

AROMATICITY AND CLASSIFICATION OF PI-ELECTRON COMPOUNDS

T.M. Krygowski

Inst. of Fundamental Problems of Chemistry, The University, Warsaw 22, Poland

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A quantum-chemical model of a chemical criterion of aromaticity has been previously proposed /1/ on the basis of which a numerical index defining susceptibility of a given pi-electron compound to addition reaction was established. This index designated by the symbol KK, defines the amount of pi-electron energy (calculated by applying the HMO-method /2/) that the molecule loses as a result of an addition reaction at the positions r and s , i.e. when in those positions a change of hybridization state from sp^2 to sp^3 occurs. The greater the value of the KK-index, i.e. the greater loss of energy, the more difficult is it for the system to undergo an addition reaction, and we postulate - the more aromatic it is. On the other hand, it is a well known fact that substitution reactions are rather typical for aromatic systems, whereas addition reactions are more likely to occur in less aromatic systems and in olefines /3/. E.g. benzene, pyridine and thiophene, recognized as typical aromatic compounds under ordinary conditions, do not undergo a Diels-Alder reaction /4/.

On the basis of the KK-index values, one may attempt to classify pi-electron compounds. The diagram on Fig. 1 presents KK-values on the ordinate and the number of pi-electrons of a given system on the abscissa.

It can be seen that the annulenes become differentiated according to the Hückel rule $4n+2$ /5/: the molecules satisfying this rule occupy higher positions on the upper curve (annulene-2, -6, -10, etc.), whereas those not satisfying the rule, i.e. the anti-Hückel ones, take the positions on the lower curve (annulene-4, -8, -12, etc.). Both curves are rather formal in character as in annulene molecules, except benzene, tension and steric actions, which are not considered in the HMO-method, play a significant role.

Polyenes are another group of molecules forming a regularity on Fig. 1. Beneath this group, among cyclic pi-electron compounds there are only quinoid systems and compounds as cyclopentadienide cation or cycloheptatrienide anion, which are antiaromatic according to Breslow /6/ and Dewar /7/.

The compounds of fulvene group with KK values near to 3 take an intermediate position between the aromatic and nonaromatic compounds.

Above the limit $KK=3$ there are the compounds which are considered to be aromatic, e.g. the benzoid hydrocarbons and their heterocyclic analogues as well as the compounds such as thiophene, pyrrole and furan. In this group there are also ions, the derivatives of cyclic polyenes satisfying the Hückel rule.

A more extensive elaboration of the problems mentioned above will be the subject of subsequent publications /8/.

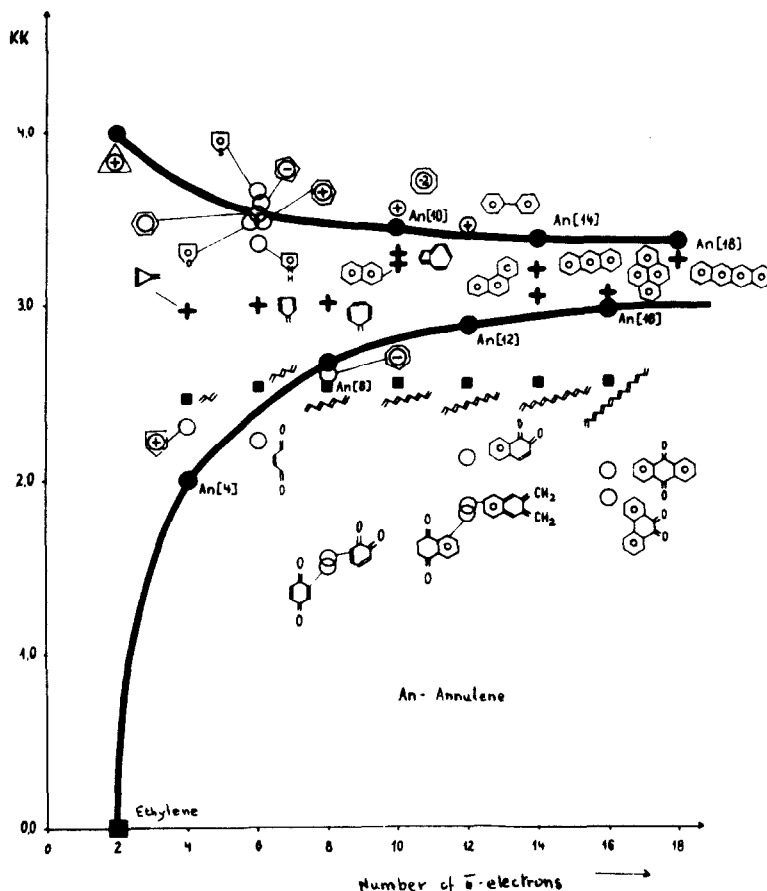


Fig.1

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