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Two Sources of the Decrease of Aromaticity: Bond Length Alternation and Bond Elongation. Part I. An Analysis Based on Benzene Ring Deformations.*

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Abstract. Decrease of aromaticity of the π-electron system may be described by two different and independent mechanisms: (i) an increase of the bond length alternation and (ii) an extension of the mean bond length (bond elongation). These two mechanisms are described by two contributions to the HOMA index: GEO and EN, respectively. These contributions correlate very well with the total Hartree-Fock energy of the benzene ring deformed in two ways: (i) when all C-C bond lengths are set equal and their length is gradually increased, and (ii) when the mean C-C bond length is fixed, and the difference in length between adjacent C-C bonds gradually increases. Both changes in geometry bear the changes in the aromatic character of the ring, and the HOMA-values as well as the Hartree Fock energies correlate excellently with Schleyer's NICS values.

Key words: Aromaticity, Benzenes, Energy.

Introduction

Recently it has been shown quantitatively[1-4] that the aromatic character of the benzene ring embedded in the benzenoid hydrocarbons depends strongly on the topological environment, as it was qualitatively known from Robinson's circle notation,[5] extended later by Clar.[6] Moreover it was also shown that the decrease of aromatic character of the π-electron system (e.g. benzene ring) may be realized in two different ways:[7]

(i) by the increase of the bond length alternation, and

(ii) by the extension of the mean bond length (i.e. elongation of bonds) of the system in question.

These two situations have been discovered due to the application of the HOMA (abbreviation from Harmonic Oscillator Model of Aromaticity) index[8] in its formula which explicitly shows these two contributions separately and present them in a numerical way:[7,9]

$$\mathrm{HOMA} = 1 - \alpha(R_{opt} - R_{av})^2 - {}^{\alpha}/_{n}\, \Sigma\, (R_{av} - R_i)^2 = 1 - \mathrm{EN} - \mathrm{GEO} \qquad (1)$$

where n is the number of bonds taken into the summation and α is an empirical constant fixed to give HOMA = 0 for the hypothetical Kekule structures of aromatic systems (with bond lengths as in acyclic polyene), and 1 for the system with all bonds equal to the optimal value R_{opt}. R_{av} stands for the average bond length, while the individual bond lengths are depicted by R_i.

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* In memory of Clive W. Bird our friend and coworker

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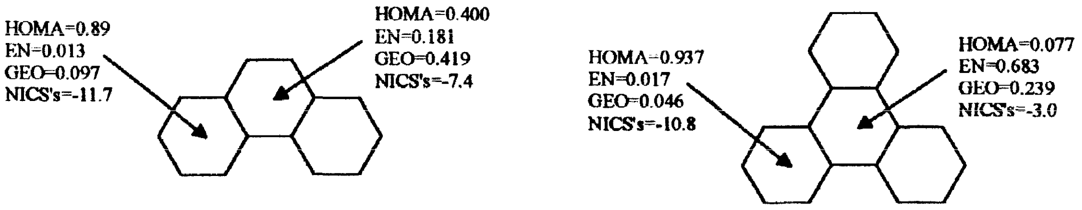
The term GEO describes the decrease of aromatization due to the increase of the bond length alternation, since it is a simple function of variance of the bond lengths (thus it describes directly a variability of the bond lengths around the mean value). The term EN describes how far the mean bond length is from the optimal bond length i.e. the EN term describes the decrease of stability due to the bond elongation.

