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Separation of the Energetic and Geometric Contributions to the Aromaticity of π-Electron carbocyclics.

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Abstract. Separation of the aromaticity index HOMA, based on experimental geometry, into energetic and geometric contributions is proposed for carbocyclic π-electron systems. The decrease of the aromatic character may be due either to an increase of bond length alternation (geometric term) or to the lengthening of the mean bond lengths of the ring (energetic term). On the basis of 169 sets of data for benzene rings in benzenoid hydrocarbons, 116 in para-disubstituted benzene derivatives and 90 in TCNQ molecules in EDA complexes and salts, as well as 48 for five-membered rings in cyclopentadienyl complexes with Rh it is shown that these two terms are uncorrelated, supporting the view of Katritzky et al.$^{1-4}$ and Jug et al.^{5} that aromaticity is a multidimensional phenomenon. The separation is applied to five-, six- and seven- membered rings in typical π-electron systems (benzenoid hydrocarbons, fullerenes, fulvene and heptafulvene derivatives).

Introduction

Aromaticity is undoubtedly one of the most important general concepts for the understanding of organic chemistry$^{6-8}$. Although it is not a unique physical or chemical property, in the 60s and 70s it was agreed$^{9-12}$ that aromatic character is associated with cyclic π-electron systems in which delocalization of π-electrons results in a few typical, partly equivalent, physicochemical features: (i) an increase of the stability in comparison with the olefinic analogues (resonance energy), (ii) averaging of the bond lengths (less bond length alternation than in polyenes), (iii) the π-electron ring current is induced when the system is exposed to the external magnetic field (typical "aromatic" proton chemical shifts in NMR spectroscopy). As a result, various indices of aromaticity^{13} have been defined, and many of them could be approximately related to the above three kinds of physicochemical properties. Application of principal component analysis^{14} to different indices of aromaticity and various groups of π-electron systems revealed that two or three orthogonal principal components are necessary to describe 75 - 80 % of the total variance due to the variation of aromatic character of the chemical species taken into account and to the variation of aromaticity indices used in the calculations. Katritzky et al. have shown$^{1-4}$ that for nine heterocyclics and twelve characteristics comprising readily available geometric, energetic and magnetic indices of aromaticity, three orthogonal factors accounted for 83% of the total variance. A similar study by Jug et al.^{5} also carried out for a group of heterocyclic systems, has lead to the conclusion that 75% of total variance may be explained by two orthogonal factors. A recent study based on experimentally determined indices of aromaticity for 169 benzene rings embedded in various chemical environments of benzenoid hydrocarbons has shown that two principal components are necessary to reproduce

95 % of the total variance[15]. Similar analysis of five families of para- disubstituted benzene derivatives consisting of 116 rings has given a similar result[16]. Clearly, aromaticity is a multidimensional phenomenon, but the nature of these factors or principal components was until now only demonstrated at the statistical level, i.e. for a group of systems and taking into account a set of indices of aromaticity.

The aim of this study is to show that aromaticity may in fact be divided into two well-defined physically meaningful contributions: the geometric and the energetic ones. Both of them are accessible for individual molecules or their fragments by applying proper analysis of experimental CC bond lengths of the systems under study.

The model

In the mid-60s averaging of bond lengths was used for the first time as a quantitative measure of aromatic character by Julg et al.[17]. They defined their index of aromaticity as the normalized function of variance of bond lengths in the perimeter of the molecule. An obvious limitation of this approach was that it could be used only for carbocyclic π-electron systems. To avoid this shortcoming a modification was suggested[18] to replace the mean bond length by the optimal bond length, R_{opt} which could be estimated for any kind of bond (including those with heteroatoms) for which the precise lengths of double and single bonds were available. R_{opt} was estimated by the minimization of the deformation energy due to the extension and compression of the double and single bonds, respectively. The above estimation was carried out assuming (i) the harmonic potential for energy of deformation and (ii) that the force constant for the stretching deformation for the double bond is twice that for the single bond. Then the HOMA index (abbreviation from Harmonic Oscillator Measure of Aromaticity) was defined[18,19]:

$$\mathrm{HOMA} = 1 - \frac{\alpha}{n}\sum\left[R_{opt} - R_i\right]^2 \qquad (1)$$

