

On the Relation between the Frontier Orbitals in Small Rings, Macrocyclic Compounds, and Linear Polymers with Extended π Systems

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Hückel theory and rotational symmetry transformations are used to demonstrate the close relation between the frontier orbitals in small rings, macrocyclic compounds and linear polymers with conjugated π systems built from the same repeating units. The concept of cycling π systems of Hückel and Möbius topology is used to interpret the results from rotational symmetry operations of the total Hückel determinant for the macrocyclic oligomers and the linear polymers. Simple rules for the location and identification of the frontier orbitals among the solutions of the subdeterminants from the symmetry transformations are presented. The method is then used to evaluate the relative band gaps (difference in frontier orbital energy) in cross-conjugated polyacetylenes and in polyarylenes in which the arene is a [4]-, [6]-, [8]-, or [10]-annulene.

Molecules with large conjugated π systems have long attracted the interest of organic chemists, and the last decade has seen an upsurge of this interest because of the unusual electrical properties of polyacetylenes and polyarenes which all contain large delocalised π electron systems. The neutral polymers are usually poor conductors but they can be oxidised or reduced ("doped") to highly conducting materials.^{1–4}

The cyclic analogues of the polyenes are the well known annulenes.^{5–6} In contrast to the linear polyenes, which only gradually change their chemical properties on extension of the π system, the annulenes show very different behaviour on increase of the ring size, (compare, *e.g.*, benzene and cyclooctatetraene). For the larger annulenes with more than 20 π electrons, the effect of increasing ring size diminishes and eventually becomes insignificant. The annulenes can be conveniently divided into two groups, those with a perimeter of $4n + 2$ π electrons which are stabilised and those with $4n$ π perimeters which are unstabilised or even destabilised as compared to the open chain counterparts. This is a consequence of the π orbital energies and usually re-

ferred to as Hückel's rule.⁷ Hückel molecular orbital (HMO) theory has contributed to the conceptual understanding of chemistry in general and of annulene and polyene chemistry in particular. The HMOs of annulenes and linear polyenes and their energies can be easily calculated from the Hückel determinant. The HMO energies can also be obtained directly by the mnemonic devices introduced by Frost as shown in Fig. 1.^{8a}

Within Hückel theory, which in its simplest form considers the topology rather than geometry of the π system, it is possible to calculate the orbital energies for cyclic π systems with one phase inversion between the p orbitals, the so called Möbius π systems.⁹ The HMO energies can be obtained directly for the annulenes of Möbius topology as shown by Zimmerman^{8b} (Fig. 1). It is obvious from Figure 1 that the combination of the HMO energies for an $[N]$ annulene of Hückel and Möbius topology results in the HMO energies for the $[2N]$ annulene of Hückel topology.¹⁰ This result can also be obtained by the use of group theory and symmetry transformations. Consider a $[2N]$ annulene which has a C_2

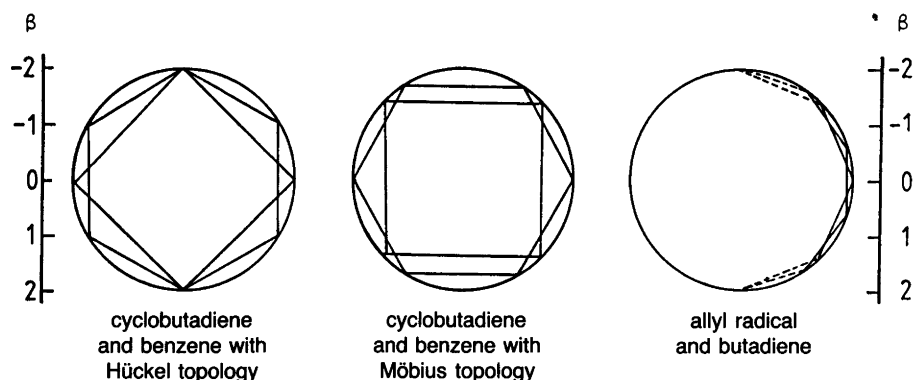


Fig. 1. Mnemonic devices for the evaluation of HMO energies for annulenes and polyenes from Ref. 4.

symmetry axis perpendicular to the planar π system. A C_2 symmetry transformation of the $|2N \times 2N|$ Hückel determinant results in a diagonalized determinant with two new $|N \times N|$ subdeterminants, which corresponds to those of an $[N]$ annulene of Hückel and Möbius topology, respectively.¹⁰ This simple picture (Fig. 2) is conceptually easy to use. Similarly, a mirror plane symmetry transformation of the $|2N \times 2N|$ Hückel determinant results in two $|N \times N|$ subdeterminants which, however, does not correspond to a similar simple geometrical picture.

