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The HOMA index was generalized to the function of a property of chemical bonds such as, e.g., characteristics in BCPs. The new HOMA indices strongly correlate with the classical one for a variety of cyclic hydrocarbons unsaturated or not. Thus, the indices reflect a more general property then aromaticity: the savoricity.

The first geometrical aromaticity index, $A$, was introduced by Julg and Françoise \(^1\) as the variance of the ring perimeter bond lengths:

$$A = 1 - \frac{225}{n} \sum_{i=1}^{n} \left( 1 - \frac{d_{si}}{\bar{d}} \right)^2$$  \hspace{1cm} (1)

where $d_{si}$ and $\bar{d}$ for CC distances: particular and averaged, $n$ is number of bonds in perimeter cycle, $r$ and $s$ are running indices over the cycle atoms, and 225 is a normalization factor.

The rationale behind the $A$ index was the observation that in the fully aromatic benzene molecule the CC bond lengths are identical whereas in the hypothetical cyclohexatriene they must be strongly alternant. However, the so-defined index has exhibited a significant drawback: it recognizes "aromaticity" in definitely non-aromatic, but non-alternant, compounds such as cyclohexane. In consequence, it also does not differentiate aromaticity of different aromatic rings such as central coronene and benzene rings. One can conclude that the sole variance of the bond distances in a ring is not sufficient to adequately express geometrical aspect of aromaticity because it does not differentiate the rings of different aromaticity with satisfactory resolution.

The drawback of the Julg and Françoise index was removed by Krygowski and Kruszewski who defined the HOMA (Harmonic Oscillator Model of Aromaticity) index (2) widely used to express geometrical aspects of aromaticity:

$$\text{HOMA} = 1 - \frac{\alpha}{n} \sum_{i=1}^{n} \left( R_i - R_{\text{opt}} \right)^2 = 1 - \frac{\beta}{n} \sum_{i=1}^{n} \left( 1 - \frac{d_{si}}{d_{\text{opt}}} \right)^2$$  \hspace{1cm} (2)

where $R_i$ and $R_{\text{opt}}$ stand for distances of i-th ring bond in the analyzed structure and the reference optimal bond in benzene (1.388 Å), $n$ is the number of CC bonds in the ring, whereas $\alpha = 257.7$ is a normalization factor which guarantees that HOMA of aromatic compound approaches 1 and of its Kekulé non-aromatic structure approaches 0, $\beta = \alpha \cdot R_{\text{opt}}$.

It is surprising that the HOMA index, which seems to be very similar to the Julg and Françoise $A$ index, is so successful and well resolves compounds of different aromaticity, while $A$ fails in this task. The "mystery" of this difference is in disparity of $\bar{d}$ and $d_{\text{opt}}$. The former refers to mean CC distance in the analyzed compounds, while the latter is the CC distance in the reference benzene molecule. The initial shortcoming of HOMA, its limitation to only carbocyclic structures, was removed by introducing parameterizations for most of important heteroatoms. \(^3\) The HOMA index was also decomposed into GEO and EN destabilizing components interpreted as geometrical and energetical factors. \(^4\) The GEO component is related to Julg and Françoise $A$ (normalized) variance index and Krygowski's et al. Bond Alternation Coefficient, BAC, \(^5\) a (normalized) standard deviation. Perfect correlations of EN with the CC bond energy and other energy parameters was also demonstrated. \(^6\)

Thus, GEO is a function of a bond variance, while EN can be interpreted as a (normalized) squared distance between a molecule and the aromaticity standard $\alpha(R_{\text{opt}} - \bar{R})$ where $\bar{R}$ is the mean CC distance in an $n$-membered molecule (n=3) and $R_{\text{opt}}$ can be interpreted as a reference CC distance in an appropriate, hypothetical, fully aromatic planar molecule of a regular $n$-gone skeleton which is benzene if $n$=6. Remark, that the (normalized) squared distance in (2) places a greater weight to more distanced points and therefore is used in optimization problems in which directions are less important then distances. Minimization of an expression very similar to (2) is basic for the K-mean clustering method introduced to cluster analysis by Steinhaus. \(^7\)