where n is the number of bonds taken into summation and α is an empirical constant fixed so that HOMA = 0 for the Kekule structure of the typical aromatic system, and is equal to 1 for the system with all bonds equal to the optimal value R_{opt}. For CC bonds $\alpha = 257.7\text{Å}^{-2}$ and $R_{opt} = 1.388\text{Å}$. The right hand side of eqn. (1) may be called the dearomatization term since it describes the degree of dearomatization of the system due to the differences of bond lengths from the optimal value, R_{opt}. This term however may be divided into two others:

$$\frac{\alpha}{n}\sum\left[R_{opt} - R_i\right]^2 = \alpha\left(R_{opt} - R_{av}\right)^2 + \frac{\alpha}{n}\sum\left(R_{av} - R_i\right)^2 \qquad (2)$$

where R_{av} is the mean bond length of all bonds taken into analysis, i = 1,2,...n. The first term on the right-hand side of (2) depends on the mean value of the bond lengths in the system under study and hence may be approximately related to the energetic contribution to the dearomatization term, abbreviated hereafter as EN. The other term chiefly represents the part of dearomatization due to alternation of bond lengths, and is therefore attributed to the geometric contribution to dearomatization, hereafter abbreviated as GEO.

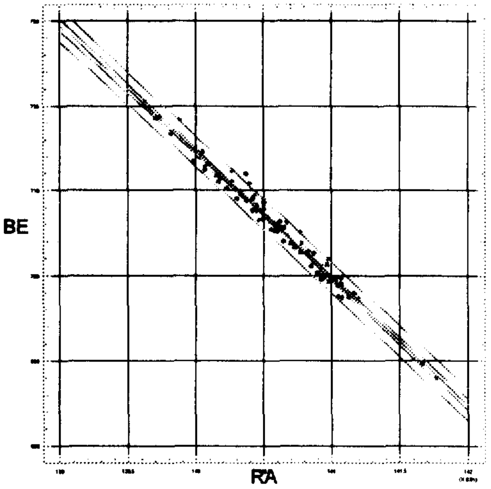


Fig. 1. Linear dependence of CC-bond energy (in kcal) of the ring in TCNQ complexes and salts calculated by use of eq. 3 on their mean bond length values (in Å). Correlation coefficient r= -0.989 for n= 90.

The dependence of the first term (EN) on the bond energy may be supported both empirically and theoretically. Fig. 1 presents the dependence of the energy of CC bonds in the ring of TCNQ molecules in 90 EDA complexes and salts on the mean CC-bond length in these rings. The correlation coefficient r=-0.989 strongly supports the above statement. The changes in bond lengths of TCNQ molecules in EDA complexes and salts represent a wide range of varying quantities and hence form a statistically good sample. The same kind of dependence for 169 benzene rings in benzenoid hydrocarbons gave r = -0.999, and for 48 cyclopentadienyl rings in complexes with Rh r=-0.996. Molecular geometries for all these systems used in calculations were retrieved from CSD[20] and only the most precise crystallographic data with AS1[20] (i.e. structures for which the mean Esd for bond lengths ≤0.005 Å) were used in these regressions. Empirically the above statement may be accepted as well justified. The energy of CC bonds in these rings was estimated using a recently described empirical formula relating bond energy (in kcal) to its length[15,21] (in Å)

$$E(n) = 87.99 \cdot \exp\{2.255[1.533 - R(n)]\} \qquad (3)$$

On the other hand, if this formula for E(n) is expanded in the Taylor series around $R_{av} = R_{opt}$ then cutting off after the first term one obtains the linear dependence of energy on the mean bond length, R_{av}. Thus we may accept that the term EN in HOMA describes that part of dearomatization which is related directly to the changes of energy of the ring in question.

The other term, GEO, is directly related to the variance of bond lengths of the ring in question. Variance[22] by definition is a good measure of variability, and in the past it was successfully applied to discuss the aromatic character of many systems. It was applied by Julg et al. as early as the mid-60s to carbocyclics[17] and later, after reformulation of the idea into the bond order form, it was used successfully in a series of papers by Bird[23] for both carbocyclics and many different heterocyclics[24]. In our case we make use of another index of aromaticity which depends directly on the degree of bond length alternation, and is hence called the Bond Alternation Coefficient, BAC[15]:

$$\mathrm{BAC} = 1 - 3.46\sqrt{\sum_{i}[R_i - R_{i+1}]^2} \qquad (4)$$

This index can be related to the bond fixation theory[25] and also resembles the Pozharskii ΔN index of aromaticity[26] in which bond lengths are transferred into bond orders. Table I presents correlation coefficients for scatter plots of EN and GEO terms *versus* other indices of aromaticity, for four samples representing numerous chemically modified five- and six-membered rings. It is immediately apparent that EN correlates very well with the energy of rings calculated by equation (3), whereas the GEO term correlates very well with Bird's I_6[23] and BAC[15].

