# A FEMO MODEL OF AROMATICITY.

## II.   THE KRUSZEWSKI-KRYGOWSKI INDEX

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One criterion of aromaticity is the pi stabilization energy, the difference in pi electron energy of a cyclic conjugated system and that of the iso-pi-electronic linear polyene.  If the pi energy decreases upon cyclization, the cyclic compound is labelled aromatic;  if the energy increases the cyclic compound is termed antiaromatic.  Paper I of this series (1) has shown that the free electron molecular orbital (FEMO) method, wherein the pi electrons of a linear molecule are treated as particles in a linear box, and those of a cyclic molecule are considered as particles on a circular ring, can be used in qualitative and quantitative explorations of the pi stabilization energy. Another index of aromaticity has been recently formulated by Kruszewski and Krygowski (2).  This parameter (KK) is the loss in pi electron energy when a conjugated system undergoes addition to form the polyene of lowest pi energy with two less carbon atoms involved in the pi system.  Kruszewski and Krygowski evaluate the energies by Hückel molecular orbital (HMO) theory and express KK in units of an average resonance integral, $\beta^{\circ}$.  The index may then be written as

$$KK = \frac{E_A^{\pi} - E_0^{\pi} + 2\alpha}{-\beta^{\circ}} \qquad (1)$$

where $E_0^{\pi}$ is the pi energy of the original conjugated system while $E_A^{\pi}$ is that

for the addition product. The term involving the coulomb integral, $\alpha$, may be viewed as an addition to $E_A^\pi$ to account for the two electrons lost from the pi system.

In a personal communication, Dr. Krygowski has suggested to me that FEMO should also be applicable to analysis of the KK index. To accomplish this it is necessary to eliminate $\alpha$ from Eqn.(1) since FEMO provides total energies directly and has no analog to this Hückel "atomic" energy. The HMO expression for the pi energy of ethylene is

$$E^\pi(C_2H_2) = 2\alpha + 2\beta° \quad (2)$$

Solving for $2\alpha$ and substituting in Eqn. (1) gives

$$KK = \frac{E_A^\pi - E_o^\pi + E^\pi(C_2H_2)}{-\beta°} + 2 \quad (3)$$

which in explicit FEMO form becomes

$$KK = \frac{h^2/8md^2}{-\beta°} h' + 2. \quad (4)$$

where h' is the energy difference $E_A^\pi - E_o^\pi + E^\pi(C_2H_2)$ expressed in units of $h^2/8md^2$ (h here is Planck's constant, m the mass of the electron, and d an average CC bond length)(3). If we take the conversion factor multiplying h' in Eqn. (4) as the ratio of the ethylene pi energy calculated via HMO (in units of $\alpha + \beta°$) to that calculated via FEMO (in units of $h^2/8md^2$)viz. 2/(2/9) = 9, we obtain

$$KK = 9h' + 2. \quad (5)$$

The utility of FEMO lies in the ease with which general formulae may be obtained. Using the theory of Paper I we get

| Series | h' |
|---|---|
| [4r]annulenes | $\dfrac{10r^2 - 16r + 3}{18r(4r-1)}$ |
| [4r+2]annulenes | $\dfrac{2(5r+1)(r+1)}{9(4r+1)(2r+1)}$ |
| [n]polyenes(4) | $\dfrac{(n+2)(n-2)}{18(n+1)(n-1)}$ |

These expressions represent three distinct curves. The two annulene series produce curves of opposite slope which however converge to the same limit, 5/36, at large ring size, indicating as in I the essential similarity in

aromatic behavior of all larger annulenes.  The polyene curve has a lower
asymptotic limit of 1/18.  Furthermore, the difference in this index between
a linear polyene and the annulene with the same number of pi electrons is just
the pi stabilization energy:

