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# HÜCKEL THEORY APPLIED TO LARGE LINEAR AND CYCLIC CONJUGATED π-SYSTEMS

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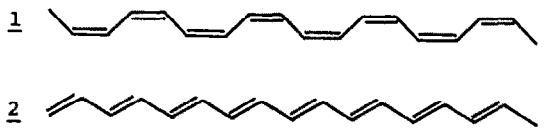
*By use of rotational symmetry ($C_n$-symmetry) a lower limit to the frontier orbital (HOMO-LUMO) gap in large molecules with linear and cyclic conjugated π-systems containing simple repetitive units has been calculated within the Hückel approximation. The frontier orbitals are shown to be the same in series of cyclic oligomers and linear polymers containing the same repetitive units. The orbital gap is calculated from the repetitive units closed on themselves to give a ring of Hückel or, alternatively, Möbius topology depending on the number of conjugated π-electrons in a linear array between the ends of the repetitive unit. For 4n (4n+2) systems the small ring of Hückel (Möbius) topology will give the frontier orbitals.*

## Introduction

Due to their potential applications as organic conductors, molecules with large conjugated linear and cyclic π-systems have regained the interest of organic and polymer chemists.[1] By far the most studied polymer of this type is polyacetylene which consists of an unbranched array of $sp^2$-hybridised carbon atoms each having one hydrogen atom substituent. In the polymer the carbon-carbon bond lengths alternate to give localised single and double bonds. As a consequence, the double bonds may be of either *cis* (*Z*) or *trans* (*E*) configuration. All-*cis*, *1*, and all-*trans*, *2*, polyacetylene are known, the latter being the thermodynamically more stable one.[2] Cyclic analogues of the linear polyacetylene, the annulenes, have

been known for more than two decades.[3] Two examples are shown below, [16]annulene, *3*, and [18]annulene, *4*, the former having alternating short and long C--C bonds[4] whereas all C--C bond lengths in *4* are almost equal.[5] Due to rapid valence isomerisation in *3* and to dynamic processes, *3* and *4* are not fixed in the configurations shown.



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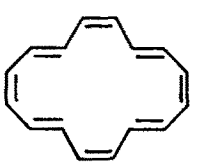

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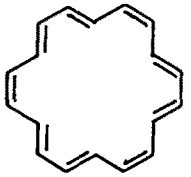

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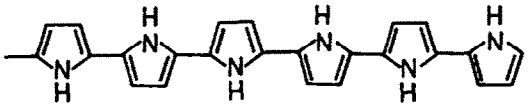
Other polymers of interest as organic conductors are polypyrrole, *5*, and polyparaphenylene, *6*, for which at present there are no cyclic counterparts known.



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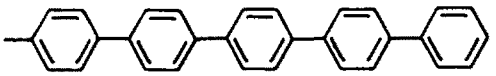

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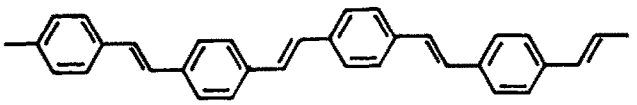
A polymer similar to *6* is poly(paraphenylenevinylene), *7*, which shows interesting conducting properties in a "doped" state.[1a,c]



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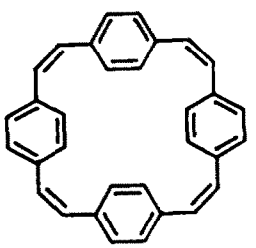
Recently we have prepared some cyclic analogues of *7*, e.g. [2.2.2.2.]paracyclophanetetraene, *8*,[6] and [2.2.2.2.2.2]paracyclophanehexaene, *9*.[7]



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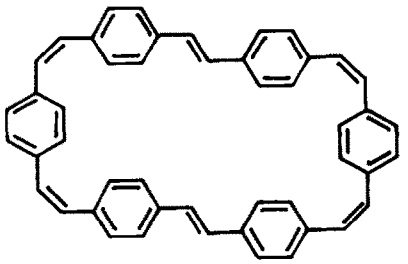

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In general, the polymers are modest conductors or semiconductors as neutral species but upon "doping" *i.e.* oxidation or reduction, they show a dramatic increase in their conductivity.[1] For the linear polymers, only bulk properties and not the conductivity of the individual polymer molecules can be measured. However, for the related cyclic molecules the "conductivity" of defined single molecules can be measured by $^1$H-NMR techniques under certain conditions as the diamagnetic ring current induced by strong magnetic fields.[3] Again, it is generally true that the neutral ring compounds show less "conductivity" *i.e.* smaller induced ring currents, than the oxidised and reduced species.[8] There is no doubt that the annulenes and unsaturated cyclophanes and their charged derivatives are useful model compounds for the study of conducting polymers with large delocalised π-systems. A large body of experimental data on the cyclic compounds has been accumulated and should be considered when discussing the corresponding linear π-systems.

## Frontier orbitals

The frontier orbitals and the gap between HOMO and LUMO orbitals are of special importance for the conducting properties of molecules with large delocalised π-systems. In the polymers the filled MOs form a quasi-continuum, as do the vacant ones.[1b] Any sophisticated MO theory which considers all the electrons in the system will be difficult to apply to the large cyclic and linear oligomers and polymers under consideration here. Due to their simplicity, approximate MO theories, such as the Hückel theory, are useful for developing a conceptual understanding of the π-electron systems. The conducting properties are due to the delocalised p-electrons which are reasonably well described by Hückel theory. A crucial condition for delocalisation of p-electrons is planarity of the π-system, a condition which is generally not met in the polymers but possibly can be achieved over a limited part of the π-system in charged ("doped") species. Although the actual HOMO-LUMO gap depends on the planarity of the real polymer the planarity assumption implicit in Hückel theory makes it possible to derive a lower limit for the energy gap between the filled and the empty band.[9] It is also believed that results from a series of similar compounds reflect the relative energy gap within the series.