Table I.Correlation coefficients for linear relationships between EN, GEO and other indices of aromaticity (BAC eq. 4, BE eq. 3, and I_6[22]) for four samples of structurally different topological patterns

sample	n	BAC/GEO	I_6/GEO	BE/EN	EN/GEO
TCNQ-EDA-complexes and salts	90	-0.991	-0.992	-0.977	0.390
Benzene rings in benzenoid hydrocarbons	169	-0.929	-0.983	-0.948	0.048
benzene ring in p-disubstituted benzene derivatives	116	-0.935	-0.995	-0.906	0.092
cyclopentadienyl rings in complexes with Rh	48	-0.949	-	-0.899	0.780

These results support strongly the conclusion that EN represents the energetic contribution to the aromaticity, whereas the GEO term represents the geometric one. Very low values of the correlation coefficient for the dependences of EN vs GEO show that these two contributions are independent of each other. The case of cyclopentadienyl derivatives is an exception. Its high value of the correlation coefficient may be easily interpreted as a statistical artefact, as shown in Fig. 2. Four points of the total n = 48 on the right-hand side of the figure form a cluster which determines the high correlation coefficient. From the statistical point of view, the correlation analysis requires normally distributed samples[22], or practically, at least the regular distribution along one of the axes. This is not the case. In view of the above-presented results, it seems reasonable to redefine the HOMA index, taking into account the above-mentioned conclusions, which may very occasionally lead to HOMA values > 1. This is possible if EN is negative and the GEO term is close to zero.

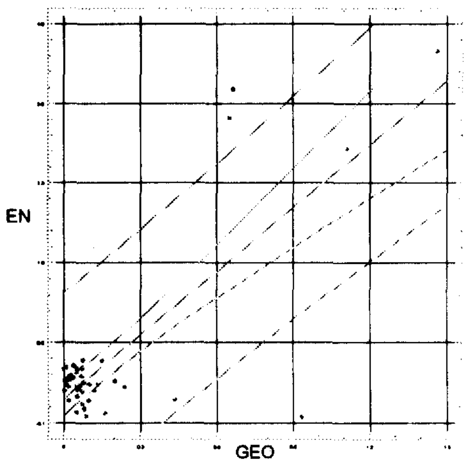


Fig. 2. Scatter plot of EN vs. GEO for 48 five-membered rings from complexes of cyclopentadienyl with Rh

Redefinition of the HOMA index

It is known from elementary chemistry, and is well illustrated by Fig. 1 or equation (1), that shortening of the bond is associated with an increase of bond energy. In the HOMA model R_{opt} is the reference bond length for which EN = 0, and for $R_{av} > R_{opt}$ EN is by definition a positive quantity. Then for $R_{av} < R_{opt}$ the EN term must be taken with a negative sign. In this admittedly arbitrary way we are able to take into consideration the rings for which the mean bond length, R_{av}, is lower than R_{opt} and which exhibit an increase of energy. Thus, in terms of energetic criteria of aromaticity, it represents stronger aromatic character since it should have a higher resonance energy. In consequence we have to reformulate the definition of HOMA as follows:

$$\mathrm{HOMA} = 1 - \mathrm{EN} - \mathrm{GEO} \qquad (5)$$

where

$$\mathrm{GEO} = \frac{\alpha}{n}\sum\left(R_{av} - R_i\right)^2 \qquad (6)$$

$$\mathrm{EN} = \alpha\left(R_{opt} - R_{av}\right)^2 \qquad \text{for } R_{av} > R_{opt} \qquad (7a)$$

and

$$\mathrm{EN} = -\alpha\left(R_{opt} - R_{av}\right)^2 \qquad \text{for } R_{av} < R_{opt} \qquad (7b)$$

The above reformulation is important for the kind of rings whose mean bond length is shorter than R_{opt}. In such cases EN terms become negative and HOMA may become larger than 1.0. The appearance of situations in which HOMA values are larger than 1.0 may seem strange and needs some comments. We should be aware here of at least three aspects.

