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Möbius π -Systems; Links Between Small Cyclic and Large Linear π -Systems

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It is found that within the framework of Hückel theory, the frontier orbital gap in a polymer with an extended π -system, built from simple repeating units, is the same as that of the repeating unit closed onto itself to give a ring of either Hückel or Möbius topology.

Organic compounds with extended π -systems such as polyacetylene, pyrrole, polyaniline and other polyarenes which are built from simple repetitive units are of current interest as new types of conductors and semi-conductors.¹ This has prompted us to point out a simple relation, within the framework of Hückel theory, between small cyclic and large linear π -systems by use of the concept of Möbius topology.² The frontier orbitals (or the band gap) are the same for cyclic oligomers and linear polymers with the same repeating unit. Thus the relative band gap, which is of prime importance for potential organic conductors, can easily be evaluated.

The link between small cyclic and large linear π -systems may be illustrated by use of the mnemonic devices introduced by Frost and Zimmerman³ for the evaluation of the orbital energies of annulenes with Hückel and Möbius topology (Figure 1).⁴ Thus by combination of the orbital energy

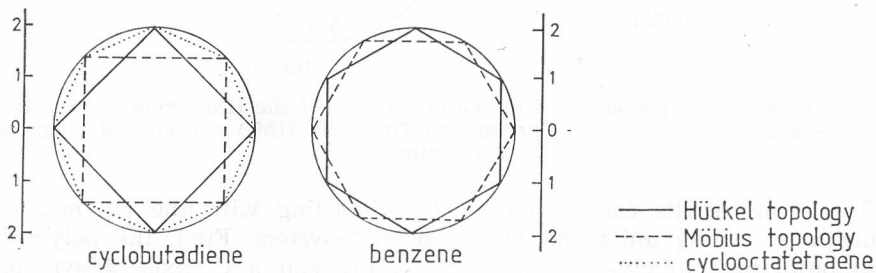


Figure 1. Mnemonic devices for the evaluation of HMO energies for annulenes with Hückel and Möbius topology.

schemes for Hückel and Möbius cyclobutadiene, the orbital energies of cyclooctatetraene are obtained. Similarly, the orbital energies of [12]annulene are obtained by a combination of the HMO:s of Hückel and Möbius benzene.²

Repetition of this process as illustrated in Figure 2 gives the HMO energies for the two series of [4]-, [8]-, [16],... and [6]-, [12]-, [24]-... annulenes, respectively. Both series will ultimately yield the HMO scheme for an infinitely large ring. The frontier orbitals (the degenerate pair of non-bonding MO:s) are the same for the two series and are already present in Hückel cyclobutadiene and Möbius benzene, respectively. These results for the annulene series can be generalized to other alternating π -perimeter cyclo-oligomers.⁵ Thus, for any such cyclic conjugated π -system the HMO energies of the $2N$ π -perimeter ring are obtained by combining the HMO energies of the N -perimeter rings of Hückel and Möbius topology (N is even, closed shell compounds). The large ring must be formed by a head-to-tail combination of the repeating unit to conform with C_2 -symmetry (Figure 2). The frontier orbitals, which give the band gap in the infinite cyclic polymer and thus the infinite linear polymer, are constant for the macrocycles with Hückel topology and $2N$, $4N$, $8N$, ... π -perimeters. They are already present in the N -sized ring of Hückel (Möbius) topology if N is equal to $4n$ ($4n+2$).