For polyacetylene and the corresponding cyclic compounds, the annulenes, simple analytical solutions to the Hückel molecular orbitals and their energies have been derived.[10a] The annulenes can be divided into two sets, those containing 4n π-electrons and those containing (4n+2) π-electrons. The former are not resonance stabilised and should have a zero-gap between the HOMO and LUMO orbitals (two electrons are shared between two degenerate orbitals) under the assumption of equal bond length, a problem which will be discussed later. The (4n+2)-annulenes are resonance stabilised and have a finite HOMO-LUMO gap which decreases with ring size as shown in Fig. 1. It is interesting to note that the linear polyenes fall between the two sets of cyclic compounds in Fig. 1.

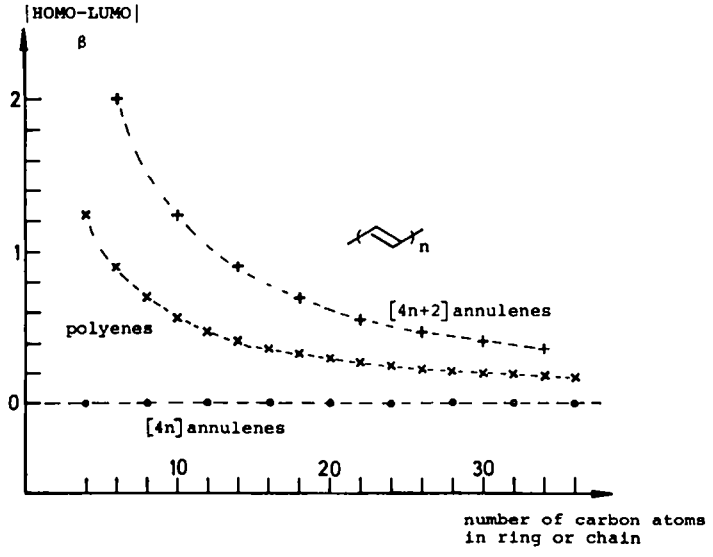



**Fig. 1** The frontier orbital gap, in β, for a series of neutral annulenes and linear polyenes as a function of the number of carbon atoms in the rings and chains.

For π-systems other than those of annulenes and linear polyenes, analytical solutions to the Hückel determinant are difficult to derive. However, for molecules consisting of repetitive units linked in a constant way, group theory provides a powerful tool for the simplification of the total Hückel determinant. We shall first demonstrate the method on simple annulenes and then use the results on larger cyclic conjugated π-systems.

## Rings of Hückel and Möbius topologies as result of $C_2$-symmetry transformations

There is a simple mnemonic device to generate the orbital energies of annulenes within the Hückel approximation. A regular polyhedron of the relevant size is inscribed into a circle of radius 2β (β is the resonance integral) with a vertex at the lowest point on the circle. The vertical coordinates for the vertices give the orbital energies as illustrated in Fig. 2 for cyclobutadiene and benzene.[11] Similarly, the orbital energies of the annulenes with Möbius topology (one phase inversion along the perimeter) are given by the vertical coordinates for the same regular polyhedron inscribed in the same circle with one side as low as possible (see Fig. 2).[12] By combining the two sets of solutions to the annulene with Hückel and Möbius topology, respectively, an operation which is equivalent to joining of the vertices of the polyhedra, the Hückel-type orbital energies of the annulene twice as large are obtained. Thus, the combination of the orbital energies of the two topologically different cyclobutadienes gives the orbital energies of cyclooctatetraene. In general, the orbital energies for a [2N]annulene correspond to the sum of the Hückel and Möbius orbital energies of the [N]annulene. This result is a consequence of the presence of a $C_2$-axis perpendicular to the π-system in the [2N]annulenes and follows from group theory.[9] The [2N]annulenes also have mirror-plane symmetry perpendicular to the π-system. However, mirror-plane transformations of the total Hückel determinant do not give simplifications which are as easily interpreted as $C_2$ transformations.

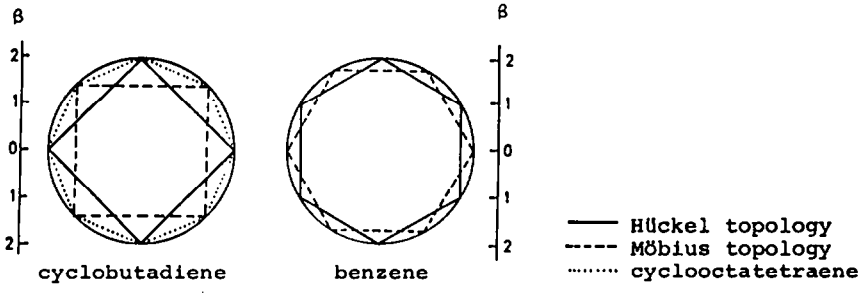



**Fig. 2** Mnemonic device to generate the Hückel molecular orbital energies for annulenes with Hückel (normal) and Möbius topology.

For the forthcoming discussion the energies of the frontier orbitals (the HOMO and LUMO orbitals) will be of central interest. These are found among the energies of Hückel-cyclobutadiene for the case of cyclooctatetraene and among the Möbius-benzene set for the case of cyclododecahexaene (see Fig. 2).