Firstly, the reference bond lengths for determining R_{opt} and the normalization factor α for CC - π-electron systems[19] are taken from the most precise electron diffraction measurements of buta-1,3diene[27]. Obviously, by taking the molecular geometry from the other measurement for the same reference molecule one gets different values of R_{opt} and α. Buta-1,3diene was chosen as the reference system so as to resemble the situation created by Hess and Schaad[28] in their approach for determining resonance energy, where the acyclic polyenes were the reference system. Most molecular geometries are actually taken from room temperature X-ray diffraction measurements. The temperature dependence of bond lengths as well as thermal motion consequences in bond length determination by the X-ray diffraction technique may suggest about 0.005 - 0.01Å margin of safety for the most precise X-ray geometric data retrieved from CSD[20].

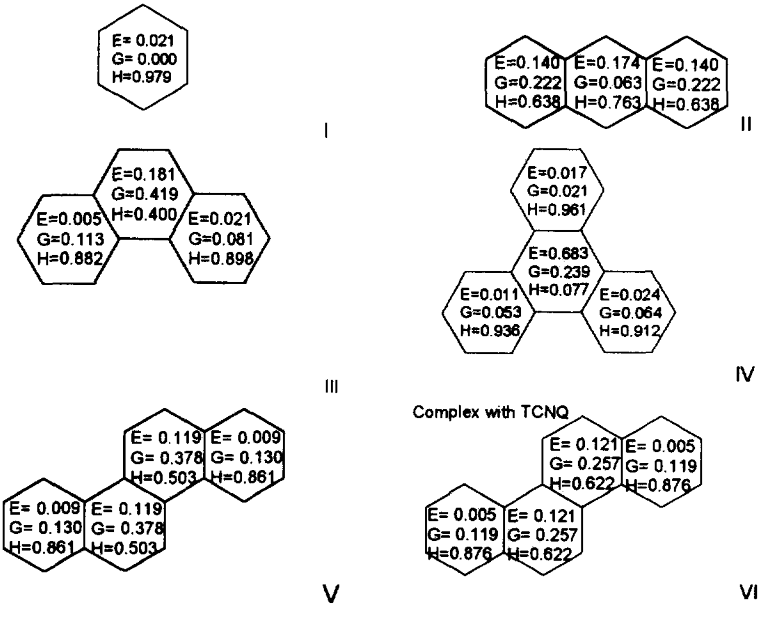
Secondly, any indices of aromaticity have to be defined on the grounds of some physical or chemical model. By virtue of that, the estimation of their aromatic character is approximate in nature. Moreover, they depend more or less arbitrarily on the reference state taken.

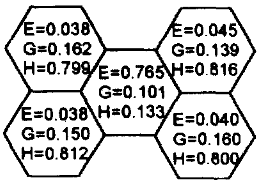
Thirdly, the GEO term is more sensitive to errors in bond length determination than EN or the HOMA, since it is equal to the sum of squares of individual differences between bond lengths and their mean value. Hence while looking at the separation of dearomatization terms in HOMA, it should also be taken into account.

Application of EN and GEO terms to selected classes of compounds.

Chart I presents the values of HOMA, GEO and EN abbreviated in charts by H, G and E, calculated from experimental geometry for a few representative benzenoid hydrocarbons. Even at first glance it is apparent that the lower aromatic character of individual rings may be due to two factors.

Chart I





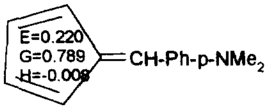
VII

(i) It may be caused by the alternation of bond lengths; then the GEO term is high. The typical cases are the central rings of phenanthrene (III) or of chrysene (V, VI).

(ii)The other possibility is when the rings have partly equalized bond lengths, but they are relatively long. Then the EN term becomes high, and determines the lower aromaticity. Typical examples are the central rings of triphenylene (IV) and perylene (VII). The latter finding neatly quantifies the Clar[29] representation of empty rings.

Another interesting observation is that the central rings in chrysene (V) are less aromatic than if they are in chrysene (VI) involved in the EDA complex with TCNQ[21]. But the change of aromaticity here is due only to the GEO term. In other words, the partial loss of π-electrons due to the intermolecular charge transfer (about 0.35e[21]) causes an increase of aromaticity observed in the decrease of bond alternation. This finding seems to be the first evidence based on experimental data which supports the Shaik and Hiberty idea[30] of the decisive role of the σ-electron skeleton in determining the averaging of the bond lengths in aromatic compounds. Pumping out π-electrons from the chrysene moiety results in an increase of its aromatic character, particularly expressed in the central rings. These changes are due to the decrease of alternation of bond length, shown by a decrease of GEO term, whereas EN terms remains practically unchanged.

