Structural Aspects of Aromaticity

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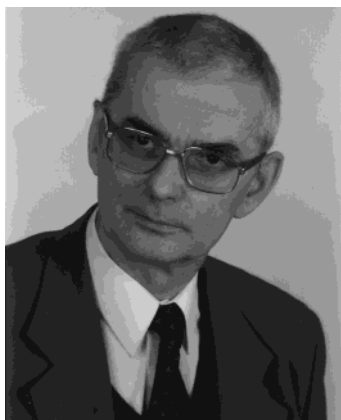
Contents

I. Introduction: Importance of a Notion in the Chemical Vocabulary and an Outline of the Criteria of Aromaticity

Aromaticity (aromatic) is considered as one of the most important concepts in modern organic chemistry.[1] There is no doubt that aromatic/aromaticity are among the terms most frequently used in chemistry, compared also to the terms in biochemistry and medicine as shown in Table 1.[2] The term aromaticity/ aromatic has a long history dating back to its first use in a chemical sense by Kekulé[3,4] and Erlenmeyer[5] in the 1860s.

Similarly, as in those days, in a modern sense the term is related either to some typical properties[6–11] or to a specific structure. In the last few decades it has been almost generally accepted that both terms, aromaticity and aromatic character, are associated with the ground-state properties of cyclic π-electron compounds which (i) are more stable than their chain analogues, (ii) have bond lengths between those typical of the single and double ones, and (iii) have a π-electron ring current that is induced when the system is exposed to external magnetic fields, leading to increased values of the magnetic susceptibility and specific values of ^{1}H NMR chemical shifts. (iv) From the point of view of chemical reactivity, aromatic compounds prefer substitution to addition, and hence, they exhibit a tendency to retain their π-electron structure.[12] However, this criterion is not based on the property of the ground state of a system, and in addition, it cannot be presented in a quantitative way for general use. That is why it is often rejected as the base for aromaticity indices, although some attempts have been made at using reactivity to define the aromatic character quantitatively.[13]

Aromaticity can be defined only by convention,[10] and since there is no unique and generally accepted definition of the term,[11] all the above-mentioned criteria may be used to develop indices of aromaticity. Aromaticity is essentially an "excess property", i.e., a deviation from an additive scheme.[1]

Aromatic properties are mostly due to π-electron systems, which are much more polarizable than the σ-core. However, the π-electron structure (the so-called π-electron delocalization observed as the equal-

Table 1. Frequency of Chemical/Biochemical/Medical Terms in Titles, Abstracts, or in Keywords of Publications Retrieved from ISI (1981−1999)

term(s)	ref
acid/acidity	639 166
AIDS	55 067
anomeric	2 273
aromatic/aromaticity	**58 872**
aqueous	114 340
base/basicity	125 694
benzene	28 327
cancer	270 647
carbohydrate/carbohydrates	44 750
catalyst/catalysis/catalytic	127 655
chiral/chirality	44 607
crystal/crystals	303 850
death	101 836
DNA	331 997
electrophilic	6982
fullerene/fullerenes	8 526
H-bond	504 236
intramolecular	32 246
intermolecular	18 868
life	146 857
molecular	453 162
molecule/molecules	262 550
nucleophilic	13 907
polymer/polymers	161 497
protein/proteins	804 002
solvent	71 519
substituent	15 492
substitution	61 397
water	404 451
virus	207 806

Tadeusz Marek Krygowski was born in Poznań, Poland (1937) and received his M.Sc. degree at the Adam Mickiewicz University (Poznań, 1961) and his Ph.D. (1969) and D.Sc. degrees (habilitation; 1973) both from the Department of Chemistry of Warsaw University. Since 1964 he has been working at this university, from 1983 as a Professor of Chemistry. He has lectured at many universities in many countries, serving as an invited Professor in Canada (Guelph), France (Nantes), Austria (Linz/D), and Israel (BeerSheva). He has been president of the Polish Chemical Society (1994–1997) and is a national representative of the IUPAC Comission on Physical Organic Chemistry. His main research interests are sedimentology (in geology, in the early 1960s), ion-pairing and generally medium effects in organic electrochemistry (in the 1960s and early 1970s), solvent and substituent effects (1970s and 1980s), problems of aromaticity, and structural consequences of inter- and intramolecular interactions (until now). His hobby is national folk music and hiking in not-too-high mountains.

Michał Ksawery Cyrański was born in Warsaw, Poland (1970). In 1994 received his M.Sc. degree and in 1999 his Ph.D. degree, both at the Chemistry Department of Warsaw University. In 1997 he was a holder of the Foundation for Polish Science grant; in 1998 he received the distinction of the Kemula Reward (by the Polish Chemical Society) and in 1999 the Kołos Reward for the best Ph.D. work (by the Department of Chemistry of Warsaw University). In 1998–2000 he was a secretary of the Executive Committee of the Polish Chemical Society (elected). His main scientific interests are the structural chemistry of small organic compounds, crystallochemistry, molecular modeling (ab initio), structural aspects of aromatic character of π-electron systems, and definition of aromaticity. So far, he has published over 30 original papers and 5 reviews and presented 5 lectures and over 30 poster and oral communications. His hobby is classical music, especially by J. S. Bach, and singing in a professional choir.

ization of bond lengths) may be considered as a byproduct of the σ-imposed geometric symmetry and not necessarily as a driving force by itself (as it is in the case of benzene).[14] There are also some arguments against the above hypothesis,[15] and hence, this topic should still be considered as disputable. In conclusion, it might be interpreted that the aromatic properties—even if they are due to the π-electron

structure—may be governed by the σ-electron demand for the equalization of bond lengths.

The term delocalization may be understood in two different ways: (a) as a result of the resonance between various canonical structures,[16] leading to the equalization of bond lengths, and (b) as a result of strong π-electron interaction (the so-called through-resonance effect) between the substituents, leading to a structure of strong quinoid character.[17]

In this review "delocalization" is used in the first sense. The first three above-mentioned properties (i−iii) are easily measurable and concern molecules in their ground electronic state. Hence, they may be readily transformed into the numerical parameters describing the aromatic character (aromaticity indices) of molecules or their fragments. The last property (iv) depends on the energy of the transition state, and hence, its value is difficult to estimate. Consequently, this criterion is usually applied mainly in a qualitative way in the practice of synthetic organic chemistry.

Criterion i leads to energy-based aromaticity indices. The beginning of the energetic criteria is associated with the early discovered low reactivity of benzene (for historical details cf. ref 18); then a numerical estimation of the thermodynamic stability, defined as the resonance energy (RE), came from the work by Pauling and Sherman[19] and Kistiakowsky et al.[20] Originally it was defined for the benzene molecule as a difference in energy between that of benzene and that of the hypothetical Kekulé structure with bond lengths as in an olefine (a model molecule called cyclohetratriene but with the double bond like in ethylene). Those first attempts were

Table 2. Stabilization Energy Values for Benzene

level of theory	scheme of reaction[a]	stabilization energy [kcal/mol]
MP2/RHF/SBK(d)	1	74.7[b]
RHF/SBK(d)	1	61.4[b]
MP2/6-31G//6-31G*	1	67.2[c]
HF/6-31G*	1	58.2[c]
MP4SDTQ/6-31G**/MP2(full)/6-31G**	2	23.9[d]
MP4/6-31G+5D	2	24.3[e]
MP3/6-31G+5D	2	23.4[e]
RMP2/6-311G**	2	28.0[f]
RMP2/6-311G*	2	28.7[f]
RMP2/6-31G*	2	28.9[f]
B3LYP/6-311+G**	2	22.2[a1]
B3LYP/6-311+G**	2[i]	34.1[g]
6-31G** (SCF)	2	24.8[f]
6-31G* (SCF)	2	24.7[f]
MP4SDTQ/6-31G**/MP2(full)/6-31G**	3	20.3[d]
6-31G* (SCF)	3	23.4[h]

[a] Schemes of reactions: (1) $C_6H_6 + 6CH_4 \rightarrow 3CH_3CH_3 + 3CH_2CH_2$; (2) $C_6H_6 + 3 CH_2CH_2 \rightarrow 3 trans\text{-}CH_2CHCHCH_2$; (3) $C_6H_6 + 3CH_2CHCHCH_2 \rightarrow 3CH_2CHCHCHCHCH_2$. [b] Matsunaga, N.; Cundari, T. R.; Schmidt, M. W.; Gordon, M. S. *Theor. Chim. Acta* **1992**, *83*, 57. [c] Bock C. W.; George, P.; Trachtman, M. J. *Phys. Chem.* **1984**, *88*, 1467. [d] Schleyer, P. v. R.; Glukhovtsev, M. N. *Chem. Phys. Lett.* **1992**, *198*, 547. [e] Haddon, R. C.; Raghavachari, K. *J. Am. Chem. Soc.* **1985**, *107*, 289. [f] Disch, R. L.; Schulman, J. M. *Chem. Phys. Lett.* **1988**, *152*, 402. [g] Schleyer, P. v. R.; Jiao, H.; Hommes, N. J. R. v. E.; Malkin, V. G.; Malkina, O. L. *J. Am. Chem. Soc.* **1997**, *119*, 12669. [h] Hess, B. A.; Schaad, L. J. *J. Am. Chem. Soc.* **1983**, *105*, 7500. [i] In scheme 2 *for cis* $CH_2CHCHCH_2$.

based on experimentally determined energies in which the enthalpy of formation[19] or hydrogenation[20] of benzene was compared with the values of formation or hydrogenation of the hypothetical Kekulé structure of benzene. In both cases, the value of RE was almost exactly the same, 36 kcal/mol. Recent developments in computer techniques and theories of quantum chemistry offered an exceptionally good opportunity for employing advanced quantum chemistry methods.[21] The ideas of isodesmic[22] and homodesmotic[23] reactions gave very effective methods for estimating various stabilization energies (SE), including those of aromatic systems, called the aromatic stabilization energy (ASE). This quantity depends dramatically on the kind of reaction, i.e., on the "reference" structure. Table 2 presents the values of ASE calculated by use of various homodesmotic and isodesmic reactions at various levels of theory.[1]

It is immediately clear that any kind of stabilization energy (SE) depends strongly on the scheme of

the (additive) reference system (reaction) and the level of the theory applied.[1]

Another insight into ASE came from the so-called graph-topological approaches. These methods are undoubtedly useful for large systems, but they do not take into account many subtle effects, and may be used for estimation rather than detailed studies.[24] An excellent review on energetic criteria of aromaticity is given in the monograph by Minkin.[11]

Criterion (ii) leads to the geometry-based aromaticity indices which are described in detail in the next section.

Criterion (iii) is associated with a few indices of aromaticity related to the magnetic properties of molecules. The earliest one was the exaltation of the magnetic susceptibility Λ—the quantity which can be estimated both experimentally[25] or theoretically.[26] As in the case of energetic criteria, its reliability depends on the assumed reference structure, since by definition
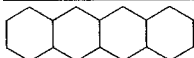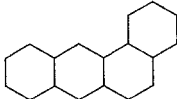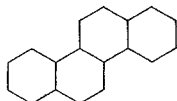
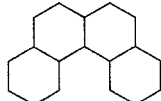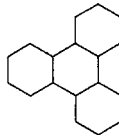$$\Lambda = \chi_m - \chi_a \tag{1}$$

where χ_m and χ_a are the measured susceptibility value and that computed from the additive scheme, respectively.[27] The final results depend on the kind of Pascal's constants employed[28] and, by definition, by the size of the ring in question.[29] In the case of theoretical treatments, reliability depends additionally on the level of theory and the extent of applied electron correlation.[11] At times the anisotropy of the magnetic susceptibility has been used as a descriptor of aromaticity,[30] but this criterion is seldom applied now. Historically, a very important criterion and one frequently used in practical work was the application of an easily measurable proton chemical shift in ^1H NMR spectra—typically aromatic protons have signals around 7 ppm or more whereas olefinic systems are around 5 ppm.[31] Very recently, a new and effective aromaticity index, NICS (abbreviation from nucleus-independent chemical shift), has been introduced by Schleyer et al.[32] It is defined as a negative value of the absolute shielding computed at a ring center or some other interesting point of the system. Rings with negative NICS values qualify as aromatic, and the more negative NICS, the more aromatic are the rings. Consequently, antiaromatic systems have NICS > 0. Table 3 presents the values of NICS and Λ for several typical π-electron systems.[32]

Table 3. Comparison of NICS and Exaltation of the Magnetic Susceptibility Values for Several Typical Compounds

compound	NICS [ppm] HF/6-31+G*	Λ [ppm][a] HF/6-31+G*	compound	NICS [ppm] HF/6-31+G*	Λ [ppm][a] HF/6-31+G*
cyclobutadiene	27.6	18.0	benzene	−9.7	−13.4
pyrrole	−15.1	−12.1	naphthalene	−9.9	−28.2
cyclopentadienyl anion	−14.3	−17.2	phenanthrene (central ring)	−6.5	−47.9
thiophene	−13.6	−10.0	phenanthrene (outer ring)	−10.2	−47.9
furan	−12.3	−9.1	anthracene (central ring)	−13.3	−49.8
phosphole	−5.3	−3.3	anthracene (outer ring)	−8.2	−49.8
cyclopentadiene	−3.2	−2.4	tropylium ion	−7.6	−20.5
alumole	6.5	11.2	azulene, 5-ring	−19.7	−42.9
borole	17.5	12.8	azulene, 7-ring	−7.0	−42.9
pentalene	18.1	30.9	heptalene	22.7	76.6

[a] Total value.

Table 4. Total Energies for Tetracene and Its Four Benzenoid Structural Isomers Computed at the HF/6-31G** Level. Only the σ-electron Structures Are Shown

System	Total energy [Hartree]	Relative Energy [kcal/mol]
	-688.66007	14.0
	-688.67834	2.4
	-688.68239	0.00
	-688.67107	7.10
	-688.68169	0.4

One more criterion may be very useful: the Hückel $(4N + 2)$ rule,[33] which states that cyclic (planar) π-electron systems with $(4N + 2)$ π-electrons are more stable than those containing $4N$ π-electrons. This is a rather qualitative criterion but has inspired numerous attempts at synthesis of the systems which could test its general validity.[34] Those attempts were particularly interesting for the π-electron systems with a small number of π-electrons ($N = 0$ or 1). Many of them were carried out in the 1960s: The triphenyl derivative of cyclopropenyl cation was synthesized and found to be stable,[35] similar to diphenylcyclopropenone[36] in which the electronegative carbonyl group stabilizes the structure. Cyclobutadiene is definitely unstable, but its complexes with $NiCl_2$[37] or $AgNO_3$[38] are known.