$$\Delta E' = h'([n]polyene) - h'([n]annulene) \qquad (6)$$

Thus the difference in the two limits, -1/12, is the limiting value of $\Delta E'$ (1).
The results of applying the expressions for h' to Eqn. (5) are presented in the
figure (5).
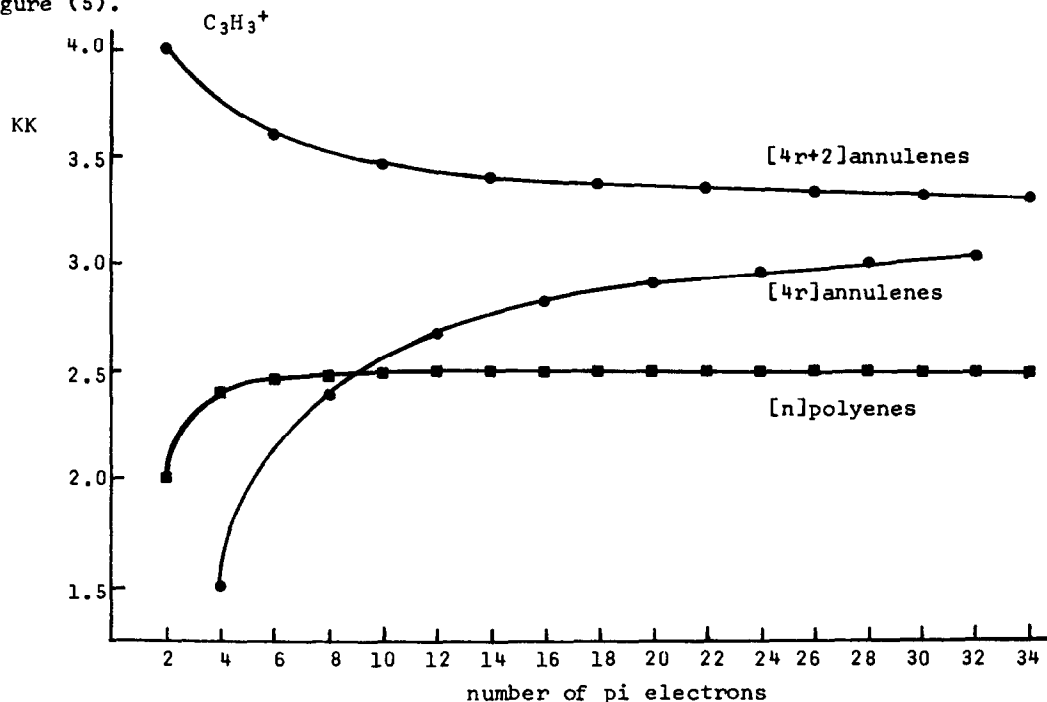


There appears to be remarkably good agreement between our FEMO calcula-
tions and the HMO results of Kruszewski and Krygowski(2,6).  The two electron
ends of both the [4r+2]annulene and the polyene curves agree exactly(7), with
the remaining FEMO numbers lower than the HMO by less than 3%.  The [4r]-
annulene curve departs more, the FEMO cyclobutadiene value being 0.50 less than
the HMO, with the remainder being lower by less than 11%.

The significance of our FEMO consideration lies not only in the ability
to reproduce the HMO curves, but more importantly in the guide it provides to

their interpretation. Through an examination of typical cases Kruszewski and Krygowski conclude that molecules with KK >3 are "aromatic" while those with KK<3 are "nonaromatic". FEMO predicts that the KK versus size curves for the [4r]annulenes and the [4r+2]annulenes converge at large r to the same limit, 3.25. If we consider the [4r+2]annulenes as "aromatic" and the [4r]annulenes as "nonaromatic" then this limit, rather than 3, may be taken as the transition point.

However, another interpretation is possible. The difference between KK for an [n]polyene and that for the corresponding [n]annulene is a measure of the pi stabilization energy. Using this criterion(1), if the annulene KK value lies above the polyene curve, the compound is aromatic, whereas, if it lies below, the molecule is antiaromatic. Here the KK transition point lies at about 2.50. FEMO then predicts that cyclobutadiene and cyclooctatetraene are antiaromatic with the remaining [4r]annulenes aromatic, while HMO predicts (cf. Fig. 1 of ref.(6)) only the former to be antiaromatic. This same difference of prediction was noted for pi stabilization energies in Paper I.

## REFERENCES

1. W. D. Hobey, J. Org. Chem., 37, 1137 (1972).

2. J. Kruszewski and T. M. Krygowski, Tetrahedron Lett., 1970, 319.

3. A thermodynamic interpretation of h' will be developed in a later paper.

4. We use the notation [n]polyene for the linear polyene with $\underline{n}$ carbon atoms contributing to the pi system.

5. $C_3H_3^+$ has been included here to establish a lower end of the [4r+2] curve. The pertinent calculation follows the same line as the others and is, coincidently the same as the expression for a [4r+2]annulene with r=0.

6. T. M. Krygowski, Tetrahedron Lett., 1970, 1311.

7. In reference (6) an incorrect value of KK for ethylene is given. The proper value is 2.0.