic damped behavior. As it is seen from Figure 5. Hückel and Möbius cyclacenes initially are out phase of each other; but as  $R$  increases damping becomes very pronounced and the fluctuations of  $O_\pi$

ceases for both types of the systems. For the initial values of R, it is evident that  $O_\pi$  function for the both types of cyclacenes has the period of 2 with the phase difference of 1 in terms of the number of benzenoid rings (R).

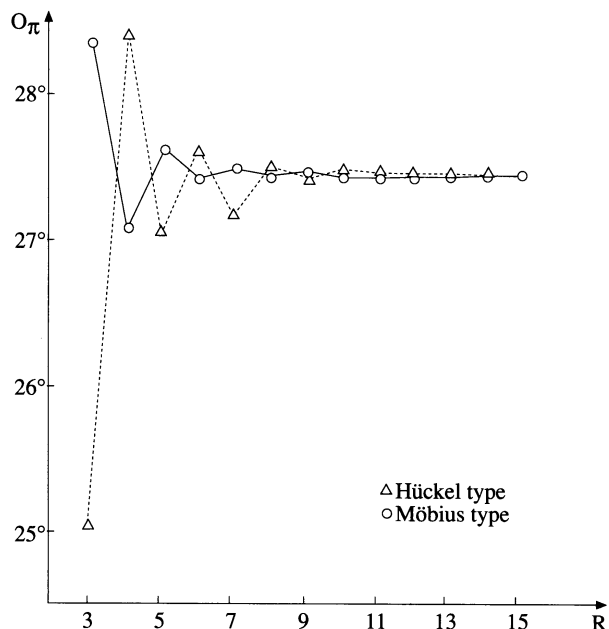


Figure 5. Variation of  $O_\pi$  of cyclacenes.

Table 1. The variation of  $E_\pi$  and  $\cos O_\pi$  values of cyclacenes.

R	Hückel type		Möbius type	
3	17.1905	.9060	16.8063	.8801
4	22.2462	.8793	22.4368	.8892
5	28.1541	.8903	28.0539	.8862
6	33.6127	.8857	33.6671	.8876
7	39.3093	.8879	39.2791	.8870
8	44.8736	.8868	44.8906	.8873
9	50.5117	.8874	50.5020	.8871
10	56.1079	.8871	56.1134	.8972
11	61.7280	.8872	61.7248	.8872
12	67.3342	.8872	67.3361	.8872
13	72.9485	.8872	72.9474	.8872
14	78.5582	.8872	78.5588	.8872
15	84.1705	.8872	84.1701	.8872

The first column under the each heading tabulates  $E_\pi$  values in the units of  $\beta$ .

## Conclusion

As R increases,  $O_\pi$  approaches the limiting value of  $27^\circ .47$ , irrespective of the type of the cyclacene being considered. The practical consequence of it is that, although Möbius cyclacenes are nonalternant systems their  $E_\pi$  values can be calculated by using Eq. (2) as if they were alternant hydrocarbons. That means,

within the constraints of HMO theory  $\sum^{OCC} x_i^2$  for large Möbius cyclacenes is equal to  $e$  as it is the case in the Hückel type. Consequently, large isomeric cyclacenes of the both types should possess the same stability as expected by  $E_\pi$ . Note that some other properties of these isomers should obviously be different.

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