

DEFINITION OF AROMATICITY BASING ON THE HARMONIC OSCILLATOR MODEL

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Among various attempts to "measure" aromaticity in pi-electron systems, those associated with aromatic stabilization energy are most popular<sup>1-4</sup>.

Usually the appropriate index of aromaticity is calculated by use of quantum-chemical methods<sup>1,2</sup>. Here, an attempt to find another way to these quantities is suggested.

According to Julg<sup>5</sup> aromaticity should be connected with averaging of the peripheral CC-bonds of the systems:

$$A = 1 - \frac{225}{n} \sum_r \frac{d_r}{d} / 1 - \frac{d_r}{d} / 2 \quad /1/$$

where  $d$  and  $d_r$  are the averaged and  $r$ -th bond lengths, respectively, and the summation runs over all  $n$  peripheral bonds. This treatment however does not differentiate benzenoid hydrocarbons, as shown in the Table.

Our proposal is to apply the harmonic oscillator model to calculate stabilization /or destabilization/ energy due to the lengthening and/or shortening of the CC-bond lengths from the optimal value.

The Model

For a molecule of a conjugated hydrocarbon the total energy may be written approximately in a following form:

$$E_t = \sum E_{CH} + \sum E_{CC} \quad /2/$$

where the first term can be assumed to be constant in respect of rather small variation of lengths for these bonds. Thus all changes of energy depending on the changes of bond lengths should be described by second term in /2/. Therefore we use here a model based on the theory of the harmonic oscillator to determine that part of the energy which results from changes of the bond

lengths from the length assumed to be optimal, namely that for equilibrium,  $X_e$ . In such a manner one can obtain from /2/:

$$E_t = \text{const.} + n E_{CC}/X_e/ + \sum_{r=1}^n \Delta E_r \quad /3/$$

where  $E_{CC}$  is the energy of a CC bond at equilibrium length. The last term in /3/ may be written, using harmonic oscillator theory, approximately as

$$\sum_{r=1}^n \Delta E_r = \frac{1}{2} \left[ k \sum_{r=1}^n /X_r - d/2 + \bar{\sigma} \sum_{r=1}^n /s - X_r/2 \right] \quad /4/$$

where  $\bar{\sigma}$  and  $k$  are force constants for "pure" single and "pure" double CC-bonds, respectively /i.e. for ethane and ethylene of lengths  $s=1.524 \text{ \AA}$  and  $d=1.334 \text{ \AA}$ <sup>6</sup>, respectively/.  $X_r$  is length of  $r$ -th bond in  $\text{Å}$ . The first sum in /4/ describes that part of the energy connected with extension of  $d$  to the length  $X_r$ / extension energy/ whereas the second sum describes that part of the energy due to the compression of  $s$  to the length  $X_r$ . The presence of bonds in the molecule for which  $X_r \neq X_e$  results in non-zero a value of the sum /4/. From the minimization of /4/:

$$\frac{d \sum_r \Delta E_r}{d X_r} = 0$$

one can find a mean bond length  $\bar{X}_r$  for which the energy of the molecule has a minimum value. This length is expressed as follows:

$$\bar{X}_r = \frac{\sum_{r=1}^n X_r}{n} = \frac{\bar{\sigma} s + kd}{\bar{\sigma} + k}$$

From the experimental data it is well known that  $k = 2\sigma^7$ , and therefore one can readily find

$$\bar{X}_r = \frac{s + 2d}{3}$$

and taking numerical values for  $s$  and  $d$  as given formerly<sup>6</sup> we obtain

$$\bar{X}_r = 1.397 \text{ \AA}$$

and this is in excellent agreement with CC bond length in benzene i.e. in the molecule of highest aromatic character. One can easily draw the conclusion therefore that benzene is so aromatic because its CC-bonds are of optimal length in respect of the harmonic oscillator model of extension and compre-

ssion of bonds from the equilibrium /i.e. optimal/ length, being just 1.397 Å.

In connection with these results and conclusions it is reasonable and profitable to postulate an index of aromaticity based upon the expression:

$$\text{HOMA}_d = 1 - \frac{a}{n} \sum_{r=1}^n /X_r - 1.397/2^2 \quad /5/$$

where  $a=98.89$  if the following conditions are fulfilled:  $\text{HOMA}_d=0$  for the Kekule structure of benzene, and  $\text{HOMA}_d=1$  for benzene,  $n$  is the total number of CC-bonds in molecule.

Thus the aromaticity index  $\text{HOMA}_d$  /5/ is nothing other than a numerical function of the excess of energy resulting from the deformation of bond lengths  $X_r$  from the optimal value  $X_e = 1.397$  Å.

Taking into consideration the known relation between calculated bond orders and bond lengths one can easily define an index of aromaticity taking into account only calculated bond orders  $p_{rs}$ :

$$\text{HOMA}_p = 1 - \frac{3.60}{n} \sum_{rs} / \frac{2}{3} - p_{rs} / 2^2 \quad /6/$$

For many cases application of /6/ can be very useful because of lack of experimental data for  $X_r$ . Both HMO and SCF bond orders can be used in formula /6/.

#### Applications

To test the validity of this approach the Table contains various aromaticity indices for some hydrocarbons.

Compound	$\text{HOMA}_d^{\text{exp}}$ 8/	$\text{HOMA}_p^{\text{SCF}}$ 9/	$\text{HOMA}_p^{\text{HMO}}$	$\Delta_{S, pb}$ 10/	REPE 11/	$\Delta^{\text{exp}}$ 5/
Benzene	1.000	1.000	1.000	1.00	1.000	1.000
Naphthalene	0.930	0.915	0.969	0.70	0.842	0.936
Anthracene	0.910	0.885	0.959	0.55	0.717	0.950
Tetracene	0.864	0.868	0.955		0.636	0.912
Phenanthrene	0.928	0.914	0.961	0.66	0.837	0.910
Chrysene	0.905	0.903	0.957	0.62	0.832	0.886
Pyrene	0.869	0.893	0.953	0.67	0.769	0.816
Triphenylene	0.938	0.929	0.960	0.67	0.865	0.932
Perylene	0.917	0.889	0.953	0.53	0.739	0.907
Cyclooctatetraene	0.531			-0.72	-0.931	
Azulene		0.641	0.969	0.30	0.353	
Pentalene		0.628	0.960	-0.22	-0.270	
Hexatriene		0.624	0.881	0.00	-0.036	
Fulvene		0.622	0.910	-0.22	-0.031	

maticity indices based upon the stabilization energies.

One can readily find almost full agreement among the data considered, despite the various ways in which it was calculated.

It seems worthwhile to point out that this approach too is based on the stabilization energies, like other indices in Table, but it is quite independent /in principle/ of quantum chemical models. The application of this index to interpret the aromaticity of a large group of pi-electron compounds is in preparation.

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