Higher order rotational symmetry can also be used to the same advantage. The general results for a C_n symmetry transformation of a macrocyclic oligomer with a C_n symmetry axis perpendicular to the plane of the π system are shown in Fig. 3.

The character tables for point groups C_n show

that the A type irreducible representation, which is symmetric with respect to C_n rotation, is always present.¹¹ This corresponds to the small ring of Hückel topology. The B type irreducible representation is present only if n is even. It is antisymmetric with respect to C_n rotation, and corresponds to the small ring of Möbius topology.

The frontier orbitals, the highest occupied and lowest unoccupied molecular orbitals (HOMO and LUMO), are the most significant molecular orbitals (MO:s) from a chemical point of view. Their separation, the frontier orbital gap, is of prime interest for polymers of potential use as organic conductors. For many purposes, knowledge of the frontier orbital energies is sufficient for the prediction of certain chemical properties.¹² The frontier orbitals and their energies are in the majority of cases easy to locate and identify among the many solutions to the total HMO determi-

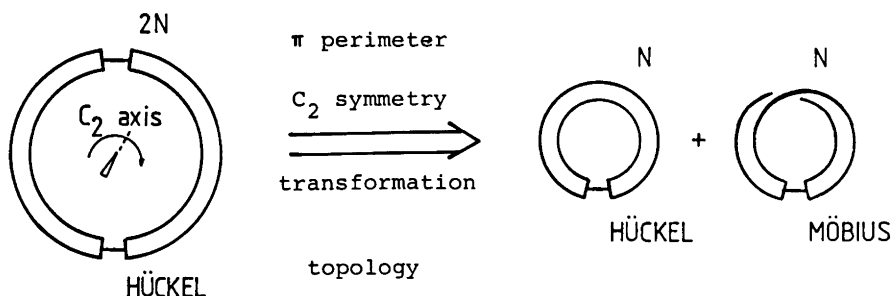


Fig. 2. Schematic representation of C_2 symmetry transformation of the HMO determinant for a $2N$ π perimeter macrocycle to give HMO subdeterminants corresponding to N π perimeter rings of Hückel and Möbius topology.

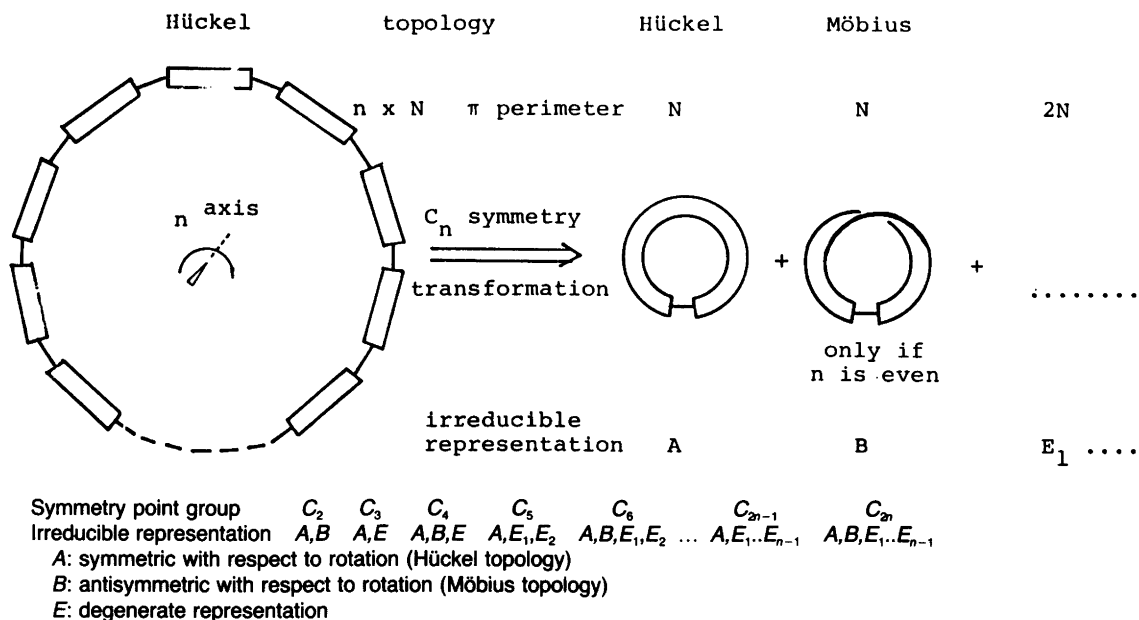


Fig. 3. Schematic representation of C_n symmetry transformation of the HMO determinant for a macrocyclic oligomer.