The above features of the HOMA index indicate that the only connection of HOMA with aromaticity lies in choosing benzene as a reference molecule and in normalization making HOMA equal to 1 for benzene and 0 for its hypothetical Kekulé form. Thus, the index can be formally used for the other (cyclic) molecules without loosing its statistical meaning. Moreover, it seems to be correctly defined also for the non-cyclic molecules if the appropriate meaning is assigned to the reference optimal distances. Here, we are showing that HOMA discriminates much larger class of molecules than sole aromatic compounds and are demonstrating that it can be generalized to obtain other valuable (aromaticity) indices.

A neural networks algorithm applied to a set of geometric, energetic, and magnetic aromaticity indices allowed for construction of a unified aromaticity index for series of unsaturated organic compounds. \(^8\) However, comparison of aromaticity indices based on different physical properties leads to the conclusion that aromaticity is a multidimensional phenomenon. \(^9\)–\(^11\) Nevertheless, some of the indices constructed on different physical bases can give quite concordant evaluation of aromaticity. A very good example is total electron energy (H), its kinetic (G) and potential (V) components, as well as the electron...
density ($\rho$) in ring critical point (RCP) which are strongly linearly correlated with the geometrical HOMA aromaticity index and also show fair linear correlations with the magnetic NICS(1)$_{zz}$ aromaticity index.\textsuperscript{12}

As pointed out above, the HOMA index can be calculated for every ring irrespectively it is aromatic or not. Therefore, we tested whether the Palusia's and Krygowski's finding\textsuperscript{12} can be extended to saturated and singly and doubly unsaturated hydrocarbon rings. Although, we found some tendencies between HOMA and electron density characteristics in RCP, the number of "exceptions" and spread of the points were significant.

Therefore, we introduced a new group of indices in which expression (2) is used as formula defining the function of a variable assigned to the bond. In this approach, the classical HOMA is a function of bond lengths, $HOMA=HOMA(R)$, but the $HOMA(\cdot)$ function can act, for example, on electron density $\rho_{BCP}$ in BCPs:

$$HOMA(\rho) = 1 - \frac{\alpha_{BCP}}{n} \sum_{i=1}^{n} \left( \rho_{BCP}^{opt} - \rho_{BCP}^{opt} \right)^{2}$$

where $HOMA(\cdot)$ is a function of a variable given in parentheses, and $\rho$ stand for electron density in $BCP$ of $i$-th bond in the analyzed structure and the optimal value in the reference benzene, $n$ is the number of CC bonds in the considered structure, whereas $\alpha_{BCP}$ is a normalization factor. The HOMA indices for other bond parameters such as potential and kinetic electron energy in bond critical points ($BCP$), $V_{BCP}$ and $K_{BCP}$, respectively, can be determined analogously.

It appeared that for cyclic hydrocarbons,\textsuperscript{1,4} the quadratic correlation between the $HOMA(R)$ and $HOMA(\rho)$ is excellent (Fig. 1) with the correlation coefficient equal to 0.9997 but the correlation coefficient of a linear fit exceeds 0.999 as well. Fig. 1 shows that the smallest values of $HOMA$ and $HOMA(\rho)$ are for the saturated 4-, 5-, and 6-membered rings in mono- and bicyclic systems. The next group of compounds, with larger values of $HOMAs$, is constituted of the singly-unsaturated rings fused in various ways to other saturated or unsaturated rings. The following group of cycles is consisted of the doubly-unsaturated rings fused in different manners to the other rings. The group of the highest values of $HOMAs$ is formed by the aromatic rings condensed in several ways in polycyclic systems (Fig. 1). The correlation has, however, some exceptions: the cyclopropane, benzene, and benzdiynes molecules. The data for these molecules were not included to establish the correlations and require further analysis and investigation. Thus, aromatic, non-aromatic, and anti-aromatic compounds served so far to construct correlations between HOMA and the other aromaticity indices form a congruent group of molecules constituting only a minor part of a more general class of cyclic molecules (Fig. 1).

