

# MNDO treatment of the Hückel and Möbius types of cyclacenes

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## Abstract

The Möbius-type cyclacenes with benzenoid rings of 8–14 are compared with the corresponding Hückel types in terms of various properties which are estimated within the framework of MNDO calculations. It has been found that, although in the homologous series of the Hückel types certain properties are dictated by the cryptoannulenic effect, they are only partly dependent on this effect in the case of Möbius cyclacenes. © 1998 Elsevier Science B.V. All rights reserved.

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## 1. Introduction

Cyclacenes which have identical peripheral circuits are a subgroup of corannulenes. Note that normally corannulenes possess non-identical inner and outer peripheral circuits [1]. Cyclacenes, which have attracted the attention of investigators during the last couple of decades [1–11], are structurally of two types, namely the Hückel and Möbius cyclacenes (Fig. 1). Many interesting features of the Hückel-type cyclacenes [11–14] and silacyclacenes [15,16] have been the subject of investigation of various aspects, such as the cryptoannulenic effect, the possibility of superaromatism etc. On the other hand, carbon tubules (nano tubes or microtubules) which recently have become the point of interest [17–19] are structurally related to cyclacenes. Moreover, Kivelson and Chapman have already mentioned cyclacenes in connection with a model for conducting conjugated polyacenes [6].

On the other hand, the Möbius-type cyclacenes have attracted less attention in the past but

nevertheless some pioneering work has been done [20–22]. Theoretically, the main difference between the Hückel and Möbius systems is that the former ones possess an even number (including zero) of phase dislocations, whereas the Möbius systems have an odd number of phase dislocations in the basis molecular orbitals [23,24] and can be visualized by use of the Möbius strip.

In the present study, MNDO treatment of certain Möbius-type cyclacenes has been considered in comparison with the corresponding Hückel types (Fig. 1).

## 2. Method

In the present treatise, the Möbius-type cyclacenes with 8–14 benzenoid rings ( $R$ ) and just one phase dislocation were subject to MNDO calculations at the level of restricted Hartree–Fock (RHF) approach. All the structures were geometry optimized (by using the steepest descent method followed by conjugate

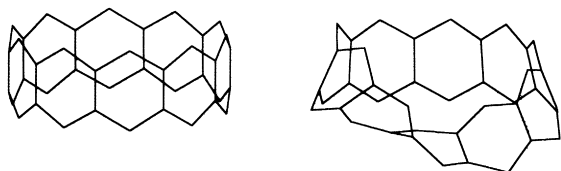


Fig. 1. The Hückel and Möbius types of cyclacenes.

gradient Fletcher–Rieves and Polak–Ribiere methods [25] in a consecutive manner) prior to single point MNDO-type molecular orbital calculations. All these computations were performed by using the Hyperchem (release 4) package program. The surface areas and volumes of cyclacenes were computed (using HyperchemPlus 1.5 package program) as suggested by Bodor et al. [26], using the atomic radii of Gavezzotti [27].

### 3. Results and discussion

Möbius systems (or anti-Hückel systems) are mathematically non-orientable surfaces [28] and have only one surface. Because of that, a Möbius-type cyclacene, contrary to the Hückel type, has just one peripheral circuit comprising all the carbon atoms in the system. Thus, the peripheral circuit is a ring of  $4R$  carbon atoms, where  $R$  is the number of benzenoid rings in the structure.

In the present study, cyclacenes with  $R = 8–14$  were considered in order to have reasonable geometries for the Möbius-type structures.

#### 3.1. The heats of formation

The total energies and heats of formation of the

Hückel- and Möbius-type cyclacenes are displayed in Table 1. It can be seen that the total energies of the Hückel and Möbius cyclacenes with the same  $R$  value are predicted to be comparable by MNDO treatment. On the contrary, the heats of formation values are very different, the Hückel types being less endothermic. However, in both cases  $\Delta H_f/R$  values are monotonously decreasing as  $R$  increases.

In the case of a Hückel-type cyclacene, the peripheral circuit, which can be dealt with as a special type of polyene ribbon with mode 0 or 2 (modulo 4), plays an important role in the stability of the molecule [11,13,29], depending on whether the peripheral circuit is of the type with  $4m$  (antiaromatic) or  $4m + 2$  (aromatic) carbon atoms ( $m$  is an integer). On the other hand, extending Zimmerman's approach [30], which states that those are energetically preferred when the number of participant electrons is  $4n$  ( $n$  is an integer), to Möbius systems, the Möbius cyclacenes with  $4m$  peripheral circuits are expected to be more stable because in cyclacenes of the Hückel and Möbius types, each carbon contributes a single electron into the conjugation. MNDO calculations evaluate cyclacenes in accordance with Zimmerman's approach. Thus, the cryptoannulenic effect [11] is valid for the Hückel cyclacenes. On the other hand, only Möbius cyclacenes with  $R = 8–11$  exhibit cryptoannulenic effect,  $4m$ -members being less endothermic, but  $R = 11$  onwards,  $\Delta H_f$  values monotonously increase irrespective of the character of the peripheral circuit.