A good illustration of this approach is given by examples of phenanthrene and triphenylene as presented in chart 1, where inside the ring is given values of aromaticity indices HOMA, its contributions EN and GEO and the magnetic index NICS.[3]

Chart 1



It is immediately apparent that both central rings have lower aromatic character than the other rings:[1] HOMA values are much less for them (0.400 for phenanthrene and 0.077 for triphenylene compared to the HOMA-values around 0.9 for other rings). Analogously the NICS (abbreviation from Nucleous Independent Chemical Shift) values are less negative for the central rings (-6.5 for phenantrene and -3.0 for triphenylene) than for the peripherial ones (-10.2 and-10.8, respectively).[2] Both indices reveal a remarkable decrease of aromaticity of the central ring compared to the peripheral ones. However **due to the possibility of the separation into two independent contributions GEO and EN, the HOMA index allows us to indicate which of the two mechanisms mentioned above acts in a dominant way in the observed decrease of aromatization of these rings**. In the case of phenanthrene the GEO term is 0.419 compared to a smaller value of the EN term equal to 0.181. It means that decrease of the aromatic character of the central ring in phenanthrene is mostly due to the increase of bond length alternation. A different situation is in the case of the central ring of triphenylene. Here the term EN = 0.683 is considerably larger than the GEO = 0.239, indicating the dominant role of bond length extension in the decrease of aromatization of the ring.

The names of the terms GEO and EN were connected with traditional criteria of aromaticity. The geometric one represent the situation where aromatic character is defined by the decrease of bond length alternation: benzene itself is typically aromatic, whereas its Kekule structure is typically non-aromatic.[10] Thus the decrease of aromaticity which is not related to bond length alternation but to the extension of their mean value was associated with the energetic criterion of aromaticity.[7,11] Extension of the mean bond length is revealed in a decrease of the ring stability, since the reference state (the Kekule structure of benzene) is the same for all cases of the deformed benzene ring.[12]

Evidently both mechanisms of the decrease of aromaticity are associated with an increase of energy (decrease of stability).[13] Additionally, in the presented above examples, none of these factors acts alone, the observed effect is a superposition of both mechanisms, (sometimes) with a dominancy of one of them. Thus it seems to be important to study how these factors function alone.

The aim of this paper is to analyse how the terms EN and GEO contribute to the general decrease of aromaticity expressed in terms of energy of the geometry changes.

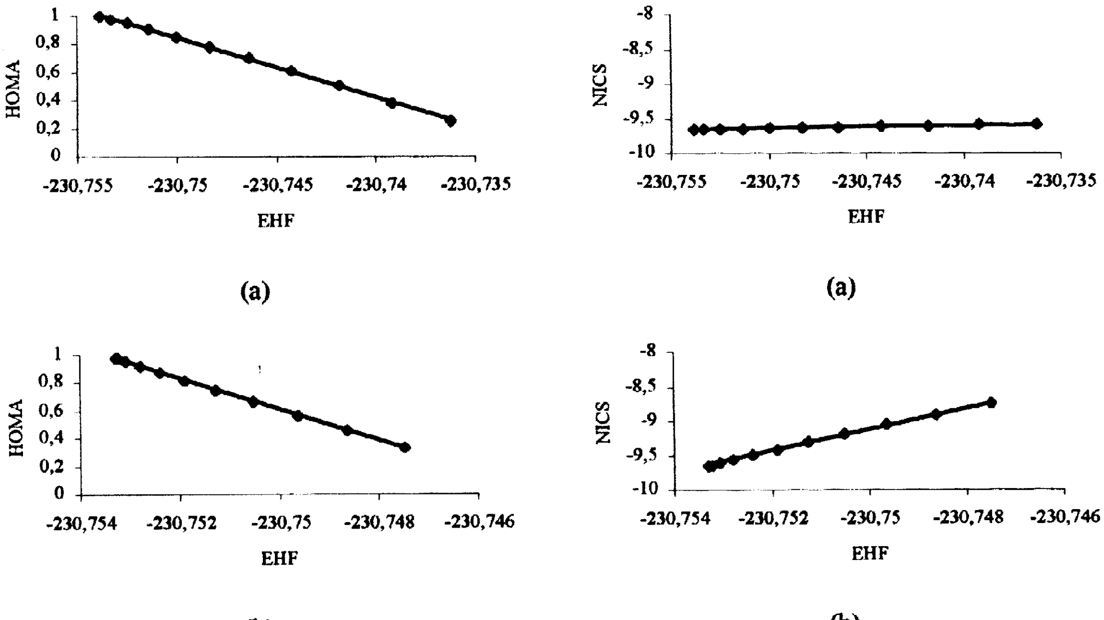
Analysis by Means of a Computational Experiment