The Hückel rule was extended onto polycyclic nonalternant systems:[39] Defining F and S as numbers of five- and seven-membered rings in a fused system, the molecule is more stable when $S = F$ and less stable for other cases. This rule was then demonstrated and proved by use of the topological theories of aromaticity.[40]

Undoubtedly, aromatic character is related to the structure of the molecule (or its particular fragment) in question. However, the term "structure" may be understood in two ways. First, it may be understood as a molecular geometry, when various geometrical parameters are used to characterize the molecules. Second, it may be understood in a topological sense, i.e., taking into account only the bond connectivity of atoms in the molecule (or its fragment). There is no doubt that the topology of the linking atoms exerts a substantial influence on any molecular property. Table 4 presents as an example the total energies[41] computed by ab initio at the HF/6-31G** level of

theory for molecules of five benzenoid hydrocarbons being the structural isomers of $C_{18}H_{12}$—the differences are meaningful and illustrate the role of topology well. The most stable chrysene is by about 14 kcal/mol more stable than the least stable tetracene! This is also well supported by the successes in estimating various stabilization energies by use of the theories based on graph theory and topological approaches.[24]

The interplay between the topology of molecules (or their fragments) and geometry can substantially change their chemical, physicochemical, and biochemical properties, including aromaticity. This kind of problem is one of the main topics which will be presented and discussed in this review. Geometry-based indices of aromaticity are almost the only ones which are readily accessible since the X-ray diffraction technique is an extremely powerful source of information on molecular geometry. Moreover, reliable theoretically obtained molecular geometries may be also used. Unlike energetic and magnetic criteria, the geometric indices can be applied to both the global and local aromatic character of a system.[42] These kind of indices are well suited for studies of the dependence of local or global aromaticity on the environment of the molecule or its fragment.

An additional encouragement of using the geometric criterion stems from the well-known statement by R. Hoffmann:[43] "There is no more basic enterprise in chemistry than the determination of the geometrical structure of a molecule. Such a determination, when it is well done, ends all speculation as to the structure and provides us with the starting point for the understanding of every physical, chemical and biological property of the molecule".

II. Geometry-Based Indices of Aromaticity

Obviously the geometry-based aromaticity indices, if they are to be applied in a reliable way, need a reliable molecular geometry. However, even though different experimental techniques, such as gas-phase electron diffraction (ED), microwave spectroscopy (MW), and X-ray and neutron diffraction, result in the molecular geometry defined in a slightly different way,[44,45] these differences are not significant for the purpose of describing aromaticity by use of the geometry-based indices. The quality of the experimental measurements or of the theoretical calculations may be of key importance only in cases of very subtle analysis of small differences in aromaticity. Therefore, some notes in this field are given below, since some typical experimental errors or trends in computational methods should be taken into account, particularly for studies of subtle changes in aromatic character.

A. Sources and Reliability of the Molecular Geometry

Dynamic development of computer techniques and experimental techniques of the X-ray diffraction measurements have given the most powerful and most frequently used method for determination of the molecular structure. Now more than 200 000 molec-

ular geometries are archived in the CSD (2000),[46] and easy access to molecular geometry is also facilitated by use of routine X-ray diffraction measurements. Some consequences for estimated values of aromaticity indices in dependence on the experimental conditions will be discussed later. Another important and useful source of molecular geometry are the ab initio techniques at a high level of theory.[21] However, in this case geometry depends dramatically on the level of theory and quality of basis set. This shortcoming may be partly diminished if the data optimized at the same level of theory are applied. The above-mentioned techniques provide most of the molecular geometries discussed in recent reports.[8,45,47] Much less useful are other techniques such as gasphase electron diffraction (ED) measurements or microwave (MW) determinations since they are applicable only to rather simple molecules (MW), often highly symmetric (ED).[45] Additionally, due to the thermal condition of the experiment, the molecules studied by electron diffraction are vibrationally excited whereas the microwave measurements are very time-consuming.

B. Outline of the Aromaticity Indices Based on Bond Length Alternation

Both archetypal aromatic systems—benzene, the paradigm of aromaticity in organic chemistry,[48] and graphite[49]—are very stable among π-electron systems and exhibit the same structural feature—just one bond length, the value of which (1.3983[50] and 1.422 Å,[51] respectively) is between the length of the typical single and double CC bonds for sp^2-hybridized carbon atoms (e.g., in 1,3-butadiene they are 1.467 and 1.349 Å,[52] respectively). Consequently, bond length alternation has been taken as a measure of the decrease of aromaticity. Annulenes following the Hückel ($4N + 2$) rule have either no (benzene) or very little alternation, whereas those which are $4N$ annulenes exhibit strong alternation.[11] Pauling and Sherman[19] and later Kistiakowsky et al.[20] considered the Kekulé structure of benzene as a reference for estimating the resonance energy of benzene (see Figure 1). This
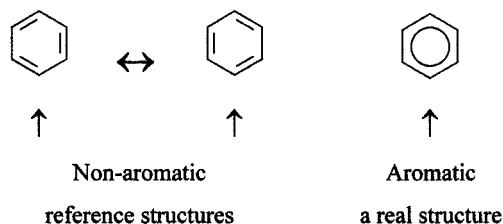

Figure 1. Model structures for the aromatic and nonaromatic forms of benzene

point has been a subject of dispute, since the systems such as benzene, which can be assumed as deformed to a localized structure by a simple "breathing" distortion, do so with little energy loss.[53,54] In any calculation of the aromatic stabilization energy (ASE), the reference structure consists of the idea of single and double bonds (of different mutual delocalization).

Following the idea that an increase in bond alternation is a good feature characterizing a decrease in aromaticity, in 1967 Julg and François[55] formulated

the first aromaticity index, A_J, based entirely on the molecular geometry (bond lengths). This index is a normalized function of the variance of bond lengths; thus, it takes the mean value of the bond lengths as a reference for estimating a decrease in aromaticity due to the bond length alternation (original formulation)[55]

$$A_J = 1 - \frac{225}{n}\sum\left(1 - \frac{R_r}{R}\right)^2 \qquad (2)$$

where n is the number of peripheral bonds with individual bond lengths R_r and R is their mean value. The constant 225 results from the normalization conditions to obtain a zero value for the Kekulé structure of benzene and 1 for any system with all bonds of equal length.

An obvious limitation of the model is the fact that it can be applied only to carbocyclic systems. Sometimes this approach has been used on species with heteroatoms, and then only CC bonds were taken into account.[56,57] This limitation results in exclusion of the contributions which are directly due to the interactions between heteroatoms and carbon−heteroatoms leading to a potential misinterpretation of aromaticity of these systems. Julg's index was applied to numerically describe the aromaticity of some π-electron systems[8,55,57] and served also to test the correctness of other aromaticity indices such as HOMA[58] as well as supporting other already accepted measures of aromaticity such as aromatic stabilization energy, ASE, and magnetic susceptibility exaltation, Λ.[56]

To overcome the problem of heteroatoms, Bird[59] applied the same idea as Julg and François, replacing the bond lengths by Gordy's[60] bond orders

$$I = 100\cdot\left(1 - \frac{V}{V_k}\right) \qquad (3)$$

where

$$V = \frac{100}{\bar{N}}\sqrt{\frac{\sum(N - \bar{N})^2}{n}}$$

and

$$N = \frac{a}{R^2} - b \qquad (4)$$

R is the observed bond length, N is the individual bond order, $\bar{N}$ is the mean bond order, and n stands for the number of bonds. Bird's indices have been defined for five- and six-membered rings, I_5 and I_6, for which the constants a and b of eq 3 are collected in Table 5.[59]

In the case of a fully delocalized heterocycle, V has a value of 1, whereas for a nondelocalized Kekulé structure with alternating single and double bonds, the value depends on the type of ring system. Thus, for a five-membered ring $V_k = 35$ and for a six-membered ring $V_k = 33.3$, and for systems consisting of a five- and six-membered rings fused together, $V_k = 35$.

Table 5. Values of Constants _a_ and _b_ Used in Calculation of Gordy's Bond Orders

type of bond	a	b
C−C	6.80	1.71
C−N	6.48	2.0
C−O	5.75	1.85
C−P	13.54	3.02
C−S	11.9	2.59
N−N	5.28	1.41
N−O	4.98	1.45
C−Se	15.24	3.09
C−Te	21.41	3.81
C−P	13.54	3.02
N−S	10.53	2.50
N−Se	13.31	2.86
O − S	17.05	5.58
S − S	19.30	3.46

Bird's indices I_5 and I_6 describe the percentage of aromaticity and have been applied to a large number of hetero-π-electron systems.[61] It is worth mentioning that a similar idea based on Gordy's bond order was published at the same time by Pozharskii,[62] but then it was not as widely applied as that of Bird. Another aromaticity index based on variation of bond lengths and bond orders was suggested by Nyulaszi et al.[63] and applied to polyphosphaphospholes.[64]

Another approach in which the bond length alternation is taken into account is based on the sum of squared differences of the sequential bond lengths. The index called BAC (bond alternation coefficient) reads[65]

$$\text{BAC} = \sqrt{\sum_n (R_n - R_{n+1})^2} \qquad (5)$$

where the summation runs over a defined cyclic route which is obvious in the case of monocyclic systems but may be a more complex problem for polycyclic systems if the overall aromaticity of a molecule is in question. This index cannot be used for systems containing heteroatoms. It also fails, at least partly, in cases where the localization of double bonds is not exactly alternant but such as that observed (for example) in the quinoidal systems, where two of the six differences of bond length are zero (for C_{2v} symmetry of the ring) or almost zero (in the lower symmetry cases).

C. Harmonic Oscillator Model of Aromaticity (HOMA)

Another approach based on bond lengths is the index HOMA.[58,66] This index differs from all other geometry-based ones by assuming another reference bond length (bond order). Instead of the mean bond length (or bond order) taken as a reference, in the HOMA model a concept of the optimal bond length is proposed

$$\text{HOMA} = 1 - \frac{\alpha}{n}\sum (R_{\text{opt}} - R_i)^2 \qquad (6)$$

where n is the number of bonds taken into the summation and α is an empirical constant chosen to give HOMA = 0 for the hypothetical Kekulé structures of the aromatic systems (with the lengths for CC bonds as in acyclic polyene, 1,3-butadiene[52]) and 1 for the system with all bonds equal to the optimal value R_{opt}. The individual bond lengths are depicted by R_i. The quantity R_{opt} is defined as a length of the CC bond for which the energy (estimated by use of the harmonic potential) of the compression to the length of a double bond and expansion to the length of a single bond in 1,3-butadiene is minimal. The same procedure can be applied to bonds containing heteroatoms, choosing the model single and double bonds as a reference for the above-presented procedure.[66,67]

Within the framework of the HOMA model, some more detailed information may be obtained. The model makes it possible to separate the two terms describing different contributions to a decrease in aromaticity:[67,68] (i) due to the bond elongation (the term called EN) and (ii) due to the bond length alternation (the term called GEO).

$$\text{HOMA} = 1 - \frac{\alpha}{n}\sum (R_{\text{opt}} - R_i)^2 =$$
$$1 - \left[\alpha(R_{\text{opt}} - R_{\text{av}})^2 + \frac{\alpha}{n}\sum (R_{\text{av}} - R_i)^2\right] =$$
$$1 - \text{EN} - \text{GEO} \quad (7)$$

where R_{av} is an averaged bond length, $R_{\text{av}} = 1/n \sum_{i=1}^{n} R_i$ and $\alpha(R_{\text{opt}} - R_{\text{av}})^2$ and $\alpha/n \sum (R_{\text{av}} - R_i)^2$ represent EN and GEO terms, respectively.

In the cases where R_{av} is shorter than R_{opt}, the term EN must be taken with a negative sign, since the shorter the bond, the greater its energy.[48,69] Hence, the proper formula for HOMA is

$$\text{HOMA} = 1 - \text{EN} - \text{GEO} \qquad (8)$$

where

$$\text{EN} = f \cdot \alpha (R_{\text{opt}} - R_{\text{av}})^2 \qquad (9)$$

$$f = \begin{cases} 1 & : R_{\text{av}} > R_{\text{opt}} \\ -1 & : R_{\text{av}} < R_{\text{opt}} \end{cases}$$

$$\text{GEO} = \frac{\alpha}{n}\sum (R_{\text{av}} - R_i)^2 \qquad (10)$$

Note that shorter R_{av} values than R_{opt} are sometimes encountered in molecular geometries obtained by X-ray diffraction technique, where the measurements were carried out at room temperature without corrections for thermal motion.

The recently developed eq 8 cannot be used directly for the heterocyclic systems since the averaging procedure is meaningless for heterogenic data (the same limitation as in the case of Julg's index[55]). Therefore, in the case of hetero-π-electron systems, a further modification of the HOMA index was made.[67] The bonds with heteroatoms are represented by the Pauling bond numbers n[70]

$$R(n) - R(1) = -c \ln(n) \qquad (11)$$

then n is calculated by use of the model bond lengths

Table 6. Structural Parameters of the HOMA Index in Its Separated Form (8) for π-Electron Systems with Heteroatoms. $n_{opt} - a$ Value of the Bond Number for R_{opt}

bond	$R(1)$	$R(2)$	R_{opt}	α^a	c	n_{opt}
CC	1.467	1.349	1.388	257.7	0.1702	1.590
CN	1.465	1.269	1.334	93.52	0.2828	1.589
CO	1.367	1.217	1.265	157.38	0.2164	1.602
CP	1.814	1.640	1.698	118.91	0.2510	1.587
CS	1.807	1.611	1.677	94.09	0.2828	1.584
NN	1.420	1.254	1.309	130.33	0.2395	1.590
NO	1.415	1.164	1.248	57.21	0.3621	1.586

^{a} Applied in the case when no separated version of eq 6 is in use.[66]

for single and double bonds, $R(1)$ and $R(2)$, respectively

$$n = \exp\frac{R(1) - R(n)}{c} \qquad (12)$$

and consequently the bond numbers are converted into the "virtual" CC bonds via the formula

$$r(n) = 1.467 - 0.1702 \ln(n) \qquad (13)$$

Finally, the $r(n)$ values from eq 13 may be applied in eq 8, leading to the HOMA index and its components EN and GEO. Table 6 collects all the constants used for the carbo- and heterocyclic systems.

Even if the choice of the reference bond lengths $R(1)$ and $R(2)$ in Table 6 is somewhat arbitrary and biased by some error (depending on the precision of measurements and the choice of model molecule(s) for a given bond length), a very narrow range of variation of the n_{opt} values, between 1.584 and 1.602 Å, makes the procedure encouraging.

D. Geometry-Based Energetic Indices of Aromaticity

One of the most fundamental and earliest criteria of the aromatic character is the high chemical stability of the systems regarded as aromatic. This feature was later quantified into measures of aromaticity named resonance energies[19] or various types of stabilization energies.[11]

Undoubtedly, the energetic descriptors of molecules are very valuable. In many cases they contribute in a decisive way to the determination and interpretation of the chemical and physicochemical properties of molecules. However, quantum chemical methods are still less useful if one wishes to know the energetic descriptors solely of some part of a molecule. In this matter, approximate models are much more helpful than the methods originated from quantum chemistry, although the latter are more sophisticated and better grounded theoretically.

1. Energetics of π-Electron Hydrocarbons Evaluated from the Exponential Relationship between Bond Length and Bond Energy[71]

It is well-known from elementary textbooks on organic chemistry[48,69] that bond energy depends on

the bond length: the shorter the bond, the more energetic it is. Very recently it has been proposed that bond lengths may be used in a model for calculating the heats of formation of π-electron hydrocarbons.[71] The idea employed the Pauling concept of the bond number, n[70] (see section C)

$$R(n) - R(1) = -c \ln(n) \qquad (11)$$

where $R(1)$ represents the length of a single bond, $R(n)$ the length of the bond with bond number n, and c is an empirical constant. Another empirical relation[72] combines bond energy with the bond number

$$E(n) = E(1) \cdot n^p \qquad (14)$$

where $E(1)$ is the energy of a single CC bond, $E(n)$ is the energy of a bond of bond number equal to n, and p is an empirical constant.