Since these results are solely a consequence of symmetry, this method for the reduction of the total Hückel determinant for ring compounds with delocalised π-systems is not limted to the annulenes but can also be applied to all systems with $C_2$-symmetry. The molecule with the π-system under discussion must consist of two identical units which are linked together in such a way as to define a $C_2$-axis of symmetry perpendicular to the plane of the π-system. It follows from group theory* that there exists a transformation which will reduce the total Hückel determinant of order $|2N \times 2N|$ into two determinants of order $|N \times N|$ which can be given a simple physical interpretation. The determinant which is symmetric with respect to $C_2$-rotation (A-type irreducible representation) corresponds to a ring of half the size of the original one with normal (Hückel) topology. The other, antisymmetric, determinant (B-type irreducible representation) corresponds to the same smaller ring but with Möbius topology (one phase inversion along the cyclic π-system) as shown schematically in Fig. 3.

* The character table for point group $C_2$ has two irreducible representations A and B which are symmetric and antisymmetric with respect to $C_2$-rotation.

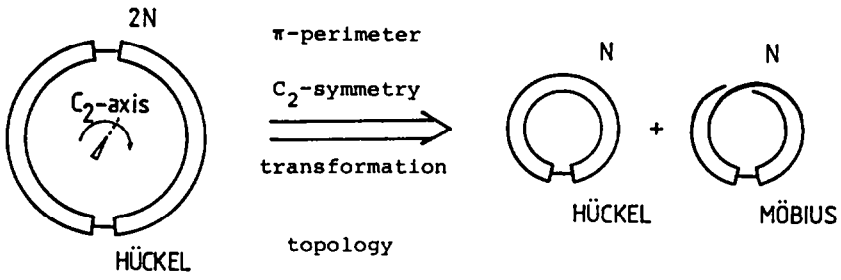



**Fig. 3** Schematic representation of the $C_2$-symmetry transformation of a ring with a planar 2N-perimeter and $C_2$-symmetry into two smaller rings with N-perimeters and Hückel and Möbius topology.

For alternant hydrocarbons, the orbital energies appear pairwise centered on the β = 0 level[10b] which means that the frontier orbitals of the 2N ring are found either among the solutions of the N ring of Hückel topology or that of Möbius topology. There is a simple rule which can be used to decide which is the case. If the simple fragment from which the smaller N rings are constructed contains a linear array of 4n π-electrons in conjugation between the points of connection, then the HOMO-LUMO pair for the 2N ring is found among the solutions to the smaller N ring of Hückel topology. If the fragment contains (4n+2) π-electrons in conjugation, the HOMO-LUMO pair is found among the solutions to the smaller ring of Möbius topology. This is the case because Hückel-type (Möbius-type) ring closure of a 4n (4n+2) π-electron chain gives the least favourable orbital energies (= frontier orbitals).

An isomer of [4.4.4.4]paracyclophaneoctaene, *10*, may serve as an example to illustrate the procedure (Fig. 4).

The first $C_2$-symmetry transformation will reduce the ring with a 32 π-electron perimeter to two 16 π-electron perimeter rings with Hückel and Möbius topology. The frontier orbitals of the original cyclophane *10* will be found among the orbitals of the ring with Hückel topology since the smaller ring has a 4n π-electron perimeter. The second $C_2$-symmetry transformation will further reduce the original π-system into two rings with 8 π-electron perimeters. The original frontier orbitals will again be found

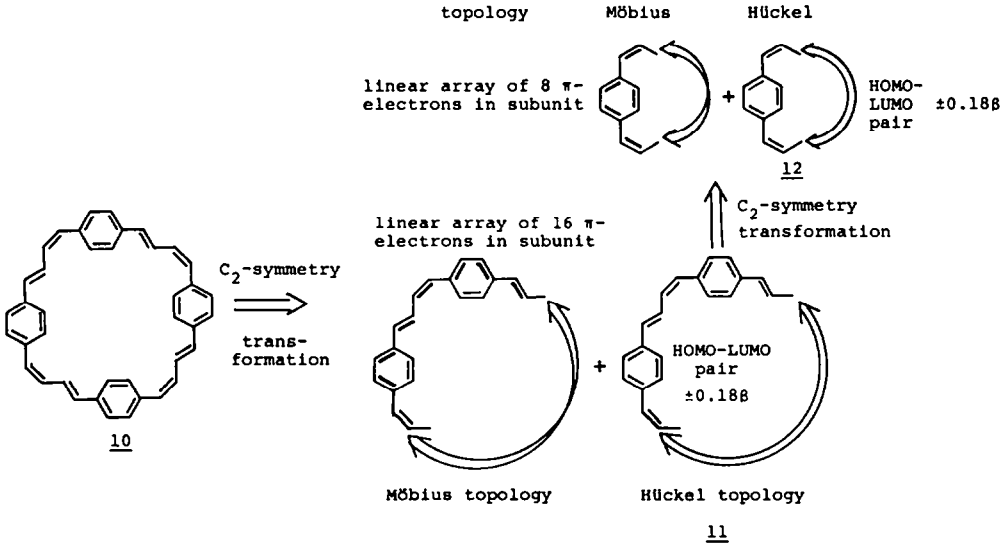



**Fig. 4** Consecutive $C_2$-transformations of cyclophane *10* into smaller fragment of Hückel and Möbius topology simplify the calculation of the frontier orbitals of *10*.

among the solutions to the Hückel topology ring as shown in Fig. 4. Instead of two consecutive $C_2$-transformations a direct $C_4$-transformation (cyclophane *10* has a $C_4$-axis of symmetry perpendicular to the π-system) can be performed to give the same result.* The total Hückel determinant is reduced from the order $|4N \times 4N|$ into three determinants of order $|N \times N|$, $|N \times N|$, and $|2N \times 2N|$. The first two which must be symmetric and antisymmetric with respect to $C_4$-rotation, respectively, are readily identified as the determinants for the 8 π-electron rings with Hückel and Möbius topology, respectively. From this example it is immediately clear that the three rings *10*, *11* and *12* with Hückel topology and 8, 16 and 32 π-electron perimeters, respectively, all have the same frontier orbitals and the same HOMO-LUMO gap which is quite analogous to the situation in [4n]annulenes.

