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# HÜCKEL MOLECULAR ORBITALS OF MÖBIUS-TYPE CONFORMATIONS OF ANNULENES

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**The different conformations of a $\pi$-electron system can be specified by listing the twist angles $\omega_{\mu\nu}$ between all pairs of bonded atomic orbitals (AOs) $\phi_\mu$, $\phi_\nu$. The resonance integral $\beta_{\mu\nu}$ of a twisted $\pi$-bond is given by (1)**

$$\beta_{\mu\nu} = \beta \cos \omega_{\mu\nu}$$

**$\beta$ being the standard resonance integral for a pair of parallel AOs. It is usually assumed that the total $\pi$-electron energy has an absolute maximum for the coplanar system (all $\omega_{\mu\nu} = 0$ or $\pi$ ). Any conformation with one or more angles $\omega_{\mu\nu}$ different from zero or $\pi$ would then have a smaller $\pi$-electron energy, assuming that the interatomic distances between pairs of bonded AOs remain constant. We shall show that, according to Hückel molecular orbital (HMO) theory this may not necessarily be so.**

**The higher members of the annulenes $(CH)_n$ (2) are presumably present in solution in a variety of non-planar conformations. Among these conformations, there are some where the $\pi$-orbital is twisted into a möbius strip. Such conformations can be obtained with standard molecular models (Dreiding or Stuart - Briegleb) without introducing any apparent bond angle or steric repulsion strain when $n > \sim 20$. The topological equivalent of such a Möbius type conformation is shown in fig. 1.**

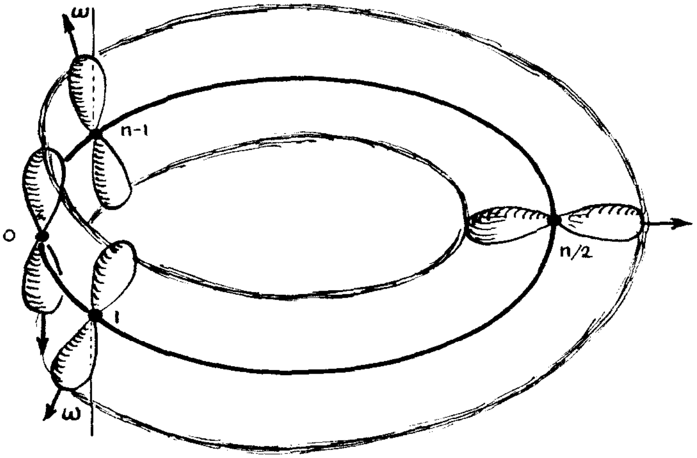

Figure 1

A closed sequence of n AOs is arranged on a ring, so that two consecutive AOs $\phi_{\mu}$ , $\phi_{\mu+1}$ form an angle $\omega = \pi/n$. The resonance integral between two consecutive AOs is $\beta^{M} = \beta \cos(\pi/n)$. It is easy to show that the orbital energies $\varepsilon_{J}^{M}$ for such systems are given in closed form by

$$\varepsilon_{J}^{M} = \alpha + 2\beta^{M} \cos \pi(2J+1)/n$$

$$J = 0, 1, 2, \ldots\ldots, n-1$$

and the corresponding HMOs $\psi_{J}^{M}$ by

$$\psi_{J}^{M} = \frac{1}{\sqrt{n}} \sum_{\mu=0}^{n-1} (\exp i\pi(2J+1)\mu/n)\, \phi_{\mu}$$

or by the appropriate real linear combinations of $\psi_{J}^{M}$ and $\psi_{J}^{M*}$.

The energy level scheme for a Möbius type perimeter differs from that of a standard perimeter in that all levels are degenerate for n even, and that only the highest antibonding level is single for n odd. This is shown schematically in fig. 2.

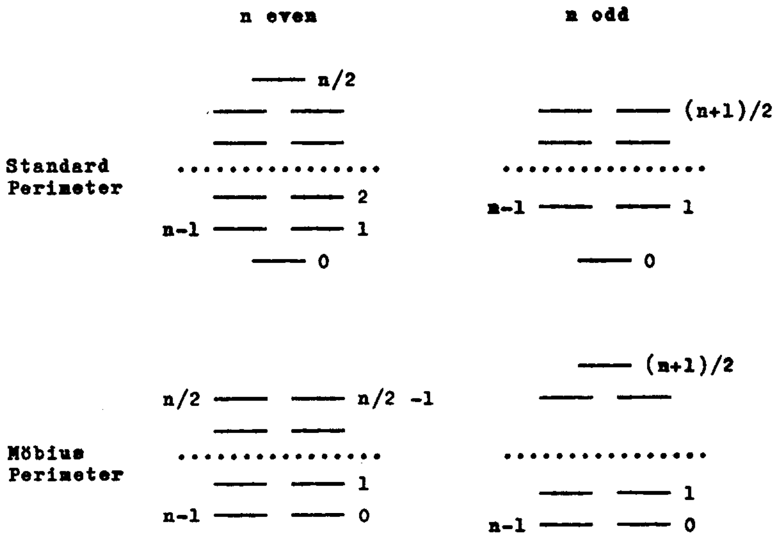

Figure 2

Closed shell configurations are thus predicted for $N^H = 2 + 4r$ electrons in the case of planar standard perimeters (Hückel's rule) and for $N^M = 4r$ electrons in the case of a Möbius type perimeter (r being a whole number).