Thus, a simple combination of eqs 11 and 14 leads to the final expression for calculation of the CC bond energy of π-electron hydrocarbons

$$E(n) = E(1) \exp\{\alpha \cdot [R(1) - R(n)]\} \qquad (15)$$

where α is an empirical constant related to p and c.

Applying the reference bond lengths and bond energies for CC single and double bonds, one obtains an expression for the bond energy, $E(R)$, calculated directly from the bond length[71]

$$E(n) = 87.99 \exp\{2.255[1.533 - R(n)]\} \qquad (16)$$

The reliability of eq 16 was tested by comparisons of heats of formation from atoms, ΔH_f, calculated directly from experimental geometries of eight benzenoid hydrocarbons (assuming a constant energy of CH bonds) with the respective data obtained from calorimetric measurements. The mean error of estimation was less than 1%. Moreover, the above-presented model is in almost perfect agreement if the bond lengths and energies based on charge density studies of six benzenoid hydrocarbons with 34 types of CC bonds are compared.[73,74]

The above results provide a good basis for using the model to estimate the energy of molecules and their fragments.[71] The treatment might be particularly useful for large and complex molecular systems, for which it is very difficult to obtain reliable energies. Moreover, it may be used for molecular fragments for which quantum chemical calculations are of limited value due to time-consuming computations.[75]

Equation 16 provides an opportunity to calculate values of the energy content of a molecule or its fragment, referred solely to CC bonds. In this way, the ring energy content, REC, or the molecule energy content, MEC, are defined.

The REC values for the benzene ring in various topological situations in benzenoid hydrocarbons vary dramatically by about 80 kcal/mol (from 650 to 730 kcal/mol).[71] The REC values correlated statistically

Table 7. Empirical Constants for HOSE Model

type of bond	R_0^s [Å]	R_0^d [Å]	$a\ (\times 10^4)$Pa	$b\ (\times 10^4)$Pa	remarks
CC	1.467	1.349	44.39	−26.02	C−C and C=C from ED data for butadiene 1,3.[52]
CN	1.474	1.274	43.18	−25.73	C−N from MW data for methylamine;[a] C=N from ED data for CH²=CH−CH=NH[b]
CO	1.428	1.209	52.35	−32.88	C−O taken from ED data for methanol;[c] C=O from ED data for acroleine[d]
NN	1.420	1.254	78.82	−52.41	N−N and N=N taken from ED of MeC=N−N=NMe[e] and MeN=NMee, respectively.
NO	1.415	1.164	33.197	−19.92	N−O and N=O taken from MW measurements of MeONO.[e]

[a] Pulay, P.; Torok, F. *J. Mol. Struct.* **1975**, *29*, 236. [b] Penn, R. E. *J. Mol. Spectrosc.* **1978**, *69*, 373. [c] Kimma, K.; Kubo, M. *J. Chem. Phys.* **1959**, *30*, 151. [d] Kuchitsu, K.; Fukuyama, T.; Morino, Y. *J. Mol. Struct.* **1969**, *4*, 41. [e] Vilkov, L. V., Mastryukov, V. S., Sadova, N. I. *Determination of the Geometrical Structure of Free Molecules*; Mir Publishers: Moscow, 1983.

well (correlation coefficient $R = 0.911$) with the Randić index,[76] which describes the energetics of the rings in benzenoid hydrocarbons computed by use of topology-based theories. A slightly worse correlation is observed for the scatter plot of REC vs HOMA (correlation coefficient $R = 0.831$).

2. Harmonic Oscillator Stabilization Energy: Estimation of Canonical Structure Weights and Stabilization Energy from Bond Lengths

Another attempt at using bond lengths to estimate the stabilization energy is associated with the empirical model enabling estimation of the canonical structure weights called HOSE (harmonic oscillator stabilization energy) for π-electron molecules or their fragments.[77] HOSE is defined as a negative value of the energy necessary to deform the geometry of the real molecule into the geometry of one of its Kekulé (or resonance) structures with localized single and double bonds of typical lengths as illustrated for benzene by Figure 2.

Figure 2. Real benzene and its Kekulé structure

The energy of deformation has been derived from a simple harmonic oscillator potential

$$E_{def} = -\frac{1}{2} \cdot \left[\sum_{r=1}^{n_1} (R_r' - R_0^s)^2 \cdot k_r' + \sum_{r=1}^{n_2} (R_r'' - R_0^d)^2 \cdot k_r' \right] \quad (17)$$

where R_r' and R_r'' stand for the lengths of π bonds in the real molecule, whereas n_1 and n_2 are the numbers of the corresponding formal single and double bonds in the ith canonical structure, respectively. In the process of deformation, the n_1 bonds corresponding to the single bonds in the ith canonical structure are lengthened whereas the n_2 bonds corresponding to the double bonds in the ith canonical structure are shortened to the reference bond lengths R_0^s and R_0^d, respectively. The force constants (k_r) follow the assumption

$$k_r = a + bR_r \quad (18)$$

Thus, the final formula for HOSE$_i$ for a given ith

Table 8. Empirical Constants to Bird's Modification[81] of the HOSE Model

type of bond	R_0^s [Å]	R_0^d [Å]	F	$a\ (\times 10^4)$Pa	$b\ (\times 10^4)$Pa
CC	1.533	1.337	85.94	44.39	26.02
CN	1.474	1.274	62.19	43.18	25.73
CO	1.449	1.250	62.33	57.10	35.51

Table 9. Resonance Energies (in kcal/mol) from Bird's Modification of the HOSE Model Compared with Experimental Data

compound	RE	RE^{exp}	compound	RE	RE^{exp}
pyridine	44.1	43.3	imidazole	34.9	40.0
pyrimidine	40.1	40.6	indole	73.3	73.8
pyrazine	38.8	40.9	isoindole	62.5	62.4
1,3,5-triazine	44.9	44.9	benzimidazole	75.1	78.9
quinoline	81.6	81.0	carbazole	113.5	111.7
isoquinoline	82.6	81.0	acridine	101.1	108.3
quinozaline	74.8	76.5	phenazine	100.3	110.3
pyrrole	31.8	34.8	phenanthridine	108.5	119.6

canonical structure is

$$HOSE_i = 301.15 \left[\sum_{r=1}^{n_1} (R_r' - R_0^s)^2 \cdot k_r' + \sum_{r=1}^{n_2} (R_r'' - R_0^d)^2 \cdot k_r' \right] \quad (19)$$

giving the HOSE values in kJ/mol. Table 7 collects parameters used in the model.[77,78]

The estimated stabilization energies from the HOSE model are in line with those obtained in other ways. It was shown[77] that HOSE correlates well with the Hess and Schaad resonance energies (correlation coefficient $R = 0.991$ for 22 alternant π-electron hydrocarbons; $R = 0.937$ for 12 nonalternant hydrocarbons).[79,80] In the last case, the Hess and Schaad RE values were given for nonalternant hydrocarbons whereas geometries used to calculate the HOSE values originated from substituted species. Since the substituent effect in nonalternant systems is quite considerable, these aspects will be discussed later.

The idea of using HOSE to estimate stabilization energies of heteroaromatics was modified by Bird.[81] To grasp molecules with a broader range of bond length variation, he used different reference bond lengths. By use of a scaling factor F, he also scaled the resulting stabilization energies to reproduce RE for benzene of 38.4 and 44.9 kcal/mol for 1,3,5-*s*-triazine. The reference data are given in Table 8,

Table 10. Geometry-Based Indices: HOMA, EN, GEO, I_6, I_5, and A_J in Comparison with NICS

system	HOMA	EN	GEO	I_6	A_J	NICS
benzene	0.979	0.021	0.000	100	1.00	−9.7
pentagons in C_{60}	0.103	0.897	0.00	100	1.00	
hexagons in C_{60}	0.550	0.248	0.202	76.2	0.912	
central ring of perylene	0.133	0.765	0.101	83.0	0.957	+6.8
outer rings of perylene[a]	0.806	0.039	0.154	79.2	0.931	−9.4
central ring of triphenylene	0.077	0.683	0.239	73.6	0.898	−3.0
outer rings of triphenylene[a]	0.936	0.017	0.046	89.0	0.979	−10.8
radialene	−2.408	3.408,	0.000	100	1.00	+2.8

[a] Mean values.

whereas a selection of the resulting RE compared with the experimental data are given for some aza-heterocycles in Table 9. In the case of five-membered rings, an energetic increment of 9.36 kcal/mol accounting for the strain was included. This value was estimated from a harmonic potential employing deformations of bond angles.

The results presented above are in quite satisfactory agreement with experimental data and encourage the use of HOSE in order to estimate stabilization energies for systems with no calorimetric data.

The HOSE model was originally successfully used[47,82] to estimate the weights of canonical structures, C_i for the i-structure, by use of a formula

$$C_i = \frac{[HOSE_i]^{-1}}{\sum\limits_{j=1}^{N}[HOSE_j]^{-1}} \quad (20)$$

The weights of canonical structures estimated in this way correlated well with those obtained by other methods. A good correlation between the HOSE weights estimated for 63 ground-state canonical structures of seven benzenoid hydrocarbons and the data calculated by use of the Randić model[83] has been found (the correlation coefficient $R = 0.985$). Similarly, a good but qualitative agreement was found between HOSE-calculated canonical structure weights for nitroaniline[84] and those computed by use of valence bond theory.[85]

The application of the HOSE model permitted estimation of aromaticity in the cases of very small changes in aromatic character of the molecule in question. This can be done by assuming equal or almost equal weights[86] of basic canonical structures as encountered in benzene or pyridine.

E. Discussion of the Pros and Cons of Molecular Geometry-Based Indices

Most of the geometry-based aromaticity indices may be applied both to describe the *local* aromaticity of the particular fragment(s) of molecules or to the *global* description of aromaticity of the whole molecules. This is not the case for most of the energetic or magnetic indices of aromaticity.

All models, based only on the variance of bond lengths or bond orders, suffer from the same disadvantage: they overestimate the aromatic character in cases where a molecule (or its fragment) has all

Table 11. Comparison of I_A with HOMA, EN, and GEO for Quinoline, Isoquinoline, Indole, and Naphthalene

compound	I_A	HOMA	EN	GEO
quinoline	132	0.710	0.004	0.286
isoquinoline	134	0.667	−0.011	0.344
indole	146	0.909	0.006	0.086
naphthalene	142	0.824	0.038	0.138

Table 12. HOMA, EN, and, GEO Values for Naphthalene for Uncorrected (u) and Corrected (c) Libration Geometries Measured by X-ray Diffraction at 92, 143, and 239 K

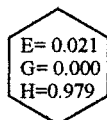| condition of geometry estimations	HOMA	EN	GEO	Δ HOMA (u−c)
92K (u)	0.8070	0.0705	0.1225	0.0155
92K (c)	0.7915	0.0852	0.1233	
143K (u)	0.8132	0.0623	0.1245	0.0239
143K (c)	0.7893	0.0852	0.1255	
239K (u)	0.8220	0.0406	0.1374	0.0460
239K (c)	0.7760	0.0852	0.1388	

bonds of equal (or almost equal) length. Table 10 provides some typical examples.

The central rings in perylene and triphenylene are definitely less aromatic than the outer rings: HOMA and NICS are in line with this, but I_6 indicates almost the same aromaticity for both kinds of rings. The ring in radialene and the five-membered ring in fullerene C_{60} are other excellent examples. In both cases, Julg's index equals 1.00 and Bird's I_5 or I_6 equals 100, whereas NICS[32] and HOMA show their weakly aromatic (fullerene) and strongly antiaromatic (radialene) character. In both cases, the fact that the bond lengths are equal results in very high values of A_J and I_5 (I_6), but this definitely does not mean that the above systems are strongly aromatic. The reasons are obvious: the bond lengths in the radialene ring and the pentagon in fullerene-C_{60} are 1.503[87] and 1.447 Å,[88] respectively, and hence, the terms EN are large and subtracted from 1 give low or even negative values of HOMA.
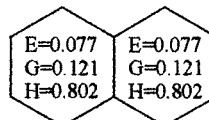
An additional problem arises when the Bird index is considered in its unified form I_A.[89] It is biased by the assumption made in the unifying procedure. The Hückel delocalization energies (DE) of benzene (2.0β), the cyclopentadienyl anion (2.47β), naphthalene (3.68β), and indenyl anion (4.17β), i.e., for the nominal parents of the I_6, I_5, $I_{6,6}$, and $I_{5,6}$, were used in the construction of an unified aromaticity index

$$I_A = I_6 = 1.235I_5 = 1.341I_{6,6} = 2.085I_{5,6} \quad (21)$$
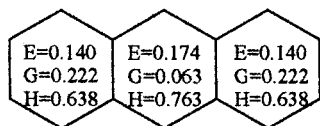
The Hückel DE's are well-known as an unreliable

Chart 1. HOMA, EN, and GEO Terms[a] for 27 Benzenoid Hydrocarbons Estimated from Experimental Geometry[182]
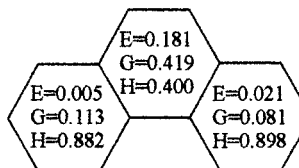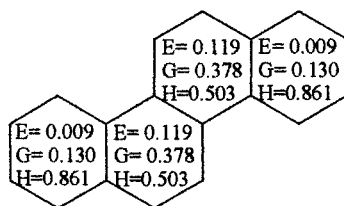
E= 0.021
G= 0.000
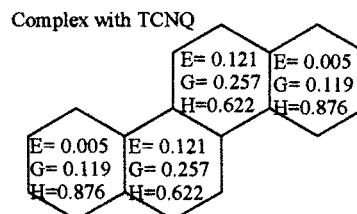H=0.979

I. BENZENE

E=0.077   E=0.077
G=0.121   G=0.121
H=0.802   H=0.802

II NAPHTHALENE

E=0.140   E=0.174   E=0.140
G=0.222   G=0.063   G=0.222
H=0.638   H=0.763   H=0.638

III. ANTHRACENE

E=0.181
G=0.419
H=0.400
E=0.005   E=0.021
G=0.113   G=0.081
H=0.882   H=0.898

IV. PHENANTHRENE

E= 0.119   E= 0.009
G= 0.378   G= 0.130
H=0.503   H=0.861
E= 0.009   E= 0.119
G= 0.130   G= 0.378
H=0.861   H=0.503

V. CHRYSENE

Complex with TCNQ

E= 0.121   E= 0.005
G= 0.257   G= 0.119
H=0.622   H=0.876
E= 0.005   E= 0.121
G= 0.119   G= 0.257
H=0.876   H=0.622

VI. CHRYSENE

E=0.168   E=0.179
G=0.326   G=0.323
H=0.507   H=0.499
E=0.009   E=0.009
G=0.131   G=0.173
H=0.859   H=0.817

VII. BENZOPHENANTHRENE

E=0.017
G=0.021
H=0.961
E=0.683
G=0.239
H=0.077
E=0.011   E=0.024
G=0.053   G=0.064
H=0.936   H=0.912

VIII. TRIPHENYLENE

E=0.146
G=0.192
H=0.661
E=0.044   E=0.032
G=0.040   G=0.053
H=0.917   H=0.915
E=0.157
G=0.136
H=0.707

IX. PYRENE (neutron diffraction)

E=0.197
G=0.230
H=0.572
E=0.058   E=0.051
G=0.062   G=0.063
H=0.880   H=0.886
E=0.204
G=0.223
H=0.572

X. PYRENE (X-ray diffraction)

E=0.038   E=0.045
G=0.162   G=0.139
H=0.799   H=0.816
E=0.765
G=0.101
H=0.133
E=0.038   E=0.040
G=0.150   G=0.160
H=0.812   H=0.800