## Generalized $C_n$-symmetry transformations

The method presented here for the analysis of macrocyclic π-systems with at least $C_2$-symmetry can be extended to macrocycles with π-systems built from $n$ identical units linked together in a uniform way to maintain $C_n$-symmetry. For such macrocycles the total Hückel determinant can be reduced using group theoretical methods to a number of simpler determinants. For the case in which $n$ is even both the A-type determinant (symmetric with respect to $C_n$-rotation, Hückel type topology) and the B-type determinant (antisymmetric, Möbius type topology) will be present together with a number of E-type determinants. The frontier orbitals will appear either among the solutions to the A-type determinant (Hückel topology) or among the solutions to the B-type determinant (Möbius topology). The rule is the same as stated above. If the simple unit contains 4n (4n+2) π-electrons in conjugation in a linear array then the frontier orbitals appear among the solutions to the smallest ring with Hückel topology (Möbius topology). For the case when $n$ is odd, only the A-type and E-type determinants will be present after the symmetry transformation and the frontier orbital energies are found among the solutions to the A-type determinant (Hückel topology) if the corresponding ring has a 4n π-perimeter, or else among the solutions to the E-type determinants. The energy of the frontier orbital gap as a function of $n$ for the two cases is shown schematically in Fig. 5 and 6. Data for the corresponding linear oligomers are also included.

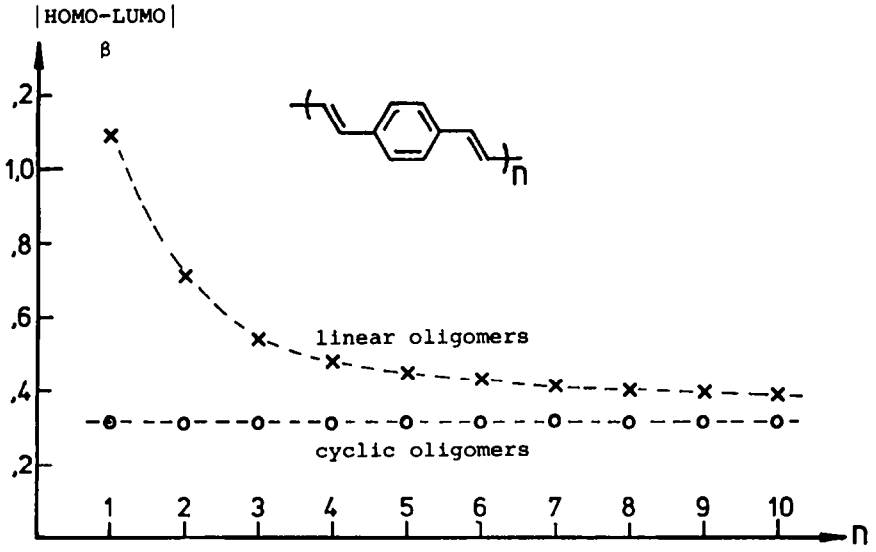



Fig. 5 The energy difference, in β, of the LUMO and HOMO orbitals from Hückel calculations as a function of size for cyclic and linear oligomers of paraphenylenedivinylene.

* The character table for point group $C_4$ contains three irreducible representations; A (symmetric with respect to $C_4$-rotation), B (antisymmetric) and E (degenerate representation).

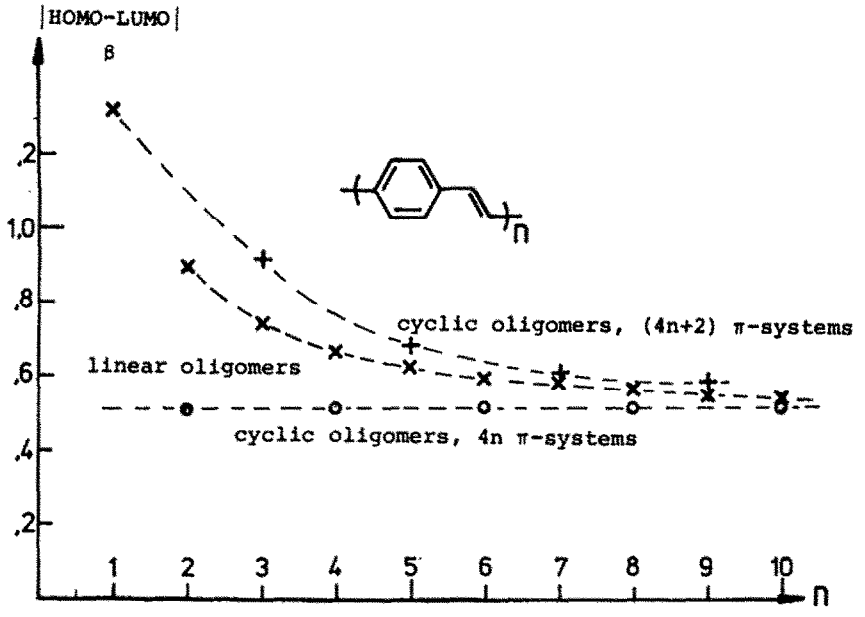



**Fig. 6** The energy difference, in β, of the LUMO and HOMO orbitals from Hückel calculations as a function of size for cyclic and linear oligomers of paraphenylenevinylene.