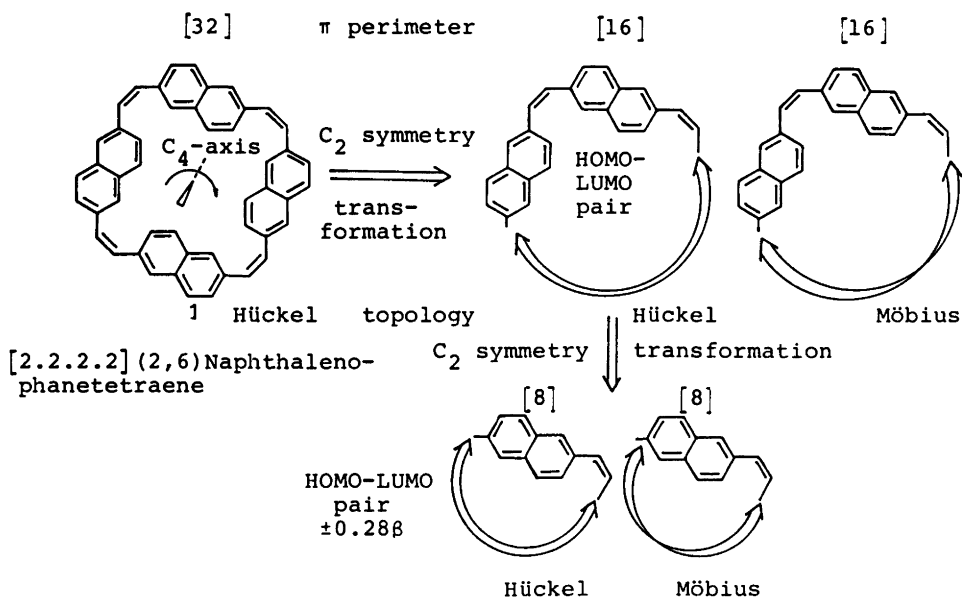


Fig. 4. Location of the frontier orbitals of [2.2.2.2](2,6)-naphthalenophanetetraene among the subsets obtained by 2 consecutive C_2 symmetry transformations of the total Hückel determinants.

nant. They will appear among the solutions to the small rings of Hückel or Möbius topology.^{10,13} One immediate consequence is that the frontier orbitals will be the same for a series of cyclic oligomers with the same repeating unit if they are found among the *A* type irreducible representation, that is, the ring of Hückel topology. If the frontier orbitals are found in the *B* type irreducible representation, that is, the ring of Möbius topology, then every second macrocyclic oligomer in the series will have the same frontier orbitals. The latter situation is observed for the annulenes for which the degenerate pair of nonbonding orbitals, the HOMO and LUMO pair, are the same for all $[4n]$ annulenes, whereas the $[4n+2]$ annulenes have different frontier orbitals. This is true even if different resonance integrals β_1 and β_2 are

used for single and double bonds.¹³ The simple rules for the location of the frontier orbitals are discussed below.

Let us first consider a *macrocyclic oligomer which is an alternant hydrocarbon and which has a π perimeter*. A π perimeter is equivalent to a conjugate chain of sp^2 carbons closed to a monocycle with formally alternating single and double bonds. For such molecules with an axis of symmetry of the order of two or more, perpendicular to the π system, the symmetry-reduced determinants of *A* and *B* type representations correspond to rings which are also alternant hydrocarbons with a π perimeter. Thus, the energies of their MOs are centered pairwise on the $\beta=0$ level¹⁴ and the HOMO and LUMOs must then appear in the same subset. If the small ring has a