The optimized geometry of benzene calculated within *ab-initio* calculation at 6-311G** level of theory[14] is a starting point for two kinds of ring deformations:

(i) the mean bond length is extended step by step by 0.005 Å from the geometry [which is in between the experimental value (1.397 Å)[15] and the theoretical one,[14] dependent on the basis set, 1.388 Å] (1.392 Å) up to 1.442 Å. In this case the GEO term equals zero and the HOMA values decrease only due to an increase in the EN term. The Hartree-Fock energy, E(HF), of the ring is calculated for each geometry for which all geometrical parameters other (except CC-bond lengths) are optimized.

(ii) the mean bond length is fixed but the bond length alternation is increased step by step by $\Delta = 0.01$ Å (i.e. lengthening of a „longer" bond by 0.005 Å is associated with a shortening of the „shorter" bond by 0.005 Å). In this case $\Delta EN = 0$) and the HOMA decreases only due to an increase in bond alternation (from Δ GEO= 0.0 to Δ GEO = 0.1 Å) i.e. due to an increase in the GEO term.

In both cases the changes in geometry are associated with the changes of the total energy E(HF) of the ring. Figure 1 presents the HOMA and NICS values plotted against E(HF). A reverse plot may give a ratio of the energy changes per unit of HOMA due to (i) the bond lengths alternation and (ii) the bond elongation. These numbers are 119.88 kJ/mole and 255.99 kJ/mole, and indicate that bond elongation is more costly than bond length alternation, if they are both measured as in the definition of the HOMA index.



(a) (a)

(b) (b)

Fig. 1. Dependence of HOMA and NICS vs. EHF. (a) in the case of expansion of the mean bond length and (b) in the case of the increase of bond length alternation.

Both changes in the ring geometry are associated with a variation in the values of aromaticity indices. Tables I and II show the mutual correlations between the aromaticity indices.

Table I

	HOMA	GEO	BAC	I_6	BE	NICS
HOMA	1.0000					
GEO	-1.0000	1.0000				
BAC	0.9631	-0.9631	1.0000			
I_6	0.9626	-0.9626	1.0000	1.0000		
BE	-0.9998	0.9998	-0.9650	-0.9644	1.0000	
NICS	-0.9997	0.9997	-0.9688	-0.9683	0.9996	1.0000
EHF	-0.9999	0.9999	-0.9605	-0.9600	0.9997	0.9993

Table II

	HOMA	EN	BE	NICS
HOMA	1.0000			
EN	-1.0000	1.0000		
BE	0.9684	-0.9684	1.0000	
NICS	-0.9956	0.9956	-0.9875	1.0000
EHF	-0.9994	0.9994	-0.9762	0.9982

For the model with bond alternation changes the indices which best correlated with E(HF) are: HOMA, and obviousely GEO, BE[1] and NICS. Typically the geometric indices measuring only the bond alternation (I_6 and BAC) have lower correlation coefficients. Obviously, the EN by definition (constant mean bond length) does not correlate at all. The changes in the mean bond length (without alternation) also generate the changes in aromaticity indices. The best correlations with E(HT) are HOMA, EN, and NICS. It may be concluded that NICS and HOMA work in the most universal way, since in both cases: (i) and (ii) they best correlate with changes of Hartree Fock energies. The possibility of using HOMA in order to show separately the two different contributions to the decrease of aromaticity of the π-electron system is an additional advantage.

As a useful illustration of the above presented ideas a few examples are presented in Table III. For all cases the collection of typical aromatic indices or criteria are presented: HOMA, EN, GEO, Bird's I_6,[16] and NICS. All the data are based on experimental geometries, except NICS and indices for benzene and its Kekule structure (indicated), which are also computed from *ab-initio* 6-311G** calculated geometries, applying for the Kekule structure bond lengths for C-C and C=C equal 1.467 and 1.349 Å,[17] respectively.