It is clear from Fig. 5 and 6 that the HOMO-LUMO gap for the linear oligomers gradually decreases to that of the cyclic species with 4n π-electron perimeters, a result which is derived below. Polymers with delocalised π-systems of interest as organic conductors are generally formed by head-to-tail polymerisation (head and tail may be equal). Although the polymer may be totally unsymmetric, the corresponding cyclic counterpart has ideally $C_n$-symmetry and thus the frontier orbitals are the same as those in the smallest repetitive unit closed with itself as shown schematically in Fig. 7.

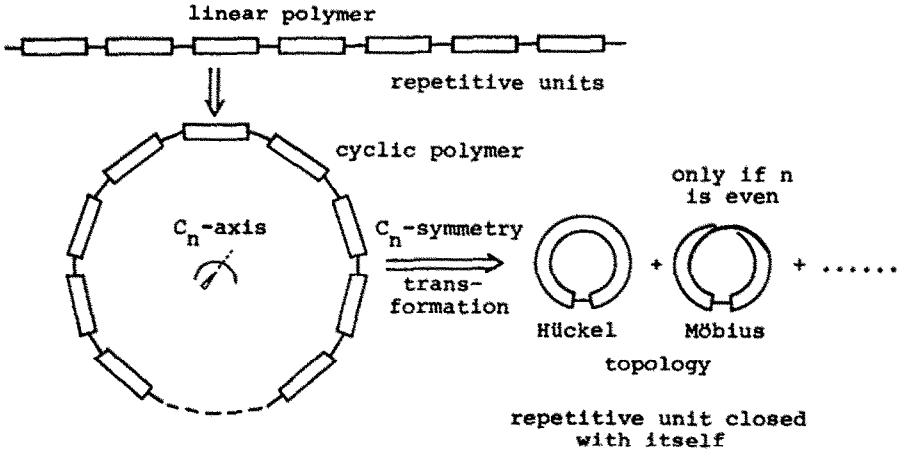



**Fig. 7** The approximation of a linear polymer with a conjugated π-system as a cyclic species with the same π-system and $C_n$-symmetry followed by $C_n$-symmetry transformation into rings of the "monomer" with Hückel (and Möbius) topology.

## Frontier orbitals in linear and cyclic polymers

In order to see the relation between the Hückel solutions for a macromolecule $M_n$ consisting of $n$ monomers M linked to form an oligomer, a polymer, or a macrocycle, and the Hückel solution for the monomer M closed on itself to form a small ring, write the Hückel matrix $\underline{\underline{H}}(M_n)$ of the macromolecule $M_n$ as an array of submatrices $\underline{\underline{H}}(M)$ and $\underline{\underline{C}}$

$$\underline{\underline{H}}(M_n) = \begin{pmatrix} \underline{\underline{H}}(M) & \underline{\underline{C}} & 0 & 0 & \cdots & \underline{\underline{C}}^T \\ \underline{\underline{C}}^T & \underline{\underline{H}}(M) & \underline{\underline{C}} & 0 & \cdots & \\ \cdots & \cdots & \cdots & \cdots & \cdots & \cdots \\ 0 & 0 & \cdots & \underline{\underline{C}}^T & \underline{\underline{H}}(M) & \underline{\underline{C}} \\ \underline{\underline{C}} & & & & \underline{\underline{C}}^T & \underline{\underline{H}}(M) \end{pmatrix} \qquad \text{(A1)}$$

where $\underline{\underline{C}}^T$ is the transpose of $\underline{\underline{C}}$. If the monomer unit M contains $k$ $p_z$-orbitals then $\underline{\underline{H}}(M)$ and $\underline{\underline{C}}$ are both ($k \times k$) matrices and $\underline{\underline{H}}(M_n)$ a ($nk \times nk$) matrix. The matrix $\underline{\underline{C}}$ describes the link between monomer units and contains one unit coefficient for each link while the rest of the coefficients are zeros. In the matrix $\underline{\underline{H}}(M_n)$ of eq. (A1) a link between the first and last unit is assumed to give a ring compound. For the linear polymer of the same size the submatrices $\underline{\underline{C}}^T$ and $\underline{\underline{C}}$ in the upper left and lower right corners, respectively, are zero. As an example, consider the annulenes as formed from ethylene subunits with the usual Hückel parameters $\beta$ and $x$

$$\underline{\underline{H}}(M) = \beta \begin{pmatrix} x & 1 \\ 1 & x \end{pmatrix} \quad ; \quad \underline{\underline{C}} = \beta \begin{pmatrix} 0 & 0 \\ 1 & 0 \end{pmatrix}$$

The key step for the elucidation of the eigenvalues (and orbital energies) of $\underline{\underline{H}}(M_n)$ is to find a symmetry transformation that takes $\underline{\underline{H}}(M_n)$ into a block diagonal form. The submatrices $\underline{\underline{H}}(M)$ and $\underline{\underline{C}}$ are considered as fixed objects and the transformation we seek must be independent of the nature of the submatrices and determined solely by the number of units $n$ and the topology of the macromolecule (a ring or a linear polymer). Since the Hückel problem for the annulenes and the linear polyenes has been solved for an arbitrary size of the ring or chain,[10a] this solution can be used to find the appropriate transformation for the general case discussed here. Clearly, for macrocyclic compounds, the transformation can be obtained by considering the rotational symmetry ($C_n$-symmetry), while for linear polymers the transformation is not discernible from the symmetry properties.