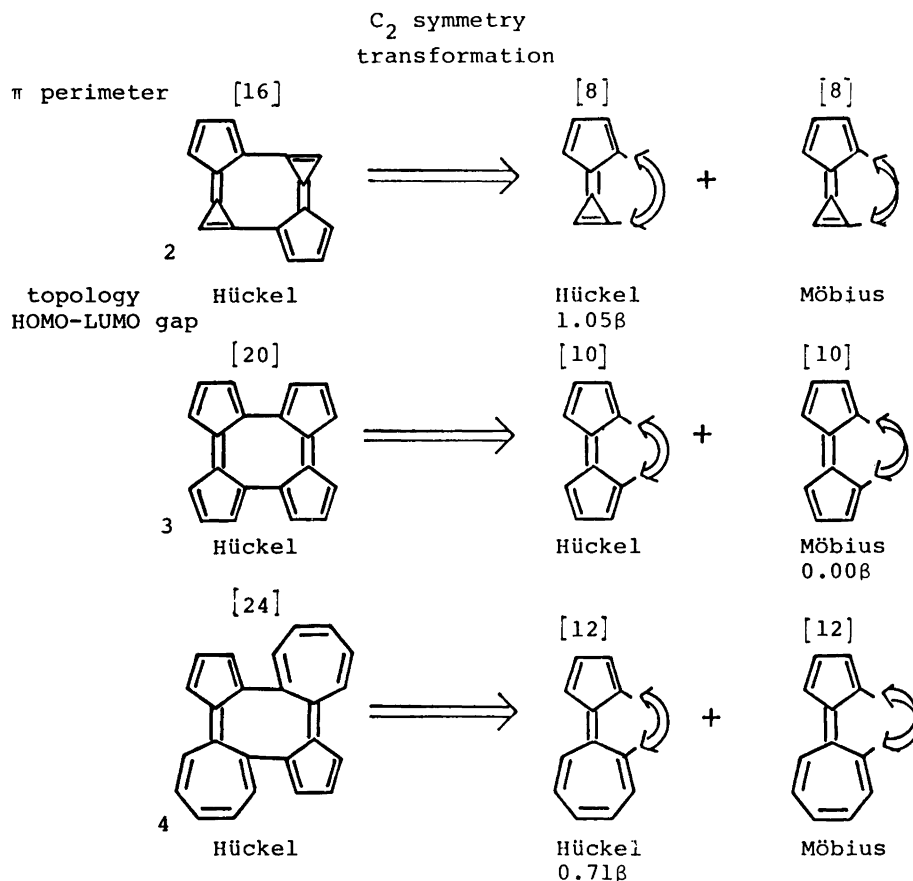


Fig. 5. The frontier orbital gap in 3 pentacyclic nonalternant hydrocarbons, 2, 3, and 4 derived by C_2 symmetry transformations of the total Hückel determinants.

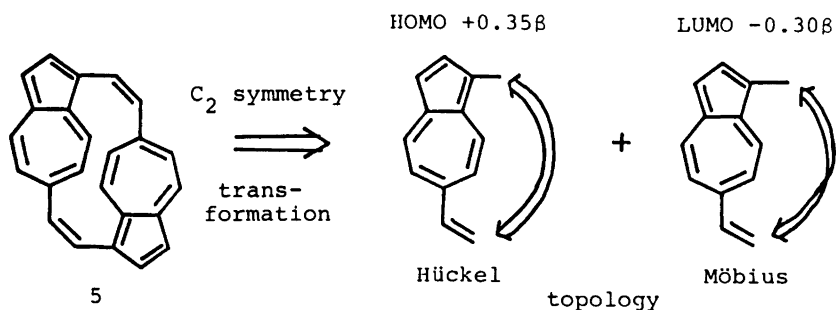


Fig. 6. C_2 symmetry transformation of the π system from a nonalternant hydrocarbon with an undefined π perimeter. [2.2](1,6)azulenophanediene 5.

$4n$ π perimeter, then the frontier orbitals are found within the Hückel topology subset. If, on the other hand, the π perimeter has $(4n+2)$ electrons, then the Möbius topology subset contains the frontier orbitals.¹⁰ The procedure can be illustrated by [2₁] (2.6)naphthalenophanetetraene¹⁵ as in Fig. 4.