XI. PERYLENE

E=0.129
G=0.299
H=0.573
E=0.168   E=0.138
G=0.406   G=0.352
H=0.427   H=0.510
E=0.006   E=0.008
G=0.161   G=0.130
H=0.833   H=0.862

XII. PENTAHELICENE

E=0.010
G=0.159
H=0.830

E=0.269
G=0.305
H=0.425

E=0.074
G=0.051
H=0.874

E=0.269
G=0.305
H=0.425

E=0.010
G=0.159
H=0.830
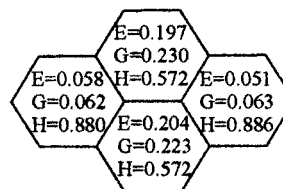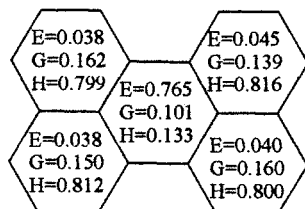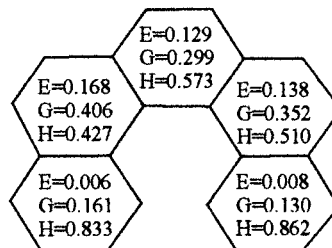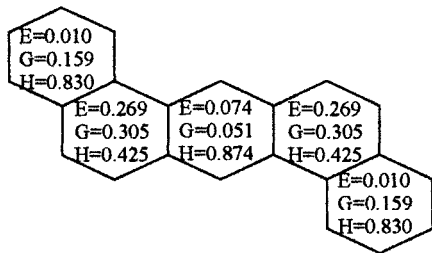
XIII. DIBENZOANTHRACENE

E=0.001
G=0.073
H=0.926

E=0.125
G=0.323
H=0.552

E=0.140
G=0.096
H=0.764

E=0.112
G=0.221
H=0.667

E=0.022
G=0.170
H=0.808

XIV. PICENE

E=0.017
G=0.102
H=0.881

E=0.006
G=0.098
H=0.895

E=0.484
G=0.203
H=0.314

E=0.462
G=0.190
H=0.348

E=0.023
G=0.134
H=0.842

E=0.006
G=0.070
H=0.924
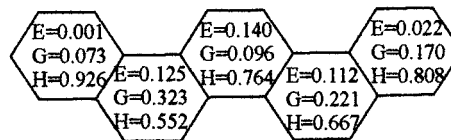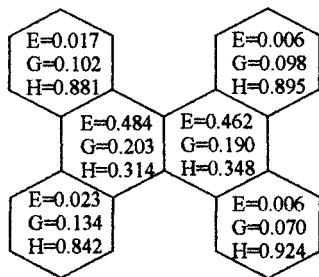
XV. TETRABENZONAPHTALENE

E=0.0.85
G=0.345
H=0.571

E=0.076
G=0.520
H=0.404

E=0.140
G=0.333
H=0.527

E=0.127
G=0.470
H=0.404

E=0.019
G=0.145
H=0.837

E=0.001
G=0.169
H=0.830

XVI. HEXAHELICENE

E=0.140
G=0.092
H=0.767

E=0.130
G=0.133
H=0.737

E=0.140
G=0.179
H=0.681

E=0.117
G=0.310
H=0.573

E=0.000
G=0.220
H=0.780

E=0.179
G=0.250
H=0.571

E=0.008
G=0.128
H=0.868

XVII. HEPTAHELICENE

E=0.019
G=0.078
H=0.903

E=0.027
G=0.053
H=0.921

E=0.179
G=0.357
H=0.465

E=0.362
G=0.225
H=0.413

E=0.416
G=0.243
H=0.341

E=0.155
G=0.250
H=0.595

E=0.019
G=0.086
H=0.895

E=0.017
G=0.146
H=0.837

XVIII. PYRENOPYRENE

E=0.115
G=0.153
H=0.732

E=0.110
G=0.182
H=0.708

E=0.101
G=0.176
H=0.722

E=0.340
G=0.002
H=0.657

E=0.127
G=0.101
H=0.773

E=0.142
G=0.107
H=0.751

E=0.101
G=0.146
H=0.752

XIX. CORONENE

E=0.038
G=0.352
H=0.609

E=0.030
G=0.208
H=0.761

E=0.013
G=0.228
H=0.759

E=0.636
G=0.177
H=0.187

E=0.275
G=0.044
H=0.681

E=0.733
G=0.164
H=0.103

E=0.012
G=0.184
H=0.804

E=0.019
G=0.223
H=0.757

E=0.040
G=0.256
H=0.704

XX. TETRABENZOPENTACENE
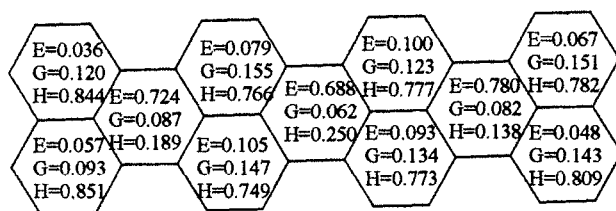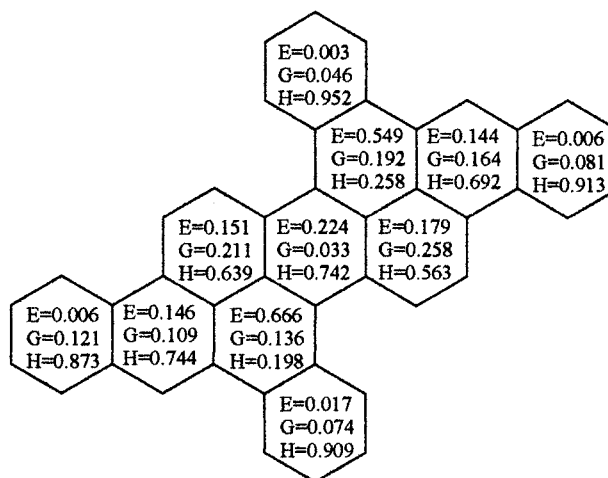
XXI. TETRABENZOPERYLENE

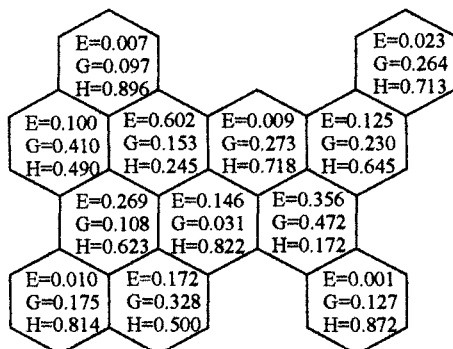XXII. OVALENE

XXIII. ANTHRABENZONAPHTOPENTACENE

XXIV. DIPHENANTHROPICENE

XXV. QUATERRYLENE

XXVI. TRIBENZOPHENANTHRAPENTAPHENE

XXVII. DIBENZONAPHTOPYRANTHRENE

[a] E, G, and H stand for HOMA, EN, and GEO, respectively.

representation of resonance energy.[79,80,90] Consequently, the aromaticity of many bicyclic hetero-π-electron systems described by I_A is overestimated, as shown in Table 11, where a comparison with HOMA, EN, and GEO values is given for a few typical examples.

In the case of HOMA, both terms (EN and GEO) contribute to a decrease in aromaticity. An important question arises, are they independent? From a purely statistical point of view, there is no reason the mean-dependent function (EN) would have to be related to the variance-dependent function (GEO). Indeed, practical correlations lead to the correlation coefficients, R, for the regressions between these two terms equal to 0.39 for 90 rings in TCNQ−EDA complexes and salts, 0.05 for 169 rings in 26 benzenoid hydrocarbons, and 0.09 for 116 rings in p-disubstituted benzene derivatives.[68] From the point of view of the total energy, any geometrical deformation of a molecule (or its fragment) requires extra energy. However, the separation provided by the HOMA model allows one to differentiate between two different mechanisms of the decrease of aromaticity.

The geometry-based aromaticity indices employ bond lengths. The bond lengths determined by X-ray or neutron diffraction may be biased by some systematic error due to data collection, method of refinement, static or dynamic disorder, or thermal motion. This is well illustrated by the differences found for benzene. Uncorrected for thermal motions, the CC bond length for benzene at 270 K is 1.378 Å;[91] with some correction for libration it is 1.392 Å, whereas the low temperature (15 K) neutron diffraction geometry corrected for libration gives 1.3980 Å, compared to 1.3972 Å for the uncorrected structure at this temperature and 1.3940 Å for the uncorrected length at 123 K.[50] These shortcomings of X-ray (and neutron) diffraction data must always be taken into account when these kinds of measurements are the source of molecular geometry. Usually such corrections are much smaller, around 0.005 Å.[45] Table 12 presents the geometry-based indices calculated for uncorrected and corrected geometries of naphthalene[92] measured at three temperatures.

As shown by the above data, the values of the indices do not vary much and 5−10% of the difference in their values may be considered as significant (depending on the precision of measurements). There are two tendencies observed: aromaticity characteristics estimated from the uncorrected room temperature geometry are the highest (for HOMA and GEO terms) and the lowest for EN. When corrections for thermal motions are applied, the aromaticity parameters for all three temperatures are much less dispersed. The parameters for the uncorrected and corrected geometries are closest to each other for the lowest temperature measurements and most dispersed for room temperature. A significant increase of the EN term for the room temperature geometry for the corrected case (0.0852) as compared with the value for the uncorrected geometry (0.0406) is quite understandable: at room temperature, much stronger thermal motion leads to an artificial shortening of most of the bond lengths; hence, corrections which

give more reliable lengths cause elongations and consequently a higher EN term. Interestingly, the EN term for the corrected geometries is constant—the extension of longer bonds is balanced by a shortening of the shorter bonds and the mean bond length does not change. This must correspond to variation in bond alternation as detected by the GEO term. The above effects are not observed for uncorrected geometry—the effect of libration on bond lengths is too high and is reflected in shortening of bond lengths, leading to a decrease in the EN value.

Independent of the precision of the diffraction experiment, if a symmetrical molecule is placed in the crystal lattice in a nonspecific position (i.e., it is not in a position of symmetry required by the space group to which the crystal belongs), then the determined molecular geometry need not follow the symmetry properties observed for the isolated molecule. This is due to an obvious experimental condition which holds that each bond length has its own, in principle independent, error of estimation. Therefore, for instance three outer rings in triphenylene (cf. Chart 1) may have different (geometry-based) indices of aromaticity, despite C_3 symmetry of the isolated molecule.

It should also be noted that there is no objection to use molecular geometries computed by use of reliable quantum chemical theories. In many cases they are a source of important data, particularly for the systems which are unstable or where the effect of some (artificial) deformation is to be studied. However, it should be emphasized here that only the equilibrium geometries should be applied, otherwise some paradoxical situation may follow. For instance, a constrained naphthalene geometry with all CC bonds of the length equal to R_{opt} would have HOMA = 1, but undoubtedly the energy of such a constrained molecule is much higher than that of the equilibrium structure. Nevertheless, in some controlled cases nonequilibrium geometries were used leading to interesting results and conclusions.

It should also be mentioned here that optimized geometries obtained by ab initio calculations depend, usually in a systematic way,[93] on basis sets and on the level of theory—taking into account electron correlation in many cases improves the situation.

III. Applications

As previously underlined, the majority of geometry-based aromaticity indices may be calculated both for the whole molecule and/or locally for given fragment(s). This is clearly an advantage in comparison with other indices, since in this way such indices may be compared with the other ones which are applicable only for the whole molecules (e.g., exaltation of diamagnetic susceptibility, ASE or RE values) or only for the individual rings (NICS, calculated ring current values). Thus, the verification may be carried out from both sides in the same way as the comparisons of the aromatic character expressed by the different indices or properties characteristic of aromaticity. Local aromaticity estimated for a given fragment of a larger molecule provides a possibility

to study the problems of the role of various environmental perturbations which may affect aromaticity. This problem is particularly important in view of the fact that the aromatic compounds (or molecules with aromatic fragments) are active species in all aspects of life processes, both negative (poisons, environmental problems, wastes, etc.) and positive ones, enabling life processes (e.g., bases in DNA, RNA, porphyrines, etc.), and also those externally affecting the quality of life (medicines, foods, etc.).[94]

Another important problem should be emphasized here. Since aromaticity is a phenomenon defined by convention, then we should be well aware of the fact that a geometry-based description of aromaticity may not always be in line with other descriptors,[71,95] although qualitatively it usually remains in agreement with them.[41,42,95]

A general view may be presented in the following way. If benzene is assumed as the ideal model for an aromatic compound, then the following way of introducing various perturbations which convert this model into many other molecules can be considered. Let us start with the simplest case: one can replace CH or CHCH fragments in a molecule of benzene by heteroatom(s). Thus, for instance, replacing CH by N and CHCH by NH leads to pyridine and pyrrole, respectively. These two molecules differ in aromatic character from benzene, and they also differ from each other. However, we can also think about greater modifications leading to some more perturbed systems, proceeding toward azoles and polyaza analogues of benzene. Further modifications of this kind may lead to macrocycles (annulenes, heteroanalogues of annulenes, etc.). Exocyclic substitution is still a new kind of perturbation modifying the properties of the π-electron system. Finally, we can consider a fusion of various systems of this kind, their interactions with other systems (EDA complexes, sandwich complexes, salts, complexes with metals, etc.). Replacing larger parts of benzene by other chemical fragments may lead to almost all imaginable systems which may exhibit aromatic, nonaromatic, or antiaromatic properties. Obviously in any of the above-mentioned cases the aromatic character of new molecules is different from the original systems. Such different perturbation(s) may affect the chemical and physicochemical properties in a nonequivalent way.

A. Topological Problems

The topology of a molecule has a fundamental influence on its physical, chemical, and biological properties. The differences in the properties of the p-, m-, and o-disubstituted benzene derivatives are well illustrated by different substituent constants σ for these three positions.[96] The energies of five structural isomers of $C_{18}H_{12}$ (Table 4) clearly show a similar aspect, namely, a connectivity of atoms (i.e., the topology of a molecule) that determines its chemical and physicochemical properties. The most stable one, chrysene, is by almost 14 kcal/mol more stable than the least stable one, tetracene! These kinds of variation in the properties due to topological reasons no doubt must affect the aromatic character of the systems or of their local fragments. Many

problems of this kind will be presented and discussed in the following paragraphs.