The submatrices of the diagonal blocks obtained after the transformation are of the form

$$\underline{\underline{H}}_j = \underline{\underline{H}}(M) + \eta_j \, (\underline{\underline{C}} + \underline{\underline{C}}^T) \qquad \text{(A2)}$$

where $\eta$ takes $n$, not necessarily different, values.

For the ring compounds one has

$$\eta_j = \cos(2\pi j/n) \qquad j = 0,1, \ldots n-1 \qquad \text{(A3)}$$

while for the linear polymer

$$\eta_j = 2\cos[\pi j/(2n-1)] \; -1 \qquad j = 1,2, \ldots n \qquad \text{(A4)}$$

In both cases $\eta$ varies between plus and minus one. To solve for all eigenvalues of $\underline{\underline{H}}(M_n)$ one has to obtain the eigenvalues of the $n$ closely related matrices $\underline{\underline{H}}_j$ of eq. (A2). For alternant hydrocarbons the orbital energies are paired on the $\beta = 0$ level and the HOMO and LUMO are thus found in the same submatrix $\underline{\underline{H}}_j$. The eigenvalues of $\underline{\underline{H}}_j$ can be regarded as functions of the coefficient $\eta$. If this function is monotonic, which is the case as long as the coupling introduced by the matrix $\eta(\underline{\underline{C}} + \underline{\underline{C}}^T)$ is weak enough so that first order effects dominate, then it is sufficient to consider the lowest and highest values of $\eta$ when looking for the frontier orbital gap (HOMO-LUMO gap). The same monotonic behaviour is also expected for chemical reasons since $\eta = 1$ corresponds to a ring of Hückel topology while $\eta = -1$ corresponds

to a ring of Möbius topology (one phase inversion between adjacent $p_z$-orbitals in the ring). Intermediate values of η correspond to intermediate situations. Depending on the type of π-electron system in the monomer unit either the ring with Hückel topology or the ring with Möbius topology is favoured energetically. For a monomer unit with (4n+2) π-electrons conjugated in a linear array between the two ends, a ring of Hückel topology is preferred over a ring of Möbius topology (Hückel's rule) which means that the smallest HOMO-LUMO gap is found for the ring of Möbius topology. For a 4n π-system the situation is reversed.

For the linear polymer the lowest η-value obtained when $j = n$ is approximately as close to -1 as the highest η-value obtained when $j = 1$ is close to +1. For a particular monomer unit the limiting values of +1 and -1, respectively, are approached monotonically with increasing $n$.

For the ring compounds the highest η-value is always +1 and thus for monomers with 4n π-systems between the ends the HOMO-LUMO gap is constant and independent of $n$. The lowest η-value is -1 if $n$ is even while if $n$ is odd there is a degeneracy (E-type irreducible representation) with $\eta_j = -\cos(\pi/n)$. Thus for a (4n+2) π-system the HOMO-LUMO gap oscillates with $n$ between a lower constant value and a larger value which asymptotically approaches the lower one for large $n$ (see Fig. 6). This latter case is well known for the annulenes where ethylene can be regarded as the monomer unit. We have shown here that this is a general property of any series of cyclic compounds built from a monomer unit which is an alternant hydrocarbon with a conjugated π-system.

## Applications to polymers with aromatic rings and unsaturated bridges

By applying the ideas presented above to a number of both known and hypothetical polymers we can estimate the lower limit of the gap between the filled and vacant orbitals in the polymers simply by solving the reduced Hückel determinants (see Table 1). As already mentioned, the method is based only upon symmetry arguments and thus the monomer must not necessarily be an alternant hydrocarbon, although this does make it easier to find the frontier orbitals.

The three polyphenylene compounds, *5*, *13* and *14*, all show a rather large gap between the filled and empty orbitals according to these Hückel calculations. The *ortho* and *para* isomers have, as expected, the smaller gaps because they contain linear, conjugated π-systems whereas the *meta* isomer contains a cross-conjugated chain. In the *para* isomer there is less steric repulsion in a relatively planar array of benzene rings as compared to the *ortho* isomer. In practice, doped polyparaphenylene is a good conductor.[1a,c,13] It is interesting to note that of the three polynaphthalenes considered here, the isomer with 1,4-substitution, *15*, is by far the most interesting candidate for a conducting polymer. The other two isomers, *16* and *17* also show reasonably small gaps. However, severe steric effects could prevent the doped polymer from becoming planar enough for an efficient overlap of the aromatic π-systems.[13] The polyazulene, *18*, also has a small calculated frontier orbital gap but larger than that of the polynaphthalene *15* . The two polyphenanthrenes *19* and *20* can also be regarded as polyparaphenylene and polymetaphenylene, respectively, with additional vinylene bridges. The polymers should be of modest interest as conductors.

The introduction of vinylene bridges as in the polymers *7* and *21-28* decreases the frontier orbital gaps and at the same time decreases the steric effects in planar conformations, as is apparent from molecular models. The introduction of more than one vinylene group between the aromatic units further decreases the frontier orbital gaps (see *7*, *21* and *22*).

**Table 1** Energy gap between the HOMO and LUMO orbitals in a series of linear polymers with conjugated π-systems, from Hückel calculations.