Let us next consider *nonalternant hydrocarbons with π perimeters* and rotational symmetry. Symmetry transformations of the total Hückel determinant for such compounds lead to new determinants corresponding to smaller rings which are also nonalternant hydrocarbons with π perimeters. However, the frontier orbitals are no

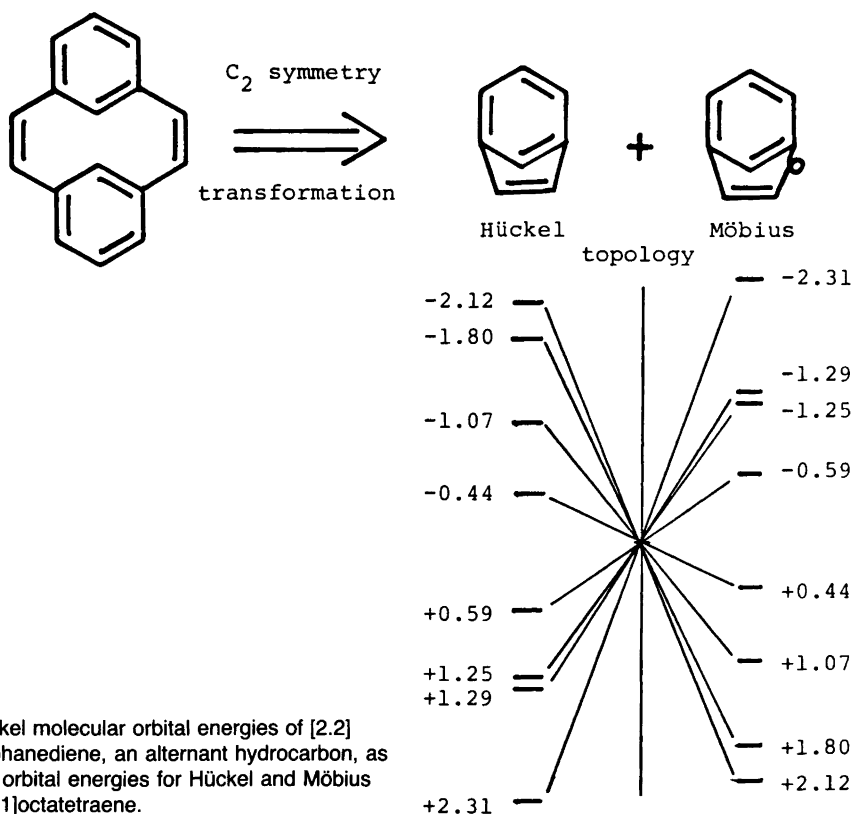


Fig. 7. Hückel molecular orbital energies of [2.2] metacyclophanediene, an alternant hydrocarbon, as the sum of orbital energies for Hückel and Möbius bicyclo[3.2.1]octatetraene.



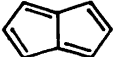
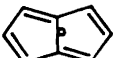
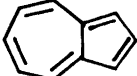
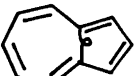
	HOMO	LUMO	Difference	Smallest difference between HOMO and LUMO in ring of Hückel and Möbius topology
	+0.62	-0.24	0.87	0.48
	+0.24	-0.62	0.87	
	+0.47	± 0.0	0.47	0.0
	± 0.0	-0.47	0.47	
	+0.48	-0.40	0.88	0.80
	+0.40	-0.48	0.88	

Fig. 8. HMO energies (in β) for fulvene, pentalene, and azulene of Hückel and Möbius topology. The bond with phase inversion in the rings of Möbius topology is indicated.

longer centered on the $\beta = 0$ level but are, nevertheless, still found within one of the subsets corresponding to the ring of Hückel or Möbius topology. The rule is the same as in the previous case: for a $4n$ π perimeter, the ring of Hückel topology is the relevant one; for a $(4n+2)$ π perimeter, the ring of Möbius topology should be chosen. This is exemplified in Fig. 5 for a series of interesting polycyclic compounds with C_2 axis of symmetry, the calicen dimer 2, the fulvalene dimer 3, and the pentaheptafulvalene dimer 4.

