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A QUANTUM-CHEMICAL APPROACH TO THE CHEMICAL DEFINITION OF AROMATICITY

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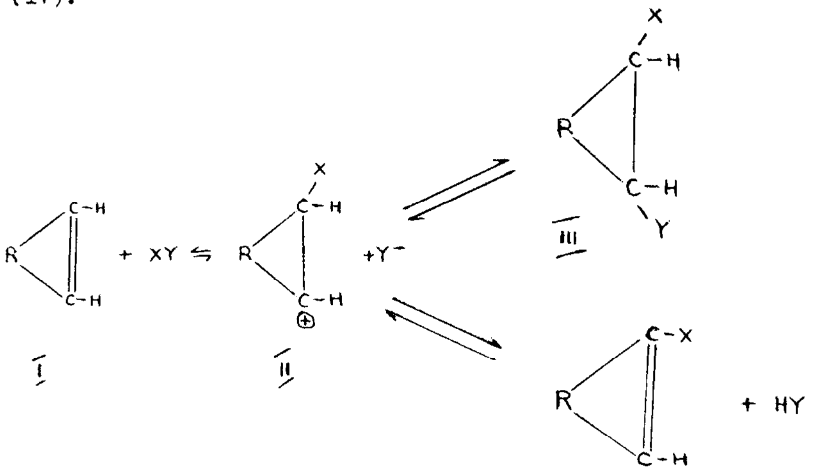
Recently, the problem of aromaticity in general as well as some attempts at a quantitative approach to it have been extensively discussed in numerous publications(1-9). The earliest chemical definition of the aromaticity was based on the susceptibility of the aromatic systems to substitution reactions such as halogenation,sulphonation or nitration. In these reactions, the olefinic analogues yield addition products (10,11).

As the basis for our considerations, we adopted a somewhat idealized reaction between a pi-electron compound (i.e. one with conjugated double bonds) and some reagent XY whose properties, we assume, are analogous to that of Cl_2 and Br_2. Furthermore, we assume that the reaction may be reversible, and that it may run from the beginning state (I) through the sigma-complex (II) to yield either the products of addition (III) or substitution (IV):



(1)

Thus, the final effect would be determined by a change of the free energy (cf. Fig. 1):

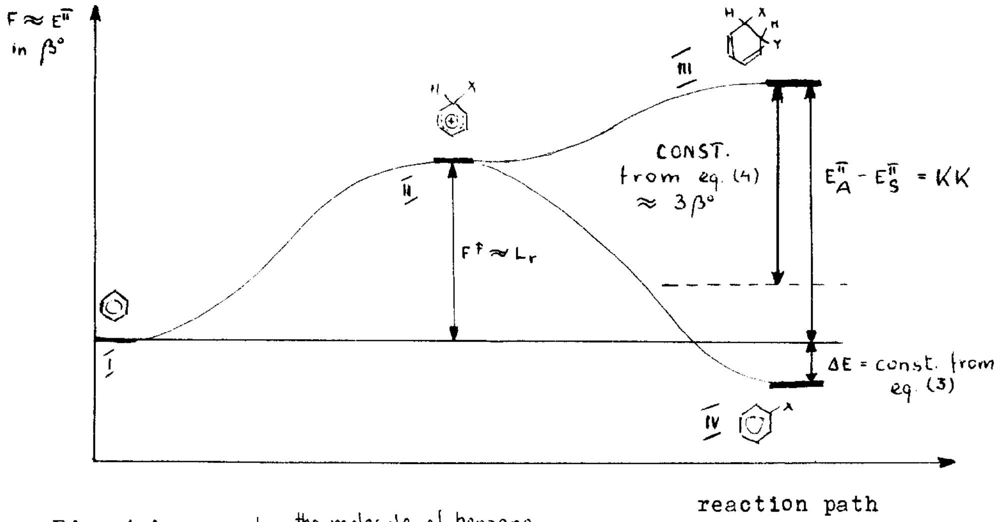


Fig. 1 An example: the molecule of benzene

The addition reaction is determined by satisfying the inequality:

$$\Delta F_A - \Delta F_S < 0, \text{ or } \Delta H_A - T\Delta S_A - (\Delta H_S - T\Delta S_S) < 0 \qquad (2a)$$

i.e.

$$\Delta H_A - \Delta H_S + T(\Delta S_S - \Delta S_A) < 0 \qquad (2b)$$

where S, H and T stand for the entropy, enthalpy and the absolute temperature, respectively.

Further we assume, as is often done (12,13), that the last term of the inequality (2b) is constant*/, if the compounds under consideration are of the same kind (a pi-electron compound always reacting with the same reagent XY), and if the reaction runs under the same conditions.

In terms of the delocalization energy model for chemical reactivity (8), we may postulate the differences in sigma electron energy between (III) and (IV) in scheme (1) for all the molecules of the pi-electron compounds under consideration to be constant. At such approximation, it is only the pi-electron energy which differentiates the molecules involved in the reaction (1) and determines its final effect. Hence, it is only the

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*/ i.e. the term $T(\Delta S_S - \Delta S_A)$ is the same for every compared pair of molecules, e.g. for benzene and anthracene or benzene and fulvene etc.

pi-energy term in the enthalpy, formula (2b), which has essential significence in the selection of the direction of the reaction. Thus, for substituents weakly interacting with the pi-electron system - we assume that X is a substituent of that kind - it is possible to write the following expression:

$$E_S^{pi} = E_O^{pi} + \text{const.} \qquad (3)$$

where E_O^{pi} stands for the pi-electron energy of the system before the reaction. Consequently, from (2b), and (3) we obtain:

$$E_A^{pi} - E_O^{pi} + \text{CONST.} < 0 \qquad (4)$$

which is an indispensable condition for the pi-electron compound to yield addition products with the reagent XY. In the term CONST. of inequality (4) are included constancy of the term $T(\Delta S_S - \Delta S_A)$, the constant from (3), and the constant term of the result of a subtraction of the sigma-electron energies for (III) and (IV) in the enthalpy.