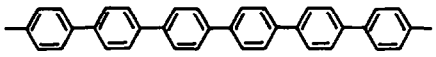
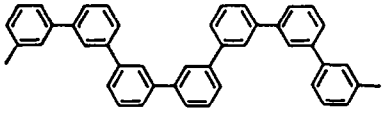
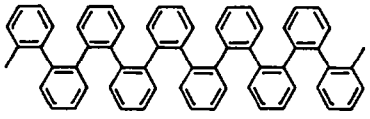
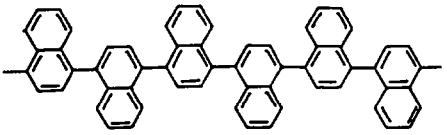
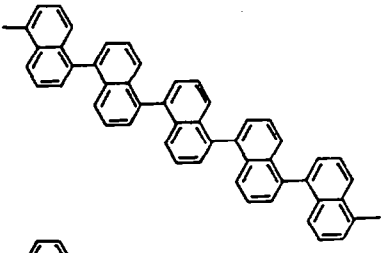
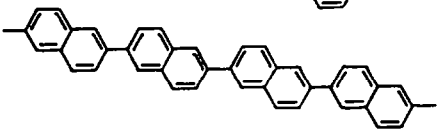
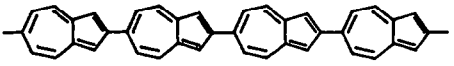
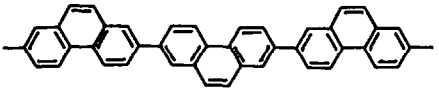
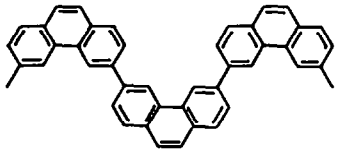
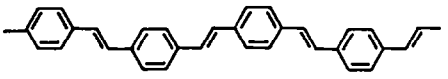
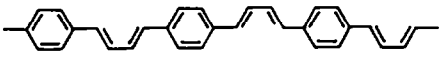
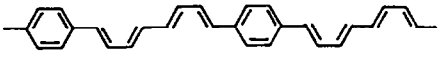
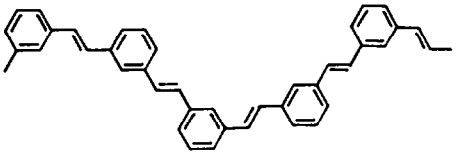
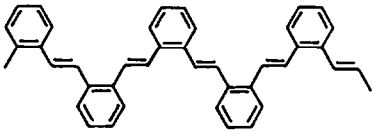
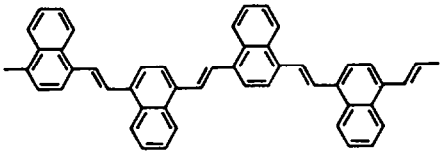
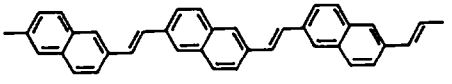
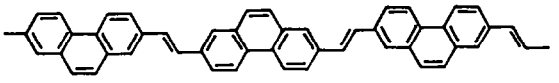
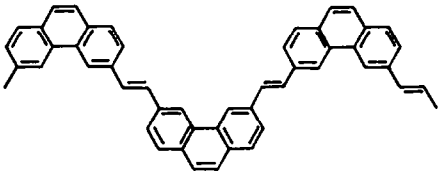
| | | lower limit of HOMO-LUMO in β | topology of repeting unit for calculations H = Hückel, M = Möbius |
|---|---|---|---|
| 5 |  | 0.83 | H |
| 13 |  | 1.24 | H and M |
| 14 |  | 0.89 | M |
| 15 |  | 0.40 | H |
| 16 |  | 0.62 | M |
| 17 |  | 0.78 | M |
| 18 |  | 0.59 | M |
| 19 |  | 0.96 | H |
| 20 |  | 0.80 | M |

**Table 1**
(cont'd)

| | | | |
|---|---|---|---|
| 7 |  | 0.51 | M |
| 21 |  | 0.36 | H |
| 22 |  | 0.23 | H |
| 23 |  | 0.89 | H and M |
| 24 |  | 0.52 | H |
| 25 |  | 0.26 | M |
| 26 |  | 0.57 | H |
| 27 |  | 0.71 | M |
| 28 |  | 0.63 | H |

## Discussion of the present method

Simple Hückel theory assumes planar π-systems and constant resonance integrals (β-values), two conditions which are seldom met in real molecules, and the effects of deviation from planarity on π-electron delocalisation can be discerned in many small neutral organic molecules. However, the effect is often less pronounced in the corresponding charged species. In order to demonstrate the value of the present method of reducing the problem of large linear conjugated π-systems to that of small rings with Hückel and Möbius topology, two questions can be considered. What is the realistic value of the resonance integral β? Are there, then, any experimental data to support the ideas presented here?