The 3 pentacyclic hydrocarbons 2, 3, and 4 which consist of 3-, 5-, and 7-membered rings fused onto an inner eight-membered ring all have $4n$ π perimeters. Still, the [16] annulene 2 and the [24] annulene 4 have large HOMO-LUMO separations whereas the [20] annulene derivative 3 has degenerate HOMO-LUMO's. The latter is a consequence of the symmetry.¹⁶ The [16] annulene derivative 2 has recently been prepared and found to be a relatively stable compound which

shows a diamagnetic rather than a paramagnetic ring current effect in its NMR spectrum.¹⁷ For this series of nonalternant hydrocarbons with $4n$ π perimeters, the simple Hückel rule is invalid. Still, simple Hückel theory gives a qualitatively correct picture of the π electron structure of the compounds and predicts that the next member of the series, the 2,2'-dimer of heptafulvalene, with a 28 π perimeter should be a true $[4n]$ annulene with degenerate HOMO-LUMOs.

There are also examples of macrocyclic hydrocarbons which are alternant with more than one possible size of the π perimeter. The [2.2] (1,6)azulenophanediene 5 is such a compound. The π perimeter size depends on the loop which is followed and varies between 16, 18, and 20. The C_2 symmetry transformation of the HMO determinant results in two new subdeterminants which correspond to small rings of Hückel and Möbius topology, respectively, with π perimeters of 8 or 10 electrons. Calculations reveal that the

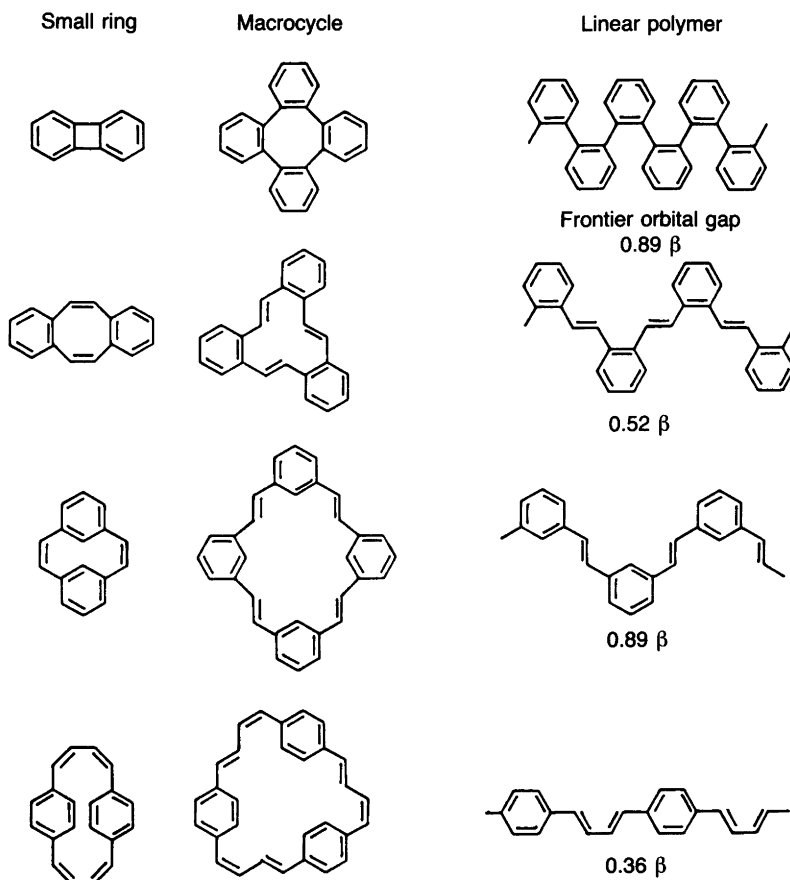


Fig. 9. Series of small rings, macrocycles, and linear polymers with a common repeating unit which have the same frontier orbitals within each series according to HMO theory.

frontier orbitals appear one in each of the two subsets with a separation of 0.65β (Fig. 6).

The symmetry transformations of the total Hückel determinant can also be useful for *alternant hydrocarbons without a conjugated π -perimeter*. The results can then be interpreted as determinants from the repeating unit closed onto itself to form the two rings of Hückel and Möbius topology. However, in this case the small rings are no longer alternant hydrocarbons. [2.2] Metacyclophanediene 6^{18} might be used as an example (Fig. 7). Since the parent compound is alternant, it follows that the two small rings must have the same HMO energies but with different signs, as illustrated. The frontier orbitals can then be identified from either of the two subsets of the molecular orbitals.