B. Benzenoid Hydrocarbons

For a long time benzenoid hydrocarbons have been used to test various hypotheses dealing with aromaticity, stability, spectral properties, or reactivity.[97,98]

A great progress started with the work by Dewar et al.[99] Using the Pariser−Parr−Pople π-electron method, they found that the bond energies of acyclic polyenes are additive. Hess and Schaad,[79] applying the additivity rule and the simple HMO method, presented a great number of REPE values (abbreviation from Resonance energy per electron) for a collection of benzenoid hydrocarbons[100] (later extended also onto nonalternants[79] and even various hetero-π-electron systems[101]). It became clear that the energy content varies dramatically in each of the groups of systems studied.

Application of HOMA and REC[47,71] allowed researchers to consider this variation by taking into account the local aromaticity (i.e., when the indices are calculated for the individual rings). Chart 1 presents relevant data for the molecules for which there are experimentally-accessible precise[102] geometries.

The data presented above show a huge variation in aromaticity (as expressed in HOMA values) for individual rings depending dramatically on the topological position of the ring. The rings which have the lowest aromatic character are those which, according to the Clar characteristics,[103] belong to the class of "empty" rings, i.e., the ones containing fewer π-electrons than other rings. The central rings in triphenylene or perylene have HOMA values as low as 0.077 and 0.133, respectively. The REC values are also very low: 668.9 and 648.1 kcal/mol, respectively. These values may be compared with that for benzene itself for which REC = 719.7 kcal/mol. An independent index, NICS,[32] also shows very low aromaticity for these two rings: −3.0 and +6.8,[32] respectively.

HOMA with its components EN and GEO well illustrate Clar's classification[103] of the rings in benzenoid hydrocarbons: empty rings (as the central one in triphenylene) are less aromatic due to the elongation of bonds, hence high values of EN and consequently low values of HOMA; rings with localized double bonds (as the central one in phenanthrene) are less aromatic due to an increase of bond alterna-

Table 13. Correlation Coefficients for the Scatter Plots between Aromaticity Indices NICS and HOMA and the Ring Critical Points for σ and π Framework (ρ_c, $\Delta\rho_c$, and the Curvature of ρ, λ) for Benzene, Naphthalene, Anthracene, Pyrene, Tetracene, Tiphenylene, Chrysene, Perylene, and Coronene[a]

index	d^b	$\nabla^2\rho_\pi$	$\lambda_{\sigma,3}$ or $\lambda_{\pi,3}$	ρ_σ or ρ_π
HOMA/π	−0.902	0.897	−0.919	0.919
HOMA/σ	-		−0.919	0.918
NICS/π	0.870	−0.860	0.860	−0.857
NICS/σ	-		0.876	−0.876

^{a} For the π framework, a correlation with the distance of the stationary points from the nodal plane for the π-structure, d, is given also. ^{b} A mean value of d is 0.8 Å.

Table 14. Aromaticity Indices HOMA, EN, GEO, ASE [kcal/mol], and MEC/n [kcal/mol] Calculated as Global Values (for whole molecules) for Linear and Angular Poliacenes (only σ-electron structures shown). Data in Brackets Are Based on Experimental Geometries
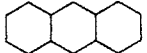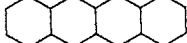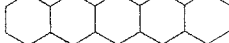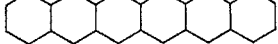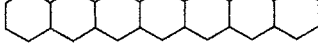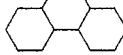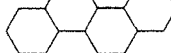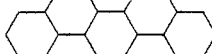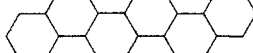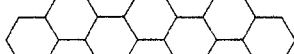
System	HOMA	EN	GEO	E	MEC/n
	0.991	0.009	0.000	3.49	120.4
	(0.974)	(0.026)	(0.000)		(119.3)
	0.811	0.064	0.125	2.61	117.9
	(0.827)	(0.036)	(0.136)		(118.9)
	0.718	0.092	0.190	2.23	117.2
	(0.710)	(0.041)	(0.249)		(118.9)
	0.668	0.115	0.217	2.02	116.6
	0.628	0.133	0.239	1.88	116.2
	0.629	0.137	0.234	1.79	116.1
	0.624	0.145	0.231	1.72	115.9
	0.741	0.091	0.168	2.40	117.2
	(0.750)	(0.005)	(0.245)		(121.1)
	0.710	0.112	0.178	2.28	116.6
	(0.658)	(0.036)	(0.306)		(119.2)
	0.685	0.132	0.183	2.21	116.2
	(0.720)	(0.065)	(0.215)		(118.0)
	0.677	0.135	0.188	2.16	116.1
	0.668	0.189	0.142	2.12	115.9

Table 15. Correlation Coefficients of Regressions between HOMA, EN, GEO, ASE/n (E), and MEC/n Calculated for Whole Molecules (12 systems)

	HOMA	EN	GEO	E
EN	−0.892			
GEO	−0.948	0.701		
E	0.989	−0.847	−0.962	
MEC/n	0.976	−0.939	−0.877	0.945

Figure 3. Linear dependence of HOMA index on the Cohen Benson ASE/n (E). Correlation coefficient $R = 0.989$. (Reprinted with permission from ref 104b. Copyright 2000 Elsevier Science.)

tion, hence higher values of GEO and consequently again lower values of HOMA.

A comparison of HOMA with other geometry-based aromaticity indices has shown[71] that the indices were not fully equivalent (even estimated for the same geometry). Since the indices BAC and particularly I_6 are "purely" bond alternation dependent, whereas HOMA depends also on the bond elongation, these two kinds of indices clearly do not correlate with each other (I_6 and BAC vs HOMA give correlation coefficients of only 0.56 and 0.67, respectively) whereas

BAC vs I_6 correlates well, −0.94, due to almost the same mechanistic background. Since both kinds of deformations, bond alternation and bond elongation, cost energy (HOMA contains components from both), the correlation between REC and HOMA exists but is rather weak, whereas correlations of REC vs

Table 16. Mean Values of HOMA, EN, and GEO Terms for the Ring of Polysubstituted Benzene Derivatives Compared with Topologically Equivalent Rings in Benzenoid Hydrocarbons
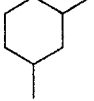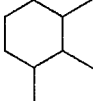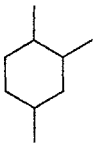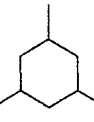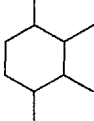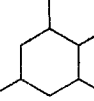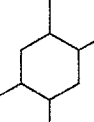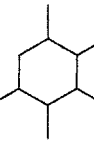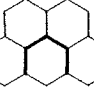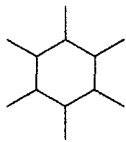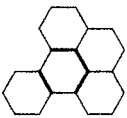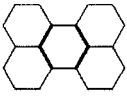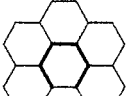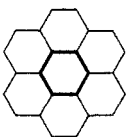
Type of ring	Class	HOMA	EN	GEO	Type of ring	Class	HOMA	EN	GEO
	1	0.994	-0.005	0.013					
	2	0.973	0.000	0.027		I	0.862	0.009	0.128
	3	0.993	-0.004	0.013					
	4	0.990	-0.003	0.014					
	5	0.866	0.006	0.115		II	0.821	0.036	0.141
	6	0.975	0.000	0.025					
	7	0.994	0.000	0.006					
	8	0.937	0.006	0.057		III	0.503	0.134	0.329
						V	0.639	0.155	0.192
	9	0.964	0.001	0.034					
	10	0.967	0.001	0.029		IV	0.818	0.124	0.057
	11	0.946	0.010	0.039		VI	0.645	0.146	0.164
						VIII	0.794	0.157	0.053

Table 16 (Continued)

Type of ring	Class	HOMA	EN	GEO	Type of ring	Class	HOMA	EN	GEO
	12	0.967	0.008	0.022		VII	0.314	0.484	0.202
						IX	0.271	0.549	0.192
						X	0.219	0.662	0.072
						XI	0.459	0.436	0.084
						XII	0.728	0.212	0.060

I_6 and BAC are practically nil (0.09 and -0.25, respectively).

Another representative sample of benzenoids studied by use of HF/6-31G** calculations has shown[41] that for the optimized geometry of 10 molecules (18 individual, symmetrically independent rings), the HOMA index correlates well with NICS leading to a regression line with a correlation coefficient $R = -0.896$. This is a quite reasonable correlation if we take into account the completely different physical basis for their definition. For the same sample the HOMA values exhibited quite good correlations with topological charge density parameters[75] such as ρ_c (charge density at the unique ring critical points), $\Delta \nabla^2 \rho_c$, and the curvature λ of ρ. Table 13 presents correlation coefficients between these parameters for σ and π electron structures.

Since the topological charge density parameters are excellent descriptors of the electronic structure, it may be concluded that HOMA and NICS alike are associated with this characteristic of π and σ electron systems, at least as far as benzenoid hydrocarbons are concerned. This result supports a view that there is an interplay between the π and σ electron structure. The charge density analysis shows that both structures contribute to the overall effect observed as aromaticity via indices as HOMA or NICS.

The molecular geometry of the whole molecule of seven linear and five angular polyacenes was used to calculate the MEC values, which are compared with the aromatic stabilization energy (ASE) calculated from the Benson and Cohen group additivity values (GAV) within the thermochemical procedure.[104] Table 14 presents normalized ASE values (divided per one π-electron) depicted as E, MEC/n (n
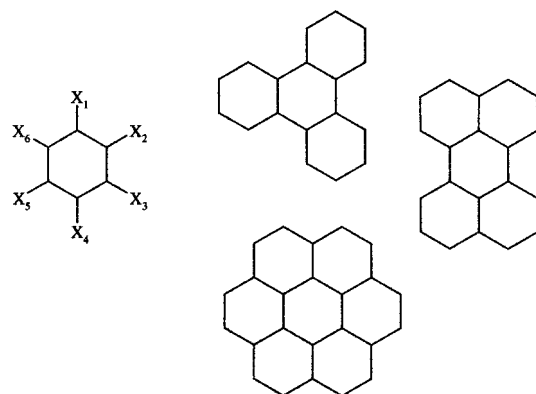
Figure 4. Analogy in the topology of the ring in hexa-substituted benzene derivatives and of the central ring in triphenylene, perylene, and coronene. (Only the σ-electron structures are shown.)

number of CC bonds), together with HOMA, EN, and GEO terms for whole molecules.

When the whole-molecule aromaticity indices are concerned, HOMA, EN, GEO, MEC/n, and Cohen–Benson E, it is clear that the aromaticity of these systems varies monotonically with the increase of the number of rings. This tendency is observed in both series, however with different sensitivity, which is in line with an observation of the changes of the position of the p-band in UV spectra in arenes. The aromaticity of the linear polyacenes is smaller than that of the corresponding angular systems, and moreover, it decreases more rapidly with an increase in the size of the system. This tendency is clearly shown by E and HOMA and is roughly in line with a decrease in the chemical stability of polyacenes. Evidently the above observation is followed by the

mutual linear relationships between the above-mentioned indices, as shown by the statistical data of Table 15.

The best correlation was found between HOMA and ASE/n (E). This dependence is shown in Figure 3.

The benzene ring has often been used as a probe of aromaticity in topologically analogous situations: benzenoid hydrocarbons vs polysubstituted benzene derivatives. Polysubstituted benzene derivatives (PBD) may lead in the ring to a topologically equivalent situation as in benzenoid hydrocarbons: the ring in naphthalene is topologically equivalent to o-disubstituted benzene derivatives, whereas the central ring in triphenylene (and, e.g., in coronene too) is equivalent to the hexasubstituted benzene derivatives. Figure 4 illustrates this point:

A question arises, how does the ring respond in these two situations in terms of aromaticity? The problem was analyzed in detail for X-ray measured molecular geometries of polysubstituted benzenes and benzenoid hydrocarbons.[105,182] According to the positions of substitution in benzene, 12 classes were defined and used for both groups of systems, as shown in the schemes in Table 16.

The range of variation of the mean HOMA values for polysubstituted benzene derivatives is much narrower (0.866−0.994) than that for the rings in benzenoid hydrocarbons (0.219−0.862). The only clear but rough conclusion is that the *ortho* substitution leads to a greater decrease of aromaticity than any other type: the mean HOMA value for eight cases where ortho-substitution is present is 0.949 as compared with 0.993 for the four other cases where ortho-substitution is absent. When the aromaticities of the rings in the benzenoid hydrocarbons are compared with substituted analogues, in all cases they are lower than those in the substituted systems. In the latter case, alternation of bond length (the GEO term) is always decisive concerning the decrease of aromaticity, whereas in the case of benzenoid hydrocarbons this is true only of the analogues of di- and trisubstituted benzene. In other cases an increase in the mean elongation of the CC bonds (an increase in the EN term) becomes decisive, leading to a dramatically low aromaticity of the central rings in groups VII, IX, X, and even XI. The following general conclusions may be drawn. (i) The terminal rings (group I) are more aromatic than in all other cases. The decrease in their aromaticity is mostly due to the GEO term (bond alternation). The same is true of the rings of group II. (ii) Angularly fused rings (central rings in phenanthrene, group III, and pyrene-type, group V) have lower aromatic character due to an increase in the GEO term (bond alternation). (iii) In the case of more than three rings fused to the ring in question (except group VI), the decrease in aromaticity results from bond elongation (the EN term) and these rings are usually of low aromaticity. (iv) Other groups, except III, are represented by small samples (groups IV, VI, VII), hence any conclusions are limited, but the decrease in their aromatic character is due to both terms.

One important conclusion may be drawn from the above results. If we consider the links between the ring in question and the closest atoms in the molecular environments, we can distinguish two situations. In the case of benzenoid hydrocarbons, all carbon atoms are bound either to other carbon atoms or to hydrogen atoms, both characterized by very similar electronegativity (Pauling's electronegativity values for C and H are 2.5 and 2.1, respectively;[106] Sanderson's values are 2.746 and 2.592, respectively[107]). In the case of the substituted benzene derivatives, the situation is quite different. The substituents are of different kinds, and electronegativities of the atom(s) linked to the ring may vary significantly. Thus, considerable inductive or resonance interactions may operate in, or through, the ring. The data in Table 16 lead to an important conclusion: perturbations due to substituent effects acting on the ring in question cause a much smaller decrease in aromaticity than the topological ones. This finding may well be a reason for successful applications of theoretical methods based on topology and graph theory[24] in describing some properties of the π-electron systems.

It is interesting to note that perturbation of the π-electron system in the benzene ring due to protonation changes the aromaticity of the sp^2 fragment only to a very small extent. MP2/4-31G* geometry optimization[108] gives HOMA = 0.9255, which may be compared with HOMA = 0.9958 for benzene optimized at the same level of theory. For the whole ring (including the saturated carbon atom), HOMA = 0.493. In that case the decrease in aromaticity stems from two $C(sp^2)-C(sp^3)$ bonds. These results seem to support a conclusion that breaking the π-electron delocalization in aromatic systems by an sp^3 carbon atom does not lead to any dramatic change in the aromaticity of the remaining part of the molecule.

C. Aza-Analogues of Benzenoid Hydrocarbons

Aza-analogues of the benzenoid hydrocarbons are well-known to be similar in aromaticity to the parent compounds. Application of the geometry-based indices of aromaticity makes it possible to analyze the problem of changes of aromaticity due to the replacement of the carbon atom(s) by aza-nitrogen atom(s), both in a local and global sense.[109] There are at least two aspects of the problem: (a) the direct effect of replacement and (b) the consequences in further fragments of the π-electron system. Chart 2 presents the HOMA, EN, and GEO values for aza-analogues of the benzenoid hydrocarbons.