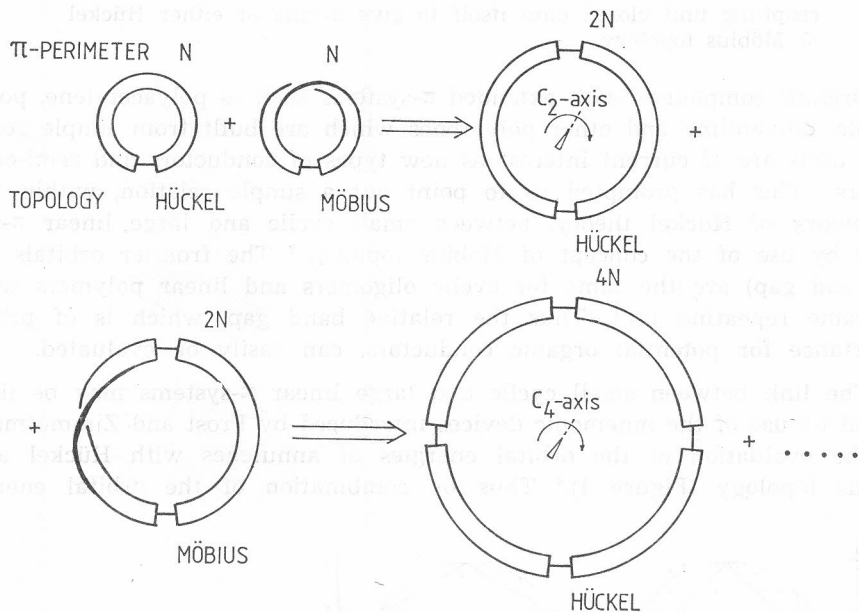


Figure 2. Schematic representation of the evaluation of the HMO energies for cyclo-oligomers with $2N$, $4N$, $8N$... π -perimeters from the HMO energies of rings with a N π -perimeter.

The same results can be obtained by starting with the polymer containing m repeating units and an extended π -system. First, the polymer is closed onto itself to give a macrocycle whereupon a C_m -axis of symmetry perpendicular to the π -system is created. A C_m -symmetry transformation of the total Hückel determinant results, if m is even, in two small deter-

minants which correspond to the repeating unit closed onto itself in a Hückel and Möbius sense, respectively, as well as a series of determinants corresponding to degenerate representations. The frontier orbitals of the polymer are found among the HMO:s of the Hückel (Möbius) topology ring if the π -perimeter contains $4n$ ($4n+2$) electrons⁶ (Figure 3).

Similar ideas to those presented here have been previously reported by Koutecky and Zahradnik.^{7,8} An elegant use of graph theory to identify linear polymers with small band gap is due to Graovac, Gutman, Randić and Trinajstić.^{9,10}