The first term in (4) is the pi-electron energy of the system after addition, as in the case when two new bonds C-X and C-Y are established in two positions, say r and s. This means that delocalization of the pi-electrons will be decreased as a result of the formation of two carbon atoms in the state of hybridization sp^3. It is obvious that this term greatly depends on the selection of the position of the new bonds, but the addition is most likely to take place in positions where there is the smallest loss of the pi-electron delocalization. In other words, the positions r and s are chosen on the condition that the modulus of the expression $|E_A^{pi}(r,s) - E_O^{pi}|$ has the minimum value. On the other hand, the position of the first attack of the electrophyllic reagent X should be determined beforehand, the position of the localization centre of the C-X bond in the sigma-complex (II) thus being defined. The position is determined on the condition that the Wheland pi-electron localization energy (12,14) be at its minimum or, more precisely, the modulus of that energy - as en energy is most often calculated in the Hückel approximation (12) - and then is measured in units $\beta^o < 0$. This energy approximately estimates the energy of activation of the process I $\dashrightarrow$ II, thus in state II of reacting molecule a C-X bond is most likely to be formed in the position of the lowest energy value.

Hence, from the inequality (4) an expression is obtained where the result $E_A^{pi}(r,s) - E_0^{pi}$ is merely the so called bi-centric pi-electron localization energy (15) which is defined as:

$$L_{r,s} = E_A^{pi}(r,s) - E_0^{pi} - 2\alpha \tag{5}$$

$L_{r,s}$ stands for part of the pi-electron energy which a molecule loses as a result of the formation of new bonds C-X and C-Y in the positions r and s, and defines the resistance of a molecule to addition reaction. The greater the absolute value of this term, the less probable the addition reaction. The last term of the inequality (4), the CONST., has a strictly opposite physical meaning: it represents the molecular energy gain which is the result of the XY reagent addition, and is the energy of the formation of two new bonds. Since, this term is constant the first term, the pi-electron one, will determine the direction of the reaction.

Keeping in mind the above objections and assumptions, we postulate the expression KK as a numerical aromaticity index which we define as follows:

$$KK = \min |L_{r,s}| \tag{6}$$

The numerical criterion of aromaticity is justified not only by the tradition of organic chemistry from which it originates, but also by a uniformity with other aromaticity indices, as presented in Table I.

Table I presents KK and DE_{sp} values (the specific Zahradnik's delocalization energy calculated for one bond (6)) and Julg's aromaticity index A(3).

It can be seen from the Table that the compounds for which KK $>$ 3 (KK-values were calculated by use the HMO-method, see (12)) generally are considered to be aromatic, whereas those where KK $<$ 3 to be nonaromatic. Thus, it can be assumed that the value of the constant term CONST. in the inequality (4) is of the range of $3\beta^0$, cf. dotted line in Fig. 1.

Table I

Compound	KK	A	DE_{sp}
1) benzene	3.53	1.00 x/	0.333
2) pyridine	3.53	1.00	0.350
3) annulene-18	3.36	0.95	0.279
4) azulene	3.31	0.91-1.00 x/	0.306
5) anthracene	3.20	0.91-0.96 x/	0.332
6) pyrene	3.06	0.81	0.342
7) fulvene	2.99	0.62 x/ -0.72	0.244
8) annulene-8 (cyclooctatetraene)	2.67	0.44	0.207
9) hexatriene-1,3,5	2.52	0.71	0.198
10) p-benzoquinone	2.51	0.39	0.164
11) Kekule's structure of benzene	1.53	0.00	0.000

x/ Ref. (3)

EXAMPLES

For benzene only one value of the one-centric Wheland's localization energy is possible, $L_r = -2.54\beta^0$, whereas three values of bi-centric localization energy are possible (in units of β^0):

$L_{1,2} = 4.47 - 8.00 = -3.53$ (butadiene - benzene)

$L_{1,3} = 2.83 - 8.00 = -5.17$ /(allyl radical +C-radical)-benzene/

$L_{1,4} = 4.00 - 8.00 = -4.00$ (2 ethylenes - benzene)

From condition (6) it follows that the aromaticity index for benzene is $KK = |L_{1,2}| = 3.53$.

Similar calculations for butadiene give the following values: $L_1 = -1.64\beta^0$ and $L_2 = -2.47\beta^0$. Hence we select the lowest value of the localization energy r=1 so that the formation of the sigma-complex II is easier. Now we can calculate $L_{r,s}$:

$L_{1,2} = 2.00 - 4.47 = -2.47$ (ethylene - butadiene)

$L_{1,3} = 0.00 - 4.47 = -4.47$ /(two C-radicals) - butadiene)

$L_{1,4} = 2.00 - 4.47 = -2.47$ (ethylene - butadiene)

As can be seen from the above calculations, within HMO-approximation, only one $L_{r,s}$ value is possible in order to satisfy the condition necessary for computing KK for butadiene: that is KK = 2.47.

The aromaticity index KK makes a convenient basis for the classification of the pi-electron compounds (16), as - it refers to the chemical properties of the molecule and also makes possible a comparison with other numerical criteria which are adopted and accepted as a measure of aromaticity.

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