Following are some observations based on the data in Chart 2, typified by the HOMA values for naphthalene and its aza-derivatives. (i) All aza-analogues have higher HOMA than naphthalene. (ii) In all cases, the decisive factor determining aromaticity is the GEO term, which is always much larger than EN. (iii) The EN term is in all cases larger for naphthalene than for any aza-analogue.

Taking into account all aza-analogues of benzenoid hydrocarbons recently studied,[109] it is apparent that in most cases replacement of the carbon atom by the nitrogen atom increases aromaticity, as compared with the parent hydrocarbon. Moreover, low-aromatic

Chart 2. Local Values of HOMA, EN, and GEO Terms[a] for Aza-Analogues of Benzenoid Hydrocarbons[109]

[a] E, G, and H Stand for EN, GEO, and HOMA, respectively. (Reprinted with permission from ref 109. Copyright 1996 Elsevier Science.)
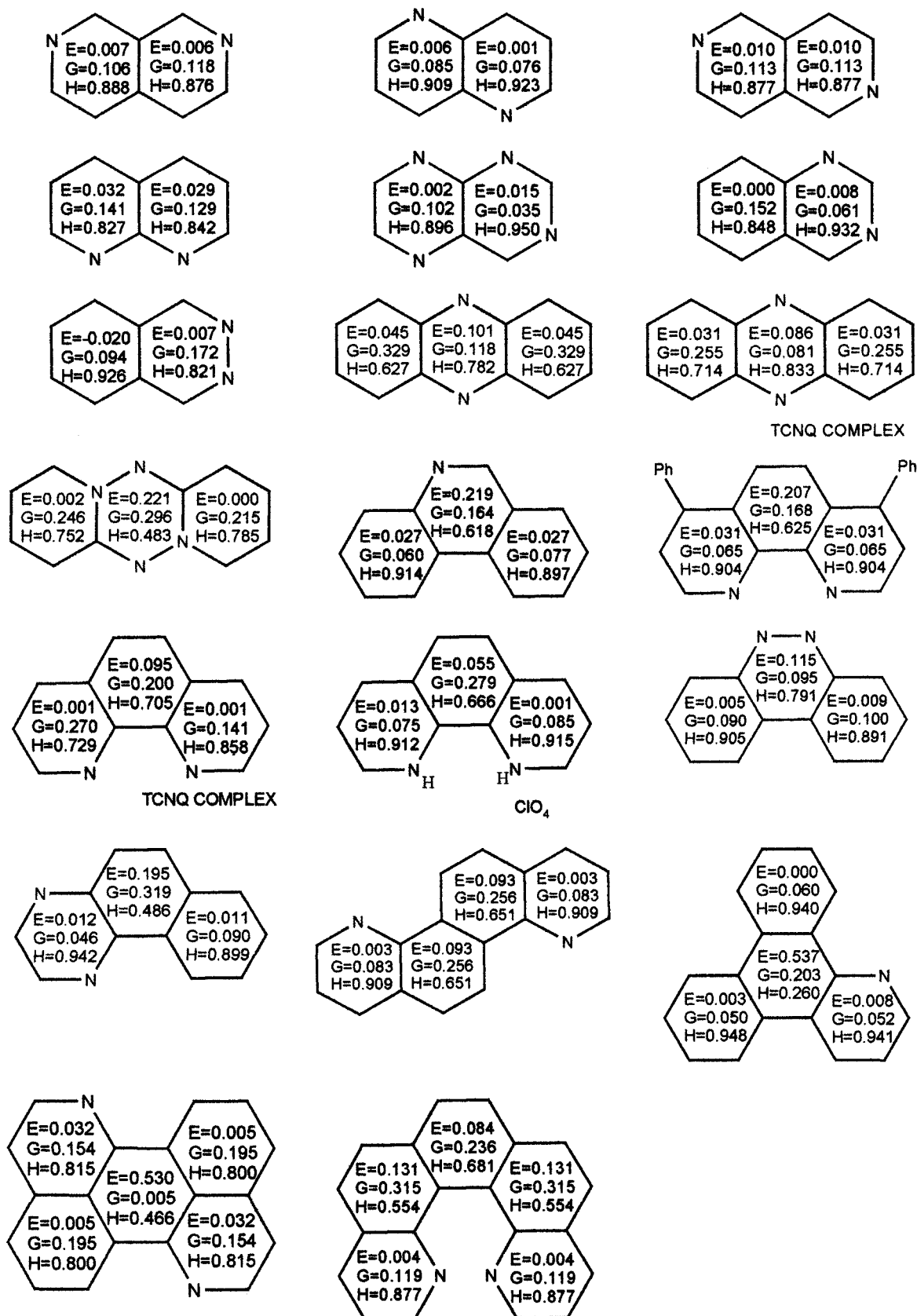
rings in the molecule are strongly affected by the substitution of nitrogen atoms into the ring, and the effect is still significant if the nitrogen atom is closest (i.e., directly linked) to the given ring.

A good illustration of the above statements is given by aza-analogues of phenanthrene. The HOMA value for the central ring in phenanthrene is 0.400. However, if the carbon atoms in position 9 and then in

Table 17. Aromaticity Parameters: HOMA (H), EN (E), GEO (G), and I_6 for Aza-Analogues of Benzene[67]

Compound	HOMA	I_6	Compound	HOMA	I_6
(pyridine)	H= 0.998, E= -0.009, G= 0.011	81.2	(triazine)	H= 0.982, E= 0.005, G= 0.012	78.8
(N⁺ BF₄⁻ C(Ph)CH₂)	H= 0.973, E= -0.025, G= 0.052	72.3	(Ph-Cl pyrimidine)	H= 0.791, E= 0.022, G= 0.187	69.8
(pyridazine)	H= 0.955, E= 0.001, G= 0.044	78.2	(pyrazine)	H= 1.029, E= -0.029, G= 0.000	100
(pyrimidine)	H= 0.999, E= 0.000, G= 0.001	84.0	(Ph(Ph)₂CH₃ triazine)	H= 0.962, E= 0.008, G= 0.030	84.4
(triazine)	H= 1.000, E= 0.000, G= 0.000	86.2			

Table 18. Aromaticity Parameters: HOMA, EN, GEO, and I_6 for Hetero-Analogues of Benzene

Compound	HOMA	I_6	Compound	HOMA	I_6
(Ph-COOH, Ph O⁺ Ph, ClO₄⁻ pyrylium)	H= 0.582, E= 0.101, G= 0.327	53.4	(CH₃ P phosphinine)	H= 0.924, E= 0.037, G= 0.039	73.1
(Ph S⁺ Ph thiopyrylium)	H= 0.829, E= 0.037, G= 0.134	63.7	(N pyridine)	H= 0.998, E= -0.009, G= 0.011	81.2

positions 9 and 10 are replaced by the nitrogen atoms, then HOMA values rise up to 0.618 and 0.791, respectively. When the carbon atoms in positions 4 and 5 are replaced, a substantial increase in the aromaticity of the central ring is observed. HOMA rises from 0.400 to 0.625. The increase in aromaticity is also observed in a CT complex with TCNQ with HOMA = 0.705 or in the protonated species where HOMA = 0.666. A similar result is shown for chrysene: HOMA for the central ring is 0.503, whereas in the aza-analogue with nitrogen atoms in positions 4 and 10 it rises dramatically up to 0.651. Also, in perylene the central ring becomes much more aromatic when the carbon atoms in positions 1 and 7 are replaced by nitrogen; HOMA increases from 0.133 to 0.466.
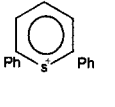
However, another question arises, namely, whether the replacement of CH by N always leads to an increase in the aromaticity of the system. Recent studies on acridine derivatives showed[110] a slightly increased aromaticity of the central ring (HOMA = 0.810 as compared with 0.763 in anthracene) in acridine and a slightly decreased aromatic character of carbocylic fragments.

Apart from the above problems, there are many aza-analogues of benzene itself. Table 17 presents aromaticity characteristics for them.[67]

The aromaticity of aza-analogues of benzene is high and not differentiated. This conclusion is qualitatively in line with resonance energies computed for reactions with proton transfer.[11,111]

As observed for aza-analogues of the benzenoid hydrocarbons, when NN bonds are present in the ring, its aromaticity is usually lowered. In contras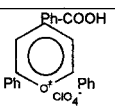t, the "meta"- or "para"-type replacements lead to higher aromaticity. *s*-Pyrazine is even more aromatic than benzene itself, but the difference does not seem to be significant. This observation is not too distant from chemical experience and intuition.

D. Other Heterocyclic Analogues of Benzenoid Hydrocarbons.

There are many possibilities of replacing the CH group in benzenoid hydrocarbons by heteroatoms, and a few good examples are presented in Table 18, which contains a few analogues of benzene.

Compared with pyridine, which shows high aromaticity, the changes observed in the aromatic character of phosphorus, sulfur, and oxygen analogues are in line with expectation.[11]

The pyrylium ring in a series of 2,6-diphenyl-4-(4-X-substituted-phenyl)pyrylium perchlorates (Figure 5) was one of the systems studied in more detail.[112]
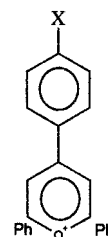
Figure 5. 2,6-Diphenyl-4-(4-X-substituted-phenyl)pyrylium perchlorates.

The aromatic character of the pyrylium ring was studied in dependence of the substituent. The heterocyclic ring is strongly electron attracting; hence, the donating substituents should affect its aromaticity.

For four substituted species with X = NMe₂, H, COOH, and NO₂, the HOMA values for the pyrylium ring depended significantly on the σ^+ substituent constants. In a similar way, the variation of the CC bond lengths (for the link between the phenyl and pyrylium rings) and of the dihedral angles between the rings were observed. The pyrylium ring is a strongly electron-accepting moiety; hence, the induction of the quinoid structure caused by the electron-donating substituents (NMe₂) results in a substantial decrease of the aromatic character of the pyrylium ring (HOMA values ranging between 0.237 for NMe₂ and 0.605 for NO₂[86]). The difference in the HOMA values ($\Delta = 0.368$) for NMe₂- and NO₂-substituted derivatives shows that the aromatic character of the ring is very sensitive to the substituent effect. For comparison, an analogous difference for the pyridinium ring in 1-X-4-(4-phenyl)-2,6-diphenylpyridinium perchlorates is equal only to 0.15.[113] In both cases the substituent effect is transmitted through the benzene ring. In the case of *p*-substituted nitro-

Chart 3. Aromaticity of Oxa-Analogues of Benzenoid Hydrocarbons

E=0.037
G=0.023
H=0.939

E=0.202
G=0.240
H=0.558

E=0.044
G=0.131
H=0.825

E=0.136
G=0.099
H=0.765

E=0.136
G=0.193
H=0.671

E=0.280
G=0.299
H=0.420

E=0.043
G=0.039
H=0.918

E=0.522
G=0.515
H=-0.037

E=0.026
G=0.090
H=0.885

E=0.058
G=0.086
H=0.856

E=0.298
G=0.885
H=-0.183

E=0.522
G=0.512
H=-0.034

E=0.058
G=0.087
H=0.855

E=0.058
G=0.084
H=0.857

E=0.016
G=0.010
H=0.973

E=0.837
G=0.224
H=-0.062

E=0.058
G=0.085
H=0.857

E=0.058
G=0.080
H=0.863

E=0.522
G=0.513
H=-0.034

E=0.037
G=0.023
H=0.939

E=0.522
G=0.512
H=-0.034

E=0.058
G=0.087
H=0.855

E=0.058
G=0.084
H=0.857

E=0.037
G=0.023
H=0.939

benzene, where the substituent effect acts directly on the ring, the difference is also very small, $\Delta = 0.11$. It is apparent that HOMA values for the pyrylium ring are much more dependent on the same changes of substituent than the highly aromatic pyridinium or benzene rings.

Replacement of the CH group in benzenoid hydrocarbons by nitrogen has been discussed in a previous section. An analogous study of replacement by oxygen has shown that the rings which contain the oxygen atom definitely become less aromatic (or even anti-aromatic) whereas the vicinal rings gain higher aromaticity.[114] Chart 3 provides a good illustration of these trends.

E. Nonbenzenoid Alternant Hydrocarbons and Their Heteroanalogues

While benzenoid hydrocarbons are the subject of long-standing studies (many of their derivatives are applied in all fields of human activities), nonbenzenoid hydrocarbons are a subject of rather moderate interest. Undoubtedly, some of these systems have substantial applications and create a significant theoretical interest. Hence, many of them have been subject to thorough structural studies. Their molecular geometries may serve as a good source of information to study their aromaticity.

The first group of alternant nonbenzenoid hydrocarbons are annulenes. Except for benzene and cyclobutadiene, all others are nonplanar. Table 19 presents the aromaticity indices for some annulenes and their derivatives calculated either from the experimental or ab initio calculated geometries.

Table 19. HOMA, EN, and GEO Terms of Annulenes and Some of Their Derivatives

system	HOMA	EN	GEO	comments
annulene [4]	−2.570	1.317	2.253	ref 11
annulene [6]	0.996	0.004	0.000	X-ray[a]
	0.974	0.026	0.000	ND[50]
annulene [8]	−0.295	0.103	1.192	ED[b]
	−0.383	0.028	1.355	X-ray[c]
annulene [10]	0.930	0.004	0.066	D_{5h}[d,e]
	0.783	0.217	0.000	D_{10h}[d,e]
annulene [14]	0.942	−0.004	0.064	X-ray[f]
Annulene [18]	0.899	0.010	0.091	X-ray[g]

[a] Cox, E. G.; Cruickshank, D. W. J.; Smith, J. A. S. *Nature* **1955**, *175*, 766. [b] Traettenberg, M. *Acta Chem. Scand.* **1966**, *20*, 1724. [c] Cobbledick, R. E.; Einstein, F. W. B. *Acta Crystallogr.* **1977**, *B33*, 2339. [d] At MP2/6-31G//HF/6-31G: Haddon, R. C.; Raghavachari, *J. Am. Chem. Soc.* **1982**, *104*, 3516. [e] At MP2/6-31G//HF/6-31G: Haddon, R. C.; Raghavachari, *J. Am. Chem. Soc.* **1985**, *107*, 289. [f] Vogel, E.; Engels, H.-W.; Huber, W.; Lex, J.; Mullen, K. *J. Am. Chem. Soc.* **1982**, *104*, 3729. [g] Bergman, J.; Hirshfeld, F. L.; Rabinovich, D.; Schmidt, G. M. J. *Acta Crystallogr.* **1965**, *19*, 227.

1

2

Figure 6. Syn (**1**) and anti (**2**) conformers of bridged [14]annulene. (Reprinted with permission from ref 116. Copyright 1986 Wiley-VCH Verlag GmbH.)

All $(4N + 2)$ annulenes clearly exhibit aromatic character, whereas $4N$ annulenes are definitely antiaromatic, with negative HOMA.