If the $HOMA(\rho)$ and $HOMA(R)$ indices reflect a more general feature than aromaticity itself than what a property is actually measured by these parameters? The plot in Fig. 1 shows an increase in the $HOMA$ indices with the increase of the cycle size and the number of the double bonds in a cycle. The relationship is slightly modified by the type of condensation. Thus, the strain of

Fig. 1. The linear correlations between the HOMA geometrical index and HOMA($\rho$) index based on electron densities in bond critical points for series of saturated, unsaturated and aromatic hydrocarbon rings.
Correlations are, however, non-linear (quadratic) but strong with the correlation coefficients exceeding 0.99 (Fig. 2). For the commonly studied aromatic and non-aromatic molecules the correlations can be fitted by a straight line with the correlation coefficients also close to 0.99. Interestingly, very recently Tokatli and Ucun constructed an aromaticity index, which would be called $\text{HOMA}(\epsilon_{\text{BCP}})$, where $\epsilon_{\text{BCP}}$ is the bond ellipticity, if the absolute value function was changed for the second power.\(^\text{13}\)

![Plot of the HOMA(R) geometrical index against the HOMA(\rho) index based on electron densities in bond critical points for series of saturated and unsaturated acyclic hydrocarbons.](image-url)  

**Fig. 3**

Correlations between the empirical structural HOMA index and functions defined on the well theoretically grounded electron density characteristics in BCP of a variety of cyclic structures (Figs. 1 and Fig. 2), are an excellent confirmation for the correctness of formulation of the empirical HOMA index and for its perfect anchoring in the quantum chemical theory. It is remarkable that the correlations are satisfied not only for aromaticity but also for its generalization, the savoricity. Notice, that regular changes of the HOMA(*) functions of bond parameters taken in BCPs with HOMA(R) are due to good correlations between $R$ and bond orders, already observed by Pauling,\(^\text{14}\) as well as $R$ and parameters in BCP reported by many others.\(^\text{5,15,16}\)

Now, taking the advantage of the fact that both HOMA(R) and HOMA(\rho) can be defined also for acyclic structures we plotted one value against the other for a series of small unbranched alkanes. Fig. 3 shows that the picture for acyclic structures is much more complex. Yet, one can probably select groups of acyclic compounds such as allenes, alkynes, alkenes, … , etc., that follow regular trends. Nevertheless, a detailed consideration of these and similar tendencies would require a careful consideration of different kind of isomerism that can occur in acyclic compounds, including for example constitutional, geometrical, and conformational isomerism which goes far beyond this study.

**Conclusions**

The HOMA index was generalized by treating it as a function of a parameter assigned to the chemical bonds. The HOMA function is...
constructed practically identically to the classical HOMA index, which in the new formulation is the function of bond lengths, HOMA(R). The generalization allows for defining the HOMA(ρ) function of electron density in bond critical points. The HOMA(R) and HOMA(ρ) indices taken for aromatic, unsaturated, and fully saturated cyclic hydrocarbons linearly correlate with regression coefficient of 0.999. This correlation reveals that the both HOMA indices are not only aromaticity indices but indices of much more general feature. This feature combines information on cyclicity, degree of cycle unsaturation, and the way of cycle condensation in polycyclic systems. We proposed to call the generalization of the aromaticity property the savoricity. Thus, we demonstrated that HOMA index is not an aromaticity index but the index of much more general property of the molecules: their savoricity. Also, HOMA functions of the potential and kinetic energy components of electron density in BCP are the savoricity indices.

Notes and references

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