Data of Table III need some comments. NICS, HOMA and I_6 are qualitatively in line in predicting a lower aromaticity of the central rings in phenanthrene and triphenylene. However, radialene, which is evidently antiaromatic, is monitored as such only by NICS (+2.8 ppm) and HOMA (-2.962), whereas I_6= 100 i.e. predicts radialene as aromatic as benzene (all bonds of the same length!). Evidently **equality of the bond length alone cannot be used as the only criterion of aromaticity, their lengths have to be taken into account. Another case of the non-aromatic systems is the Kekule structure of benzene, which is well accepted as a non-aromatic reference state.[10] For this case HOMA = 0, by definition, if the double and single bonds are taken into account as in butadiene-1,3,[17] however NICS is only slightly different from the value for benzene itself, indicating considerable aromaticity of this structure**. A similar result is found while using I_6, which for this geometry is equal to 50.5. If the Kekule structure is for the geometry like CC bonds in ethane (1.533 Å)[20] and ethene (1.337 Å),[21] i.e. closely to the geometry of the reference structure in the Pauling[22] and the Kistiakowsky[23] estimations of resonance energy, then I_6 for such a ring geometry is still 17.1.

Table III

	HOMA	EN	GEO	I_6	NICS[2]
Benzene[13]	0.979	0.021	0.000	100	-9.7
Kekule structure of benzene[18]	0.0	0.103	0.897	50.5 (17.1)*	-8.6[18]
Central ring of phenanthrene	0.400	0.181	0.419	64.2	-7.4
' of chrysene	0.503	0.119	0.378	66.1	-8.7
' of perylene	0.133	0.765	0.101	83.0	+6.8
'of triphenylene	0.077	0.683	0.239	73.6	-3.0
Outer rings of (3)-(6), mean values	0.867	0.023	0.110	83.2	-10.8
Radialene[19]	-2.962	3.962	0.000	100	+2.8

*) Kekule structure with bond lengths as in ethane[20] and ethene[21]

The above presented results show that the criteria of aromaticity and non-aromaticity are not always in line when various indices are compared for some testing situations, for which chemical intuition clearly defines systems as non-(Kekule structure of benzene) or anti-aromatic (radialene) systems.

General Discussion and Conclusions

The HOMA index may be used only for the equilibrium geometry of molecules, since only in these cases does the geometry reflect the natural structure of molecules and the natural interactions in them. Any deformation leads to an artificial situation, and the results obtained in this manner may have only a qualitative value. However, in some cases, the artificial geometry is applied in order to show some trends which would not be accessible if only the experimental data were used. In this way natural geometries of benzene rings in cyclophanes[12] and benzenoid hydrocarbons[12] were used to show the interrelations between the energetics of these rings and the aromaticity indices: NICS, HOMA, EN, GEO and I_6.

In this report a similar procedure was applied to show the energetic relation between two kinds of deformation of the benzene ring, which lead to a decrease in aromaticity: an increase in bond length alternation and bond elongation. **Both these mechanisms are present in molecular geometry of π-electron systems and application of the HOMA model allows us to detect them and to identify the nature of the decrease in aromaticity.** Bond elongation is energetically twice as costly as bond alternation.

It should also be mentioned here, that the HOMA model with the separation into GEO and EN terms allows illustration of how the Clar classification[24] of rings in benzenoid hydrocarbons work. The „empty" rings, such as eg. central rings in triphenylene or perylene are less aromatic and EN is a dominant factor of the decrease in aromaticity.[7] The rings with a migrated sextet are aromatic, HOMA is large and EN and GEO terms are small. The rings with localised double bonds (central rings in phenanthrene, chrysene, etc) are less aromatic due to an increase in bond alternation, i.e. HOMA is smaller due to a larger value of the GEO term.[7]

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