A slightly different class of molecules is bridged annulenes, which are often close to the benzenoid

Table 20. HOMA, EN, and GEO Values for Bridged [14]Annulene Derivatives Estimated from Perimeter Bond Lengths

compound	HOMA	EN	GEO
anti-1,6:7,12-bismethano[14]annulene[116]	0.241	0.034	0.215
syn-1,6:7,12-bismethano[14]annulene[115]	0.749	0.036	0.215
syn-1,6;8,13-bisoxido[14]annulene[a]	0.992	0.000	0.008
1,6:8,13-propanediylidene[14]annulene[a]	0.900	0.052	0.048
syn-1,6:8,13-biscarbonyl[14] annulene[b]	0.939	0.017	0.044
7-methoxycarbonyl-anti-1,6:8,13-dimethano[14]annulene[c]	0.021	0.066	0.913

[a] Vogel, E. *Pure Appl. Chem.* **1971**, 355. [b] Destro, R.; Simonetta, M. *Acta Cryst.* **1977**, *B33*, 3219. [c] Gramaccioli, C. M.; Mimun, A. S.; Mugnoli, A.; Simonetta, M. *J. Am. Chem. Soc.* **1973**, *95*, 3149.

hydrocarbons. A very interesting situation is observed for bridged [14]annulenes with a phenanthrene perimeter.

Table 20 presents HOMA, EN, and GEO values for these two kind of conformers of bridged [14]annulene.

The syn[115] and anti[116] conformers of bridged annulene[14] derivatives differ much in aromaticity. Application of HOMA and its components to the perimeter bond lengths allowed us to look at it in a more subtle way. Low aromaticity for the anti conformers of the bridged [14]annulenes is documented by the low values of HOMA (<0.24) with a dominant contribution to the decrease in aromaticity from the geometric factor (large GEO terms). The situation is quite different for the syn conformers for which HOMA values for the perimeter bond lengths are always high, thus pointing to their aromatic character. The above values may be compared with the value obtained for [14]annulene with HOMA = 0.942 and phenanthrene (HOMA = 0.750.)

F. Nonalternant π-Electron Hydrocarbons

There are four classical nonalternant π-electron hydrocarbons which have long been the subject of many studies of their aromatic character: fulvene, heptafulvene, azulene, and pentalene.[117] Fulvene, heptafulvene, and pentalene have been considered for a long time as nonaromatic (or even antiaromatic), both for their chemical instability and the negative REPE values.[79] More recent studies strongly support this hypothesis. The X-ray determined geometry of heptafulvene[118] allowed us to estimate the aromaticity: the HOMA value for the ring is equal to 0.257. The case of fulvene is more complicated—only geometries for the substituted species are known. The mean HOMA value calculated for 11 exocyclically substituted fulvenes is 0.001.[65]

The situation changes dramatically if fulvene and heptafulvene are substituted exocyclically by electron-donating (e.g., NMe$_2$) and electron-accepting (e.g., CHO) groups, respectively. In both cases, aromaticity strongly increases to the values for HOMA of 0.669 and 0.769, respectively. In both cases an increase in the REC values is also observed: for fulvene rings from 576.7 to 591.6 kcal/mol and for heptafulvene rings from 842.2 to 850.3 kcal/mol. In both cases the rings very clearly tend to follow the Hückel ($4N + 2$) rule and may serve as good examples of the substituent effect on aromaticity. Electron-donating groups

in the case of fulvene and electron-accepting ones in the case of heptafulvene strongly stabilize the rings, leading to a substantial increase in their aromatic character, which is in line with Figure 7.
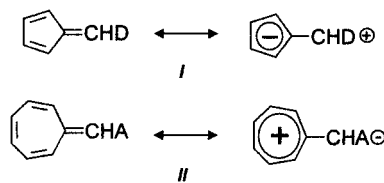
Figure 7. Illustration of the Hückel rule for the fulvene and heptafulvene derivatives. (Reprinted with permission from ref 65. Copyright 1995 Slovak Academy of Sciences.)

The changes in aromaticity are unlike those for the substituted benzenes, where they are much smaller.[105] Recent studies on exocyclically substituted fulvene derivatives have demonstrated a very good systematic dependence between aromaticity and the nature of substituents, as shown in Figure 8.
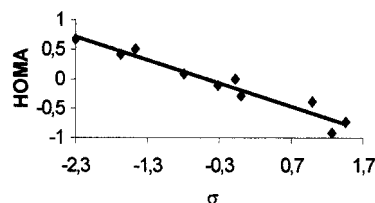
Figure 8. Dependence between aromaticity index HOMA and the substituent constants σ^+. The correlation coefficient $R = 0.970$.

Pentalene is undoubtedly antiaromatic, with a large negative value of REPE which equals −0.018, large and positive value of NICS (+18.0 at HF/6-31+G* for the geometry at DFT B3LYP/6-311+G** level of theory), and HOMA = −0.381.[119] Following the Hückel rule, its dianion is considered to be aromatic, and hence, the metal complexes are well-known.[120] Schleyer's NICS value for the pentalene dianion is −12.1, indicating its strong aromatic character.[32,121] Similarly, the HOMA value calculated from the optimized geometry at the DFT B3LYP/6-311+G** level of theory is 0.468, in a qualitative agreement with NICS.

Azulene is a valence isomer of naphthalene, and the fusion of five- and seven-membered rings allows them to interact in order to fulfill the Hückel rule. Old estimations of its aromaticity via REPE = 0.023[79] indicates a moderate aromatic character, in line with HOMA values for the whole molecule[122] (HOMA = 0.665). Individual rings may be treated by NICS and HOMA: for the five-membered ring the values are −19.7 and 0.286, respectively, and for the seven-membered ring −7.0 and 0.514, based on the lowest energy isomer at B3LYP/6-31G*.

Tropolone is another famous nonalternant system whose aromaticity has long been disputed. Recent studies of its anion and two conformers of protonated tropolone[123] have given us a good opportunity to analyze how the aromaticity is affected by the protonation. The HOMA for tropolone is equal to 0.642. Its anion is definitely less aromatic, HOMA = 0.176, whereas cis and trans conformers of protonated

tropolone are highly aromatic, HOMA = 0.924 and 0.910, respectively. This is a nice illustration of the Hückel rule: a positively charged hydroxy group in the cationic form withdraws electrons from the ring, leading closer to the $(4N + 2)$ number of electrons, whereas a negatively charged phenolic oxygen acts in the opposite direction.

Finally, we should mention some more complex fused systems with nonalternant rings. A good example is dicyclohepta[*cd,gh*]pentalene derivative (methyl 10-ethyldicyclohepta[*cd,gh*]pentalene-5-carboxylate)[124] for which the hydrocarbon skeletone is shown in Figure 9:

Figure 9. Dicyclohepta[*cd,gh*]pentalene.

The molecule is aromatic (global HOMA value is 0.734), resulting from the rule[39] stating that when the numbers of five-membered and seven-membe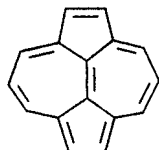red rings are equal, then the system should maintain the aromatic character. Interestingly, the aromatic character is different in these two kinds of rings: the seven-membered rings are more aromatic and have HOMA equal to 0.818, whereas the five membered rings have only 0.500. This difference between the aromatic character of seven- and five-membered rings becomes even more dramatic if in positions 7 and 14 carbonyl groups are attached.[125] Then the five-membered rings become antiaromatic with HOMA equal to −0.258, whereas aromaticity of the seven-membered rings is almost unchanged: HOMA = 0.822. In an unsubstituted molecule,[126] five-membered rings are also less aromatic with a HOMA value 0.663 whereas a seven-membered ring has HOMA = 0.823, with global HOMA = 0.791. It seems that five-membered rings are sensitive to substitution, and the perturbation does not go further to seven-membered rings.

G. Cyclopentadienyl and Cyclopentadiene Moieties Embedded in Various Chemical Environments

Cyclopentadiene is known to be a relatively strong Brønsted acid ($pK_a = 16$[48]), and as such it is able to form salts. It also forms covalent compounds with most nonmetal elements as well as complexes with metals.

Until the mid-1990s, the CSD base[46] archived 4079 derivatives of cyclopentadienyl and cyclopentadiene bound to almost all elements from Li to Tl.[127] Table 21 presents the values of HOMA index estimated as a mean value for the subsamples built up of the compounds of cyclopentadiene or cyclopentadienyl moieties with particular elements. In most cases the data observed are greatly dispersed; hence, statistical characteristics are given as averages and the interquartile ranges of HOMA values as well as the mean C−X interatomic distances are given with their interquartile ranges (variances could not be used for

Table 21. Statistical Parameters for HOMA and C−X Interatomic Distances[127]

element	sub-sample size	HOMA$_{av}$	inter-quartile range	RC−X interatomic distance (averaged)	inter-quartile range	averaged variance of C−X in rings
Li	18	0.602	0.424	2.394	0.085	0.051
Be	3	0.927	0.111	1.887	0.031	0.000
B	13	0.303	0.098	2.943	0.043	0.916
N	14	0.466	0.349	2.724	0.067	0.889
O	15	0.331	0.746	2.682	0.062	0.891
Na	2	0.729	0.398	2.954	0.153	0.015
Mg	6	0.703	0.344	2.412	0.148	0.002
Al	5	0.429	0.695	2.648	0.911	0.280
Si	104	0.540	0.384	3.143	0.023	0.835
P	132	0.614	0.156	3.123	0.045	0.881
S	43	0.636	0.255	3.087	0.015	0.895
Cl	12	0.795	0.091	3.034	0.012	0.876
K	1	0.851	0.000	3.035	0.000	0.003
Ca	9	0.816	0.038	2.649	0.014	0.001
Ti	68	0.788	0.192	2.352	0.024	0.004
V	64	0.822	0.178	2.292	0.033	0.003
Cr	145	0.778	0.220	2.235	0.055	0.009
Mn	214	0.752	0.151	2.158	0.020	0.006
Fe	1222	0.723	0.237	2.076	0.061	0.005
Co	398	0.709	0.268	2.083	0.038	0.008
Ni	105	0.689	0.238	2.124	0.025	0.002
Cu	2	0.931	0.055	2.213	0.004	0.001
Zn	5	0.758	0.293	2.447	0.340	0.075
Ga	3	0.599	0.000	3.484	0.300	0.636
Ge	7	0.741	0.157	2.754	0.751	0.266
As	4	0.592	0.107	2.843	0.760	0.413
Se	6	0.630	0.094	3.224	0.004	0.891
Br	8	0.675	0.300	3.183	0.030	0.873
Y	2	0.728	0.045	2.654	0.002	0.000
Zr	15	0.888	0.127	2.528	0.055	0.000
Nb	35	0.868	0.101	2.423	0.046	0.002
Mo	481	0.781	0.175	2.350	0.027	0.005
Tc	2	0.497	0.175	2.299	0.018	0.001
Ru	332	0.690	0.231	2.241	0.067	0.014
Rh	231	0.584	0.261	2.237	0.048	0.002
Pd	15	0.642	0.289	2.444	0.039	0.063
In	10	0.777	0.004	2.863	0.396	0.008
Sn	23	0.597	0.299	2.864	0.766	0.243
Sb	1	0.865	0.000	2.682	0.000	0.092
Ba	12	0.760	0.064	2.971	0.067	0.001
La	2	0.896	0.018	2.813	0.022	0.003
Hf	5	0.769	0.183	2.498	0.022	0.000
Ta	13	0.673	0.307	2.457	0.063	0.002
W	122	0.764	0.181	2.345	0.030	0.002
Re	76	0.600	0.352	2.319	0.038	0.017
Os	8	0.185	0.323	3.063	0.775	0.571
Ir	44	0.539	0.192	2.225	0.058	0.001
Pt	7	0.656	0.140	2.635	0.951	0.259
Au	1	−0.025	0.000	2.961	0.000	0.347
Hg	10	0.300	0.553	3.393	0.011	0.920
Tl	4	0.570	0.077	2.925	0.336	0.003

characteristics of the dispersion since the distributions were frequently not normal).[128]

Cyclopentadienyl rings form different compounds depending on the element linked to them. In some cases, a more or less deformed cyclopentadiene-like ring is involved in the complex systems of interactions with atoms (ions) other than carbon elements. The typically nonmetallic elements are bound via a covalent link C−X. Typical ionic interactions are encountered for compounds with s-block elements of the Periodic Table. Coordination compounds are formed mainly with transition metals. These kind of compounds are the most complex, since they are often built up of several ligands which are located in various places in the spectrochemical series and may
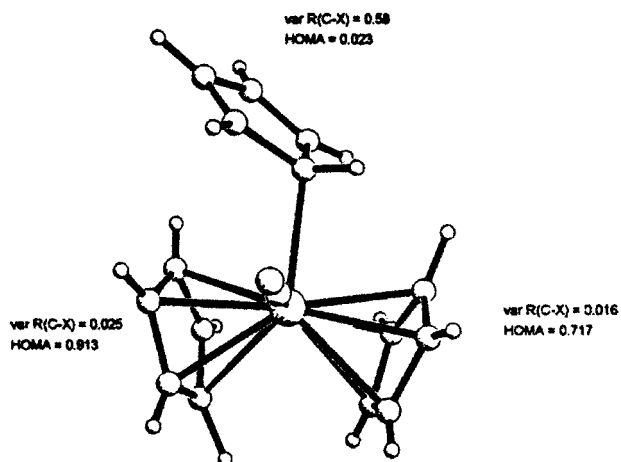
Figure 10. Molecular structure of tris(cyclopentadienyl)-nitrosomolybdenum. (Reprinted with permission from ref 127. Copyright 1996 Elsevier Science.)

differ considerably in their power of interacting with the central atom, affecting its interactions with the cyclopentadienyl moieties. Consequently, dramatic differences in aromaticity of these rings may be observed. A good example is the structure of tris-(cyclopentadienyl)nitrosomolybdenum[129] shown in Figure 10. Two rings interact with the Mo central atom in almost the same way. The variances in the C−Mo distances for those two rings are small: 0.025 and 0.016 Å². Both rings are still aromatic, with HOMA = 0.913 and 0.717. The third ring is bound to the Mo atom in a quite different way—one carbon atom is sp³ type and much closer to the Mo atom than any others, and hence the variance of C−Mo interatomic distances for this ring is large (0.58 Å²), which is responsible for a significant decrease of aromaticity, HOMA = 0.016. The ring simply resembles a cyclopentadiene ring.

From the data in Table 21 it is easy to draw conclusions based on a similar method of interpretation. In the right-hand column are collected averaged variances of C−X distances calculated for each ring separately and the variances averaged for the whole subsample. Low values of these quantities mean that all carbon atoms of the five-membered ring are a very similar distance from the X atom. This is encountered mostly in the case of sandwich-type complexes and in ionic derivatives of cyclopentadienyl anion in the crystalline states.

H. Heterocyclic Analogues of Nonalternant Hydrocarbons

Monocyclic systems, heteroanalogues of the cyclopentadienyl anion, are most often encountered in organic synthesis. Application of HOMA, EN, and GEO to this class of compounds allows one to estimate their aromaticity from experimental geometries. Table 22 presents a collection of data.

A classical problem of the changes in aromaticity in the series, pyrrole, thiophene, and furan,[56,130−132] is also shown by the present data and is in line with chemical expectation.