Chart II



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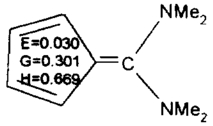

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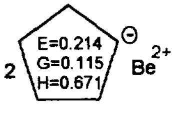
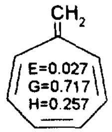
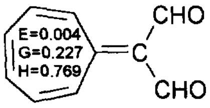


X



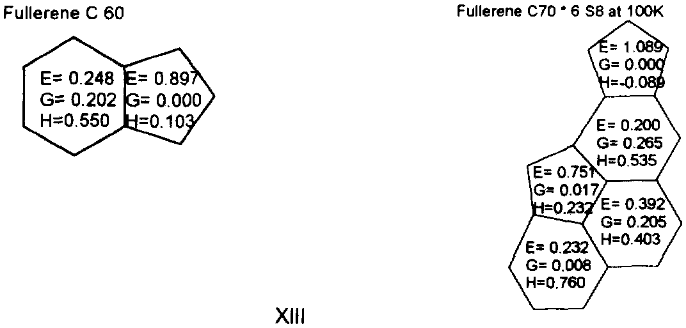
XI



XII

Another interesting group of systems is provided by nonalternant π-electron hydrocarbons and their derivatives. Chart II presents HOMA, EN and GEO values calculated from the experimental geometry of a few typical cases, which serve as a good illustration of the Hückel 4N+2 rule[31]. The fulvene VIII exocyclically substituted by a substituted phenyl group displays antiaromatic property: HOMA values are negative for both independent molecules (in the crystal lattice), but the largest contribution comes from the GEO term, i.e. it is due to the localized double bonds. If the exocyclic substituent becomes strongly electron donating as in IX, the aromatic character increases, but again the change is more exhibited in GEO than in EN terms. In the case of the anion of cyclopentadienyl (X) the aromatic character is even more exaggerated, and the GEO term is close to zero. A similar situation is observed in the case of heptafulvene XII. The unsubstituted molecule is nonaromatic with a low EN term but a strong dearomatization term GEO. If it is substituted by strongly electron-accepting formyl groups at the exocyclic carbon atom, the aromatic character of the ring increases, mostly due to the decrease of the GEO term, i.e. due to the decrease of bond alternation.

Chart III



XIII XIV

Application of this separation to fullerene C_{60}, XIII and the complex $C_{70}.6S_8$, XIV gives insight into the aromatic character of fullerenes which has hitherto been controversial[32-35]. The results are presented in chart III. The most important finding is that 6-membered rings in both XIII and XIV have similar EN values ca 0.2 - 0.4, and the changes in their aromatic character are equally due to the changes in GEO and EN terms. A different situation is encountered for 5-membered rings. They are much less aromatic, but their changes of HOMA values are almost solely due to the energetic term EN. The lower aromaticity of pentagons in comparison with hexagons of fullerenes is in line with magnetic susceptibility measurements and their interpretations[34-36].

The substituent effect on ring geometry, later reflected in changes in GEO and EN terms, is presented for a series of para-substituted anilines. When the HOMA, EN and GEO terms are plotted against the Hammett σ, one obtains the correlation coefficients -0.74, -0.49 and 0.87, respectively. The significance levels for these regressions are 0.42%. 8.9% and 0.01%. Undoubtedly the last mentioned correlation is highly significant, whereas that for EN vs σ is not. It may be concluded that the substituent effect on aromaticity of the ring in p-substituted anilines is mostly due to changes in bond alternation, whereas the energy of the ring depends insignificantly on substitution. The above results are supported by direct correlations of other indices like BAC, BE and I_6 with σ, as shown in Table II.

Table II. Correlation coefficients for scatter plots of aromaticity indices vs. Hammet's σ for 13 para-substituted derivatives of aniline. α stands for significance level of the regression line; α =0.001 means that in one per 10000 cases this linear dependence may occur by chance.

	HOMA	EN	GEO	BAC	BE	I_6
σ	-.7346	-.4894	.8723	-.9079	.4155	-.9243
α	.0042	.0896	.0001	.0000	.1579	.0000

In conclusion, it may be said that molecular geometry by means of bond length may be translated into indices of aromaticity which reflect geometric (GEO term) and energetic (EN term) contributions to the overall aromaticity which is represented by the HOMA index. The above-presented separation may be carried out for any fragment of π-electron system built up of CC bonds.

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