We shall now prove that a planar perimeter of $n = 4r$ AOs, which would yield an open shell configuration when occupied by 4r electrons, can be twisted into a closed shell Möbius strip perimeter without loss in $\pi$-electron energy. The orbital energies of the planar ring of n AOs are

$$\varepsilon_J = \alpha + 2\beta \cos 2\pi J/n$$
$$J = 0, 1, 2, \ldots\ldots, n-1$$

The occupancy of these levels is shown in fig. 3. The two non-bonding orbitals of energy $\varepsilon_r = \varepsilon_{3r} = \alpha$ each contain a single electron. In the corresponding Möbius model all bonding orbitals are occupied by pairs of electrons (fig. 3).

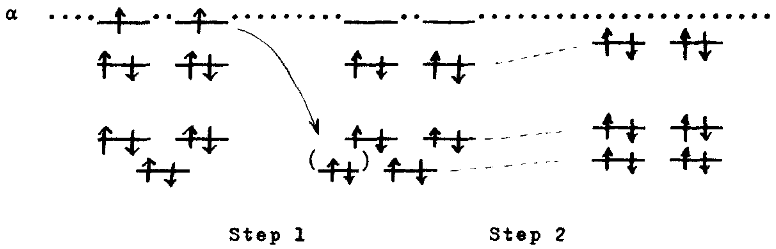

Figure 3

We transform the first model into the second one as follows:

Step 1 : The two electrons in the non-bonding orbital pair are put into a phantom orbital of energy $\mathcal{E}_0 = \alpha + 2\beta$, so that each energy level is now occupied by four electrons. In this step we gain 4β in π-electron energy.

Step 2 : The energy of each quadruply occupied level $\mathcal{E}_J$ is altered to the energy $\mathcal{E}_J^M$ of the Möbius model. We lose thereby for each level energy equal to

$$4(\mathcal{E}_J^M - \mathcal{E}_J) = -8\beta \left[\sin \pi/n\right]\left[\sin \pi (2J+1)/n\right]$$

Summing over all quadruply occupied levels, from J = 0 to J = r-1, we get

$$4\sum_{J=0}^{r-1} (\mathcal{E}_J^M - \mathcal{E}_J) = -4\beta$$

The net change in π-electron energy for both steps is therefore zero.

As far as zeroth order HMO theory is concerned, we can therefore obtain a closed shell configuration for an annulene of 4r AOs without loss in $\pi$-electron energy by twisting the system into a Möbius strip conformation. However, twisting a closed shell perimeter of 4r+2 AOs into an open shell Möbius strip conformation is always accompanied by a loss of $\pi$-electron energy.

Those results are, of course, subject to the well known limitations of zeroth order HMO theory (1). No account has been taken of bond alternation (3) or of alternation in twist angles.

For even n the Möbius strip HMOs show the usual pairing properties of alternant systems (4). For odd n the energy level diagram $x_J^M = (\mathcal{E}_J^M - \alpha)/\beta^M$ is the mirror image of $x_J = (\mathcal{E}_J - \alpha)/\beta$ of the standard HMOs of a perimeter with the same number of AOs. A free electron model analogous to the Hückel treatment yields the following changes in delocalisation energy on changing a simple ring of perimeter length L and width $B \ll L$ into the corresponding Möbius strip: for 4r electrons $rh^2/2mL^2$ energy gain (stabilisation), for 4r+2 electrons $-(2r+1)h^2/4mL^2$ energy loss (destabilisation).

One or two-dimensional models (such as the HMO or the free electron model) yield reasonable approximations if the three-dimensional wave function of the system can be written as a product of functions of lower dimension(5). For instance the movement of an electron in a potential of cylindrical symmetry is described by a wave function of the type $\varphi(\omega)\eta(\rho, z)$, $\rho$ being the distance to the z axis and $\omega$ the angle of rotation. The solutions $\varphi_J(\omega)$ may be thought of as those which pertain to an "electron on a ring" ( $\omega = 2\pi x/L$, L = length of the perimeter). In the foregoing discussion we have implicitely assumed that HMOs on a Möbius strip are acceptable factors of the corresponding three-dimensional problem. It is, however, not obvious that three-dimensional potentials exist for which this is exactly, or even approximately true. It could well be that the results quoted above are artefacts of the essentially two-dimensional HMO model and that they have no three-dimensional counterpart.

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