#### 3.2. Frontier molecular orbital energies

MNDO calculations reveal that both of the Hückel

Table 1  
The total energies and heats of formation of various Hückel- and Möbius-type cyclacenes (kJ/mol)

$R$	Hückel type		Möbius type	
	Total energy	$\Delta H_f$	Total energy	$\Delta H_f$
8	– 415497	1508	– 415007	1998
9	– 467645	1486	– 467059	2072
10	– 519673	1584	– 519214	2043
11	– 571804	1579	– 571324	2058
12	– 623800	1709	– 623429	2079
13	– 675927	1707	– 675519	2115
14	– 727900	1860	– 727598	2161

Table 2

The frontier molecular orbital energies and interfrontier energy gaps ( $\Delta E$ ) for various Hückel- and Möbius-type cyclacenes

<i>R</i>	Hückel type			Möbius type		
	HOMO	LUMO	$\Delta E$	HOMO	LUMO	$\Delta E$
8	– 1.063	– 0.333	0.730	– 1.122	– 0.266	0.856
9	– 1.111	– 0.296	0.815	– 1.124	– 0.287	0.836
10	– 1.064	– 0.345	0.718	– 1.064	– 0.333	0.730
11	– 1.104	– 0.313	0.791	– 0.971	– 0.425	0.546
12	– 1.066	– 0.350	0.715	– 0.962	– 0.433	0.528
13	– 1.099	– 0.322	0.776	– 0.964	– 0.432	0.530
14	– 1.068	– 0.353	0.714	– 0.962	– 0.432	0.523

Energies  $\times 10^{-18}$  J.

and Möbius cyclacenes are closed-shell systems. The frontier molecular orbitals (HOMO and LUMO, respectively), which usually play an important role in UV-VIS spectra and chemical reactions, exhibit different characteristics in the cases of the Hückel and Möbius cyclacenes. For example, as the homologous series of the structures are considered, FMO energies of the Hückel cyclacenes fluctuate alternately, producing a series of local maxima and minima. Thus, the interfrontier energy gaps ( $\Delta E$ ) for the Hückel types alternate in value (Table 2), whereas the Möbius cyclacenes generally have a tendency in the direction of increasing HOMO and decreasing LUMO energies as *R* increases. The overall effect is such that for the Möbius cyclacenes,  $\Delta E$  values generally decrease as the structures become larger.

### 3.3. Charges and dipole moments

Although, MNDO calculations for the Hückel-type cyclacenes predict some minute negative and positive

partial charges on the carbons and hydrogens, respectively, and this behavior is also exhibited by Möbius cyclacenes with *R* = 11–14, the others (*R* = 8–10) possess positively and negatively charged carbons.

As for the dipole moments, the Hückel-type cyclacenes have zero value of dipole moments, whereas the Möbius types, in an interesting manner, exhibit certain local minima and maxima (in the range of 0.3–3 debye) in the series of *R* = 8–12 (Table 3). Also note that the maxima occur for structures with a peripheral circuit of *4m*-type (*R* = 8, 10 etc.). It seems that, *R* = 13 onwards, the Möbius cyclacenes tend to lose their characteristic feature in terms of dipole moments.

### 3.4. Some additional properties of cyclacenes

Table 3 tabulates some other properties of cyclacenes in addition to dipole moments. By the inspection of the table, it is evident that for lower members of the cyclacenes, volume and area are comparatively

Table 3

Some estimated properties of cyclacenes

<i>R</i>	Hückel type		Möbius type		
	Area	Volume	Area	Volume	Dipole moment
8	534	1030	532	1009	0.578
9	604	1156	581	1128	0.393
10	667	1285	641	1270	2.551
11	739	1409	700	1406	0.650
12	793	1539	774	1545	0.873
13	866	1663	877	1678	0.944
14	931	1794	938	1810	1.112

Area:  $\times 10^{-20}$  m<sup>2</sup>; volume:  $\times 10^{-30}$  m<sup>3</sup>; dipole moment: debye.

less for the corresponding Möbius types. However, as the peripheral size increases, this time the Hückel types possess smaller values.

#### 4. Conclusion

The comparison of MNDO data for the Hückel and Möbius types of cyclacenes reveals the effect of any phase dislocation along the strip of  $\pi$ -skeleton present in these presently non-existent structures. The Hückel types are predicted to be less endothermic, although in terms of the total energy they are comparable with the corresponding Möbius types, thus inferring that the formerly mentioned types with a pronounced cryptoannulenic effect may have more likely future synthetic availability.

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