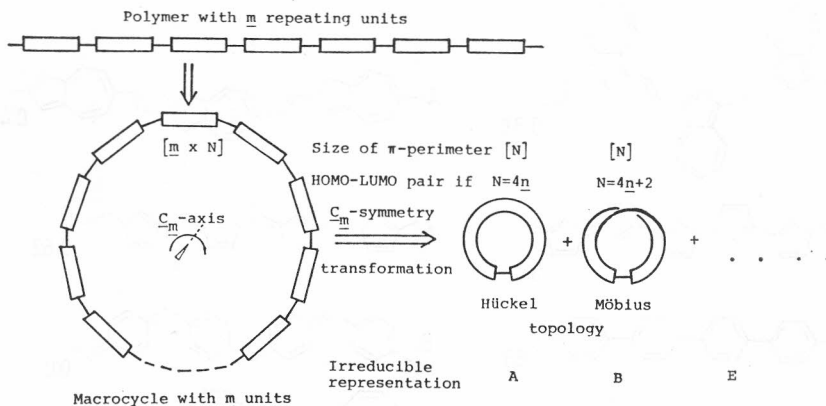


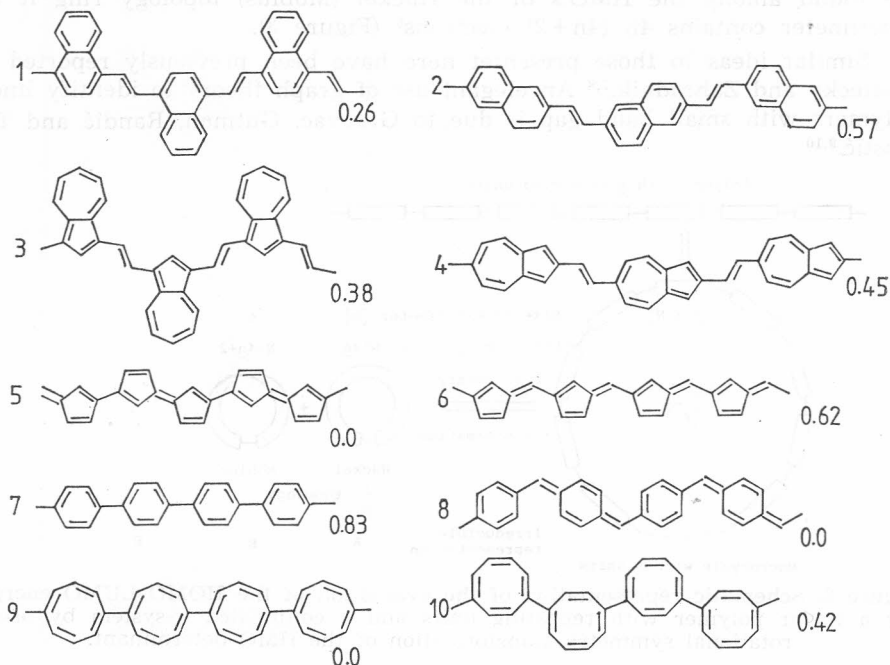
Figure 3. Schematic representation of the evaluation of the HOMO-LUMO energies for a linear polymer with repeating units and a conjugated π -system by use of rotational symmetry transformation of the HMO determinant.

To illustrate the use of the present method for a rapid evaluation of the relative band gap in a series of polymers we have chosen two examples. The first concerns the poly(naphthalenevinylene) and poly(azulenevinylene) with small band gaps. The vinylene groups have been included to lower the band gaps but also to partly eliminate the geometrical restrictions for an effective π -overlap along the chain in eg. poly(1,4-naphthalene). It may also be noted that the 2,6- and 1,4-naphthalenevinylene groups have been incorporated into cyclophanes which show large diatropic ring current effects when reduced to their dianions.¹¹ The HMO calculations indicate that the 1,4-naphthalenevinylene- (1) and 1,3-azulenevinylene-polymer (3) should have smaller band gaps than their 2,6-isomers (2 and 4) as depicted in Table I.

The second example concerns the minimisation of the band gap in polymers built from conjugated five-, six-, and eightmembered rings. Some answers are given in Table I. It is clear that polyfulvalene (5) has a smaller band gap (0.0β)¹² than polyfulvene (6, 0.62β). Of the three polyphenylenes, the *para* isomer (7) has a slightly smaller band gap (0.83β) than the *ortho* isomer (0.89β), while the *meta* isomer has a large band gap (1.24β). However, a much smaller band gap should be observed for polyparaphenylene with one sp^2 -carbon atom between the unsaturated six-membered rings (8, 0.0β). Of the polycyclooctatetraenes, the 1,5-isomer (9) show a small band gap (0.0β), whereas that of the corresponding 1,4-isomer (10) is considerably larger (0.42β).

TABLE I

Calculated Band Gaps (in β) for Ideal Polymers with Conjugated π -electrons Within the Framework of Hückel Theory.



The conceptually simple method presented in this paper for the calculation of the band gap in ideal polymers using simple Hückel theory is ideally suited for rapid calculations on series of similar polymers. In the polymer, the frontier orbital gap (band gap) should be small for the polymer to be of potential interest as a conductor. Once an interesting polymer has been found, more elaborate calculations should be carried out, with due consideration of geometrical constraints. However, there is no reason to believe that HMO theory combined with symmetry arguments (a combination which has previously proven so successful in numerous cases) should fail to give qualitatively correct results.¹³

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SAŽETAK

Möbiusovi π -sustavi: Veza između malih cikličkih i velikih linearnih π -sustava

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Separacija graničnih orbitala unutar Hückelove teorije kod π -elektronskih polimera sagrađenih od jednostavnih kopija jednaka je onoj kod Hückelovih i Möbiusovih prstenova nastalih zatvaranjem lanca kopija. Izabrani su samo oni Hückelovi (ili Möbiusovi) prstenovi kojima je π -elektronski perimetar $4n$ (ili $4n + 2$). Ta je veza upotrebljena kao kvalitativni kriterij za identificiranje polimera s malom separacijom graničnih orbitala.