The example of [2.2] metacyclophanediene in Fig. 7 shows the interesting relation between the HMO energies of the Hückel and Möbius topology rings of certain nonalternant hydrocarbons. If the compounds can be transformed into alternant hydrocarbons by removal of one bond only, then the Hückel and Möbius rings have the same HMO energies but with different signs. Some examples of such nonalternant hydrocarbons of interest for the following discussions are shown in Fig. 8.

From the rules for the identification of the frontier orbitals in cyclooligomers with conjugated π systems and rotational symmetry, it follows that, within the framework of Hückel theory, there exists series of macrocycles of different sizes, built from a common repeating unit, which

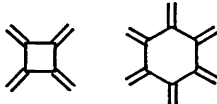
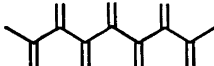

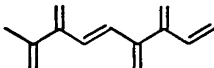
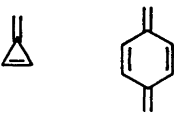
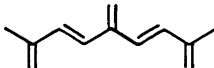

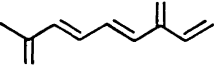

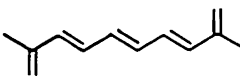
Monocyclic compounds	Polymers	Calculated band gap in β for the polymer
		0.83
		0.69
		0.62
		0.51
		0.43

Fig. 10. Cross-conjugated polyacetylenes and some related monocyclic compounds.

have the same frontier orbitals. The $[4n]$ annulenes are just one example of such a series, others are shown in Fig. 9. We have also shown that the HOMO and LUMOs of such series are upper and lower limits, respectively, for the frontier orbitals in the linear polymers with the same building blocks.¹³ Thus, there exists a close relation between small rings, macrocycles and linear polymers with a common repeating unit as exemplified in Fig. 9.

Conceptually, the use of C_n rotational symmetry transformations has many advantages and immediately reveals the close relation between polymers, macrocycles, and small ring compounds built from a common repeating unit. Furthermore, the method makes use of the Möbius ring concept which again is useful for the understanding of important symmetry-based regularities of compounds with extended π systems.

As already mentioned, the $[4n]$ annulenes and polyacetylene have the same frontier orbital energies as well as alternating single and double bonds. Quite analogously, the radialenes are related to the completely cross-conjugated polyacetylene. Other cross-conjugated polyenes can

be derived from small rings with exocyclic double bonds as shown in Fig. 10.

From the series of polyenes in Fig. 10 and their frontier orbital gap, it should be possible to evaluate the effect of cross-conjugation on the band gap in polyacetylene.

The incorporation of monocyclic conjugated π systems, the annulenes, into polyacetylene leads to an interesting series of hypothetical as well as real polymers. What is the effect on the band gap in the polymer? What ring size and substitution pattern lead to the smallest calculated band gaps? Some of the answers are given in Figure 11 where the small molecules used for the calculations are shown together with the polymers.

Some general conclusions can be drawn from the data in Fig. 11. A band gap of zero, which is equivalent to the situation in polyacetylene, is calculated only for poly-(1,3)-cyclobutadienylene, poly(1,3-cyclooctatetraenylene), and poly(1,5-cyclooctatetraenylene). Considerably larger band gaps are found for the corresponding isomers with conjugated chains, *i.e.*, poly(1,2-cyclobutadienylene) and poly(1,4-cyclooctatetraenylene). Of the three isomeric polyphenylenes,

Bicyclic or polycyclic compound	Polymer	Frontier orbital gap in polymer in β
		0.76
		0.0
		0.89
		1.24
		0.83
		0.0
		0.42
		0.0
		0.80
		0.51

Fig. 11. Calculated frontier orbital gaps (HMO-theory) in polymers containing cyclic π perimeter units linked in various positions.

the *para* isomer has a slightly smaller band gap than the *ortho* isomer, whereas the *meta* isomer shows a very large gap. The incorporation of a [10] annulene ring into polyacetylene results in relatively large band gaps with a slightly smaller calculated value for the 1,6-isomer over the 1,5-isomer.

Conclusions

The Hückel-Möbius topology concept provides a simple representation of the results of C_n symmetry transformation of the total Hückel determinants for linear polymers with extended π systems. By use of this method, we have focused the attention on series of cyclic oligomers other than

those of the annulenes. Such series of compounds should have the same frontier orbital energies and might possess interesting chemical and physical properties as a result of the delocalised π electrons. On oxidation or reduction, they may form model compounds of use for the elucidation of the fundamental properties of organic conductors.

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