

MACROCYCLIC π -SYSTEMS WITH C_2 -SYMMETRY AS THE SUM
OF π -SYSTEMS WITH HÜCKEL AND MÖBIUS TOPOLOGY

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Abstract: The π -system of a macrocycle with twofold rotation symmetry and $2N$ conjugated π -electrons can conveniently be regarded as the sum of two cyclic N - π -electron systems having Hückel and Möbius topology, respectively.

From our experimental studies of cyclophanes with unsaturated bridges it has become increasingly apparent that some properties of the π -electron systems in these compounds bear strong similarities to those of the annulenes.¹ To obtain a qualitative theoretical description of the π -system in the cyclophanes we have turned our attention to simple Hückel theory, which has been so successful in developing a conceptual understanding of the electronic properties of the annulenes.

One significant property of a $[2N]$ annulene, which can be generalised to cyclophanes, is illustrated in Fig. 1 by using a mnemonic device to obtain the orbital energies. By inscribing a regular polygon in a circle of radius 2β with a vertex at the bottom of the circle, the orbital energies for the annulene with Hückel topology are obtained from the vertical displacement of the vertices from the horizontal diameter. Similarly, if the polygon is placed with the lowest side horizontal, then the orbital energies of the annulene with Möbius topology are obtained.² Clearly, the $[2N]$ annulenes

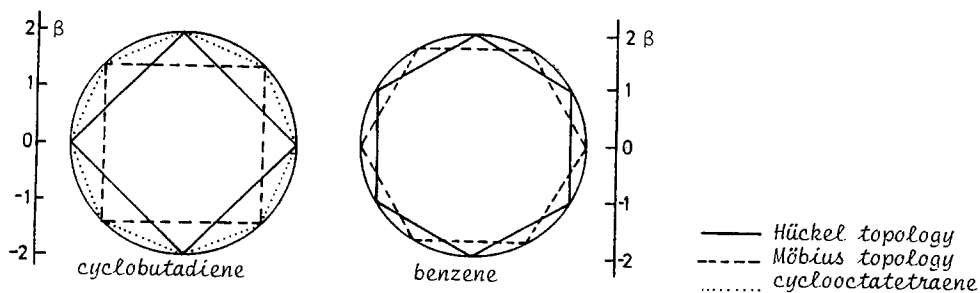


Fig. 1. Mnemonic device for the evaluation of orbital energies of cyclobutadiene and benzene within the Hückel approximation.

can be viewed as combinations of two [N]annulenes with Hückel and Möbius topology, respectively. Thus cyclooctatetraene can be viewed as a composite of normal (Hückel) cyclobutadiene and Möbius cyclobutadiene, while for cyclododecahexaene the orbitals and their energies are easily obtained from those of benzene and Möbius benzene.

For the [2N]annulenes, the frontier orbitals and their energies, which are the chemically most significant ones, are easily obtained from the subset from the smaller ring of Hückel topology in the case of cyclooctatetraene and from the subset from the smaller Möbius topology ring in the case of cyclododecahexaene. This idea of reducing a macrocyclic π -system to two smaller cyclic π -systems with Hückel and Möbius topology, respectively, is not limited to annulenes since it is a general consequence of \underline{C}_2 -symmetry and thus can be applied to all rings with a delocalised π -system having a \underline{C}_2 -axis of symmetry perpendicular to the plane of the π -system. For such molecules consisting of two identical subunits linked to each other in such a way that the resultant species has at least \underline{C}_2 -symmetry, group theory provides a method to reduce the total Hückel determinant of order $|2N \times 2N|$ into two determinants of order $|N \times N|$ by a symmetry transformation.³ The two resulting determinants, one symmetric and one antisymmetric with respect to the \underline{C}_2 -symmetry, correspond to those from two smaller rings, one of Hückel and one of Möbius topology (Fig. 2).⁴

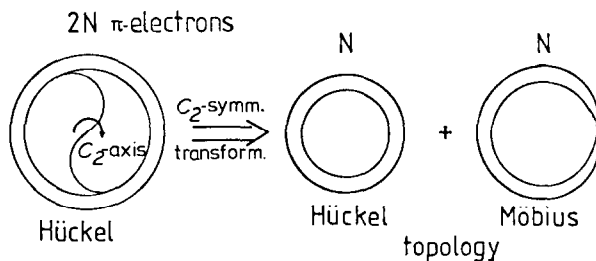


Fig. 2. Schematic representation of \underline{C}_2 -symmetry transformation of a $2N$ macrocyclic π -system into two N π -systems with Hückel and Möbius topology, respectively.

For alternant hydrocarbons the orbital energies within the Hückel approximation are centred pairwise on the $\beta=0$ level. If the parent macrocycle is an alternant hydrocarbon with a π -perimeter, then the smaller rings will also be alternant hydrocarbons which means that the HOMO and LUMO orbitals appear together in one of the two subsets from the smaller rings of Hückel and Möbius topology. A simple rule can be used to decide in which of the subsets the frontier orbitals and their energies are to be found. If the subunit used to construct the hypothetical smaller rings contains a linear array of $4n$ conjugated π -electrons between its two ends, then the frontier orbitals of the larger ring are found in the Hückel-type subset. If the subunit has $(4n+2)$ π -electrons, then the frontier orbitals are found within the Möbius subset.