Both questions can be answered with examples from cyclophane chemistry. Recently, we have prepared a series of cyclophanes with unsaturated bridges, molecules large enough to maintain efficient overlap between the local double bonds and the aromatic rings to form a macrocyclic π-perimeter. Two such compounds are the cyclophanes **8** and **9**. In the neutral compounds, $^1$H NMR spectra show no sign of ring current effects from the macrocyclic perimeter (*i.e.* low "conductivity"). In solution, the benzene rings

rotate rapidly on the NMR time-scale. In contrast, the dianions of cyclophanes *8* and *9* show large ring current effects from the macrocyclic perimeter (*i.e.* high "conductivity") and the benzene rings now rotate slowly.[8b] Both cyclophanes *8* and *9* contain the same simple unit with six π-electrons in a linear array between the ends and (see Fig. 6) thus the frontier orbitals of the macrocycles should be of the same energy and are to be found in the reduced determinant of Möbius-type. The HOMO-LUMO gap is 0.51 β. The two dianions are both formed upon electrochemical reduction *via* a reversible two-electron process in DMF solution at a mercury drop, as studied by cyclic voltammetry. As predicted, the reduction potentials are identical (-1.70 V *vs* SCE).[7,14] Similarly, other cyclophanes with unsaturated bridges and analogous cyclic conjugated π-systems undergo such reversible reduction to dianions. The values for the HOMO-LUMO gaps from Hückel calculations and the experimentally observed reduction potentials show a good linear correlation from which a β-value of *ca.* 50 kcal mol$^{-1}$ was calculated.[15] When applied to frontier orbital gaps in organic conductors, the β-value determined in this way from the LUMO:s might be more relevant than the smaller values previously determined from heats of hydrogenation or combustion, where the LUMO:s are not involved.

From simple Hückel theory it follows that [4n]annulenes and long linear polyenes should have the same zero-energy gap between the filled and vacant orbitals, but due to bond alternation this gap increases to a finite value. Hückel theory can accomodate the phenomenon of bond alternation by adopting alternating resonance integrals $\beta_1$ and $\beta_2$ for the formal single and double bonds in the chain or ring (Fig. 8).

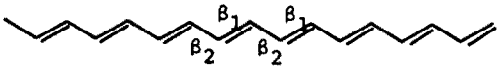



**Fig. 8** Bond alternation in a long polyene with two values for the resonance integral.

For an infinite chain of alternating single and double bonds the frontier orbital gap is $2|\beta_1 - \beta_2|$ [10c] which also has to be the HOMO-LUMO gap in small [4n]annulenes with bond alternation. From structural data on [8]annulene (cyclooctatetraene) and [16]annulene,[4] both of which show bond alternation, the average double bond length is calculated to 1.340 and 1.333 Å, respectively, and the single bond length to 1.476 and 1.454 Å, respectively. By use of a Morse function for the relation between the resonance integral and the bond length,[16] the frontier orbital gaps of 0.46 β for [8]annulene and 0.44 β for [16]annulene are obtained. For polyacetylene, the experimental value is *ca.* 1.4 eV[1b,d] which corresponds to 0.64 β (β = 50 kcal mol$^{-1}$). The calculated frontier orbital gap has to be taken as a lower limit for an ideal polymer. It should be remembered that no corrections for the deviation of the π-system from planarity have been made. In addition, the interesting problem of how the electrical current is transported between the polymer strands has not been addressed, but this must also affect the size of the gap between the filled and vacant orbitals in neutral polyacetylene.

More sophisticated calculations on the band gap in conducting polymers than those presented here have been reported.[17] It is interesting to compare our results with those of more accurate calculations (*ab initio* quality valence effective Hamiltonian method) on polyacetylene, polyparaphenylene, polymetaphenylene and polyvinylparaphenylene, which represent examples of good to modest conductors. The data from ref. 17 are plotted against the results of Hückel calculations (this paper) with a β-value of 50 kcal mol$^{-1}$ in Fig. 9. No correction for deviations from planarity nor for different β-values for the formal single and double bonds has been made. Three of the four points fall on the line which corresponds to the same relative energy gap differing by a constant of 1.4 eV. The qualitatively good agreement between the Hückel data and the more elaborate calculations for the admittedly small number of polymers is encouraging and lends support to this extremely simple treatment of a very complex problem.

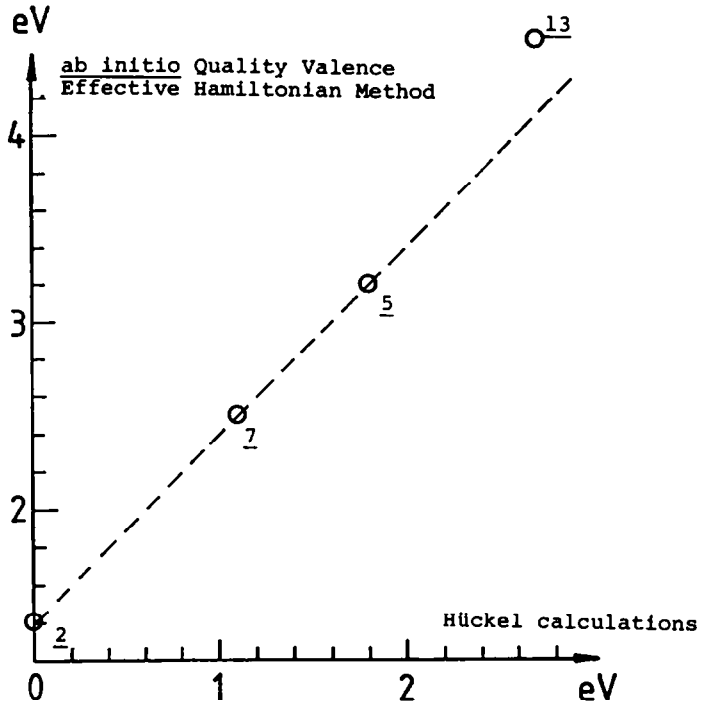



Fig. 9 Calculated band gaps for organic conductors assuming planar π-systems, *ab initio* Quality Valence Effective Hamiltonian Method from ref. 17 vs Hückel calculations from this paper. Dotted line represents the same relative band gaps.

**Acknowledgement**

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