[2.2.2.2] Paracyclophanetetraene, 1, may serve as an example to illustrate the procedure. The cyclophane contains a 24 π -electron perimeter and can be divided into two equal parts (only \underline{C}_2 -symmetry is used) of Hückel and Möbius topology, respectively. The energies of the frontier orbitals are obtained by solving the Hückel-type determinant of the subunit because the subunit has a linear array of 12 π -electrons between its ends. However, this subunit can itself be further divided into two parts as shown in Fig. 3. The original frontier orbitals are now found by solving the Möbius-type determinant since this new subunit contains only six π -electrons in a linear array. As an alternative to this procedure a \underline{C}_4 -symmetry transformation will give the same results.

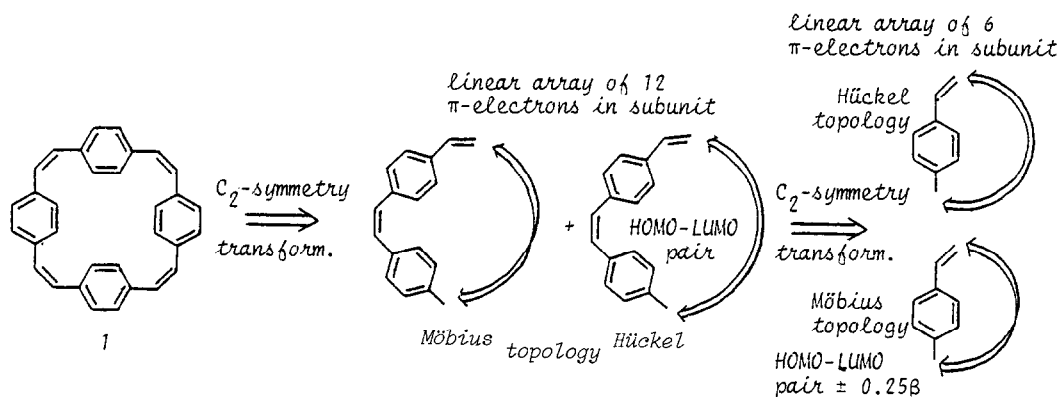


Fig. 3. Transformation of the π -system of cyclophane 1 by consecutive \underline{C}_2 -symmetry transformations.

It follows from the example above that there must exist a number of macrocycles built from the same subunit but with different sizes which have the same frontier orbital energies.¹ The $[4n]$ annulenes are just one example of such a series of macrocycles with π -perimeters.

Alternant hydrocarbons with π -perimeters provide the simplest examples of the use of \underline{C}_2 -symmetry for evaluation of the frontier orbitals and their energies in cyclic π -systems. However, the procedure can also be applied to nonalternant hydrocarbons, as illustrated below (Fig. 4). The total Hückel determinant can still be transformed into two smaller ones since the symmetry arguments are valid, but the orbital pairing scheme is no longer obtained. The subunit of the macrocycle in Fig. 4 is a vinylfulvene which has six π -electrons in a linear array between its ends. Thus the frontier orbitals are found among the solutions to the hypothetical smaller ring with Möbius topology.

The use of \underline{C}_2 -symmetry can simplify the solution of the Hückel determinant for macrocyclic rings with delocalised π -electrons but symmetry arguments are also valid beyond the Hückel approximation.

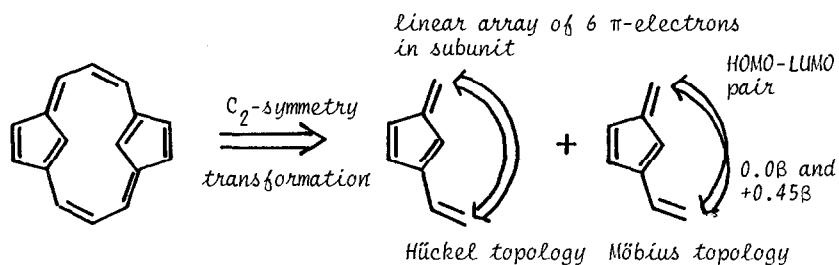


Fig. 4. C_2 -Symmetry transformation of a nonalternant macrocycle (a fulvene derivative) into two smaller rings of Hückel and Möbius topology, respectively.

A most interesting consequence of rotational symmetry is revealed on extending the method to macrocyclic π -systems of the type discussed here consisting of \underline{n} identical units linked in a head to tail fashion (head and tail may be identical) resulting in $C_{\underline{n}}$ -symmetry. Using group theory one can show that for alternant hydrocarbons with \underline{n} even, the Hückel frontier orbitals of the macrocycle can be found among the solutions to the species formed by internal linkage of the subunit to give rings of Hückel and Möbius topology. If \underline{n} is odd the symmetry transformation will give a determinant which correspond only to the smaller ring of Hückel topology. The previously mentioned rule for finding the frontier orbitals is still valid. Furthermore, these calculated frontier orbitals give lower and upper limits for the frontier orbital energies of the corresponding linear polymers with extended π -systems. Such polymers are of great current interest as organic conductors and their critical property is the gap between the filled and empty molecular orbitals. The use of the method presented here for an estimation of the lower limit of the band gap in such polymers will be discussed in a forthcoming paper.

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References and notes

1. See e.g. U. Norinder, D. Tanner and O. Wennerström, Croat. Chim. Acta **56**, 269, 1983, and references therein.
2. H.E. Zimmerman, Accounts Chem. Res. **4**, 272, 1971, and references therein. H.E. Zimmerman, Tetrahedron **38**, 753, 1982.
3. See e.g. F.A. Cotton, "Chemical Applications of Group Theory", Wiley, New York, 1963, or H.E. Zimmerman, "Quantum Mechanics for Organic Chemists", Academic Press, New York 1975.
4. Similar results have been obtained by graph theoretical methods by R.E. Merrifield and H.E. Simmons, Chem. Phys. Lett. **74**, 753, 1982.

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