Recently Schleyer et al.[121] studied the aromaticity of bicyclics, furofuran, thienothiophene, benzofuran,

Table 22. HOMA, EN, GEO, and Bird's I_5 Indices for Five-Membered Heterocyclics[67]
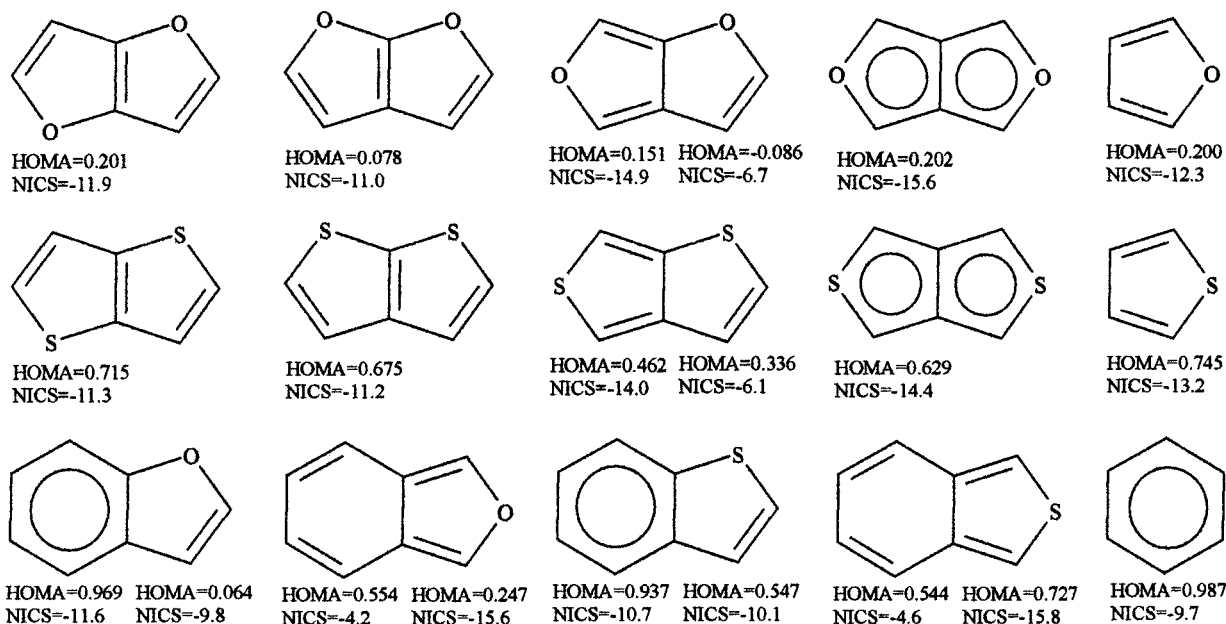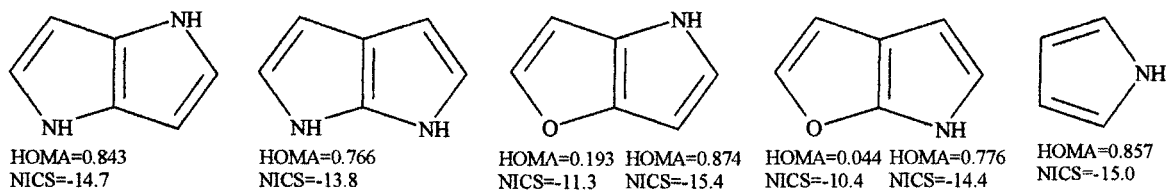
Compound	HOMA	I_5	Compound	HOMA	I_5
(O)	H=0.029		(Naphtyl triazole)	H=0.839	
	E=0.108	32.8		E=0.001	64.1
	G=0.863			G=0.160	
(S)	H=0.654		(H triazole)	H=0.911	
	E=0.113	67.9		E=0.027	82.0
	G=0.233			G=0.062	
				(1)	(1)
			(H triazole (1)(2))	H=0.907	
(CH₂Ph, P)	H=0.346			E=0.003	79.0
	E=0.065	37.0		G=0.090	
	G=0.588			(2)	(2)
				H=0.753	
				E=0.019	63.3
				G=0.228	
(H, N, CHCCH₂CHO)	H=0.899		(H triazole, Ph)	H=0.885	
	E=0.004	65.4		E=0.015	78.1
	G=0.097			G=0.100	
(H, pyrazole)	H=0.922		(CH(Ph-Cl)₂ tetrazole)	H=0.973	
	E=0.019	75.9		E=0.001	88.3
	G=0.059			G=0.026	
(H, imidazole)	H=0.918		(Ph-NMe₂ tetrazole)	H=0.952	
	E=0.007	67.8		E=0.021	88.6
	G=0.074			G=0.026	

and benzothiophene, calculating optimized geometries and a collection of aromaticity indices. Chart 4 presents these data enriched by HOMA values computed from the optimized geometry.

The topology of the heteroatoms in benzofuran and benzothiophene exerts different effects on aromaticity, as seen in a different way by HOMA and NICS: in both cases, 1-endo-substitution decreases the aromaticity of the benzene ring in terms of HOMA, 0.969 and 0.937 compared with benzene (0.987), but it increases the aromaticity in terms of NICS, −11.6 and −10.7 compared with −9.7 for benzene. In the case of HOMA, a similar situation is observed for the five-membered rings: 0.064 and 0.547 compared with 0.200 and 0.745 for the oxygen- and sulfur-containing rings. In the case of 2-endo-substitution, both NICS and HOMA exhibit a decrease in the aromaticity of the benzene ring, but again there is no full agreement in the description of five-membered rings.

The aromatic character of furofuran and thienothiophenes strongly depends on the topology of endo-substituents. The same observation is found for pyrropyrrole and a mixed system—furopyrrole for which the calculations were carried out at the same level of theory.[119] Chart 5 presents these data.

In all cases, the [1,4]-derivatives are more aromatic than [1,6]-di-endo-substituted pentalene. Interestingly, only pyrrole fused to furan with [1,4]-endo-

Chart 4. Aromaticity Indices HOMA and NICS of Furofuran, Thienothiophenes, Benzofuran, and Benzothiophene

HOMA=0.201
NICS=-11.9

HOMA=0.078
NICS=-11.0

HOMA=0.151 HOMA=-0.086
NICS=-14.9 NICS=-6.7

HOMA=0.202
NICS=-15.6

HOMA=0.200
NICS=-12.3

HOMA=0.715
NICS=-11.3

HOMA=0.675
NICS=-11.2

HOMA=0.462 HOMA=0.336
NICS=-14.0 NICS=-6.1

HOMA=0.629
NICS=-14.4

HOMA=0.745
NICS=-13.2

HOMA=0.969 HOMA=0.064
NICS=-11.6 NICS=-9.8

HOMA=0.554 HOMA=0.247
NICS=-4.2 NICS=-15.6

HOMA=0.937 HOMA=0.547
NICS=-10.7 NICS=-10.1

HOMA=0.544 HOMA=0.727
NICS=-4.6 NICS=-15.8

HOMA=0.987
NICS=-9.7

Chart 5. Aromaticity Indices of Pyropyrroles and Furopyrroles

HOMA=0.843
NICS=-14.7

HOMA=0.766
NICS=-13.8

HOMA=0.193 HOMA=0.874
NICS=-11.3 NICS=-15.4

HOMA=0.044 HOMA=0.776
NICS=-10.4 NICS=-14.4

HOMA=0.857
NICS=-15.0

substitution exhibits an increase of the aromaticity compared with the individual ring. In all other cases the fusion leads to a decrease in aromaticity. These effects are supported by both NICS and HOMA and are in line with the topological charge stabilization rule.[133]

Another problem is when the changes in aromaticity of heterobicyclics are considered as a result of exo-substitution. X-ray and ab initio studies[134] of eight derivatives of furo[3,2-*b*]pyrrole and five derivatives of furo-[2,3-*b*]pyrrole lead to the conclusion that the aromaticity of both π-electron systems exhibits a strong dependence on the substituent effect, much stronger than that observed in benzene derivatives.[105]

Very recently experimental geometries of 1,3,4-thiadiazole derivatives have been studied with regard to their aromatic character.[135] It was shown that the aromaticity of the ring in these systems depends significantly on the nature of the substituent. The electron-donating NH_2 group increases the 1,3,4-thiadiazole ring aromaticity by about 0.06−0.07 unit of HOMA as compared with the systems substituted by less donating groups such as NHCOMe or S. Moreover, the ring in thiadiazoles is significantly less aromatic than in triazole.[135]

In the case of nonalternant heterocyclic systems fused to benzene, an interesting case is that in indazole two existing tautomers (Figure 11) differ by 2.9 kcal/mol, thus indicating 1H tautomer to be more stable.[136,137] HOMA shows the values equal to 0.808

and 0.792 for 1H and 2H tautomers, respectively, which is in line with the energetic expectation. However, a really dramatic difference is observed for the benzene fragment in these two tautomeric forms: for the 1H tautomer HOMA for this ring is 0.897 compared with HOMA = 0.810 for the 2H tautomer. The decrease in aromaticity of the benzene ring is associated here with the shortening of both CN and CC bonds from the five-membered rings.

A similar picture was observed in the case of bispyrazolo[3,4-*b*;4,3-*e*]pyridine derivatives.[138] The pyrazole rings fused to pyridine have much lower aromaticity (HOMA around 0.65) than unfused species, for which HOMA is about 0.92. These data based on experimental geometries are extended by the theoretically computed geometries onto a wider range of substituted systems, as shown in Table 23. The pyrazole ring becomes less aromatic when exocyclic bonds to substituents (or in the fused ring) and are shortened as shown in the schemes in Figure 12.

As can be seen in Table 23, a decisive component of the decrease in aromaticity in those cases is an increase in bond alternation measured by an increase
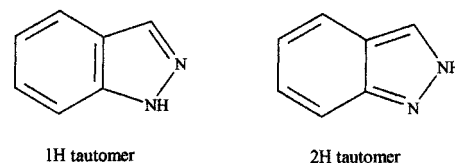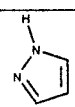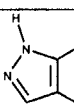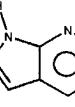

1H tautomer   2H tautomer
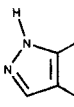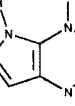
Figure 11. Tautomers of indazole.

Table 23. Aromaticity Indices for the Pyrazole Fragment of Model Molecules Based on RHF/6-311G Geometry**

Formula	Aromaticity indices	Formula	Aromaticity indices
	H=0.900 E=0.000 G=0.100 NICS= -14.7		H=0.917 E=0.003 G=0.080 NICS= -14.3
	H=0.819 E=0.031 G=0.150 NICS= -13.0		H=0.904 E=0.002 G=0.094 NICS= -12.9
	H=0.782 E=0.032 G=0.186 NICS= -11.8		H=-0.011 E=0.443 G=0.663 NICS = -0.5
	H=0.782 E=0.025 G=0.193 NICS= -11.5		H=-1.025 E=0.777 G=1.248 NICS= +9.8

Figure 12. Scheme of the decrease of aromaticity for pyrazole ring. (Reprinted with permission from ref 138. Copyright 1998 Elsevier Science.)

of the term GEO. A very good agreement between the HOMA estimation of aromaticity and the values of Schleyer's NICS is observed.

Porphyrins are a good example in which the local aromatic properties in pyrrole moieties is associated with a global property measured in the center of the mac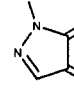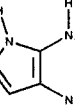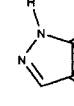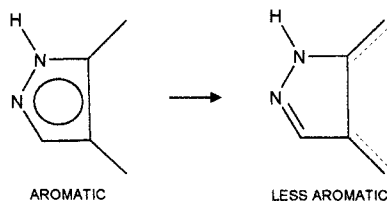rocycle.[42] An extensive sample of 456 porphyrines including complexes with metals (424) of which the molecular geometry was released from CSD[46] was treated by the HOMA model. On the other hand, the ab initio optimization of the unsubstituted porphyrine, its Mg^{2+} complex, and dianion at the B3LYP/6-31G* level of theory allowed us to look at these systems in an independent way including application of the magnetic index NICS.[32] In spite of the quite different sources of data, the conclusions drawn from experimental and theoretical data were very similar. Table 24 presents the resulting data.

In the free base porphyrin, the most aromatic part is the "internal cross" (Figure 13). The pyrrole rings with NH groups are clearly more aromatic (HOMA = 0.666, NICS = −15.2) than the other five-membered rings (HOMA = 0.452, NICS = −4.5). Hence, the NH groups are not the inert bridging groups as suggested by the [18]annulene model[139] but

Table 24. HOMA, EN, GEO, and NICS Values for Porphyrins, Their Metal Complexes, and the Dianion[a]

	HOMA[b]	HOMA[c]	EN[b]	GEO[b]	NICS (ppm)[c]
porphyrine	0.652	0.666	0.107	0.240	−16.5[d]
ring (1,3)	0.666	0.702	0.132	0.202	−15.2
ring (2,4)	0.452	0.381	0.175	0.373	−4.5
internal cross	0.880	0.932	0.075	0.045	−21.7
porphyrine−metal	0.656	0.671	0.094	0.249	
ring (1,3)	0.566	0.556	0.158	0.276	−10.0
ring (2,4)	0.524	0.556	0.153	0.323	−10.0
internal cross	0.872	0.906	0.071	0.057	−21.0
porphyrine dianion		0.448			−14.9[d]
ring (1,2,3,4)		0.287			−4.0
internal cross		0.908			−17.5
porphyrine−M^{II}	0.638		0.102	0.259	
porphyrine−M^{III}	0.682		0.084	0.233	

[a] M^{II} and M^{III} stand for divalent and trivalent metals, respectively [b] Mean experimental geometries. [c] Calculated geometries. [d] Ring center value, see Figure 13.
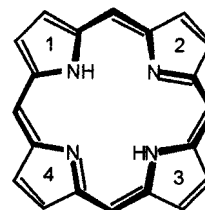
Figure 13. Enumeration of the rings in porphyrine. "Internal cross" shown in bold (see text). (Reprinted with permission from ref 42. Copyright 1998 Wiley-VCH Verlag GmbH.)

instead are an integral part of the aromatic system. The unprotonated five-membered rings have low aromatic character, implying that the C_2H_2 groups function as exocyclic "bridges". A more appropriate description of the free base porphyrin should probably be as a 22 π-electron system rather than the [18]annulene model as shown at Figure 14.

Lower aromaticity of both kinds of pyrrole moieties is associated with an increase of the double-bond character of CC(H)C bridges, leading to more localized structures.[42] This kind of effect has been discussed in detail in the case of porphyrins[42] and pyrazoles.[138]

In the case of metal complexes, all four pyrrole rings are incorporated into the aromatic system, while in the case of dianions, the π-electronic structure is more strongly-localized on the central part, which can genuinely be considered as an 18 π-electron species plus four C_2H_2 bridging groups.

I. Dependence of Aromaticity on Intermolecular Interactions

Since aromaticity undoubtedly depends on the electron structure of the system in question, it should also depend on the intermolecular interactions. Indeed, it was shown[140] that the geometry of the ring in hydrated nitrosophenolate anions in salts with sodium and magnesium cations varies significantly. When the HOMA, EN, and GEO indices are calculated from the molecular geometry of the ring, in these two cases the changes in the aromatic character are significant, as shown in Figure 15.
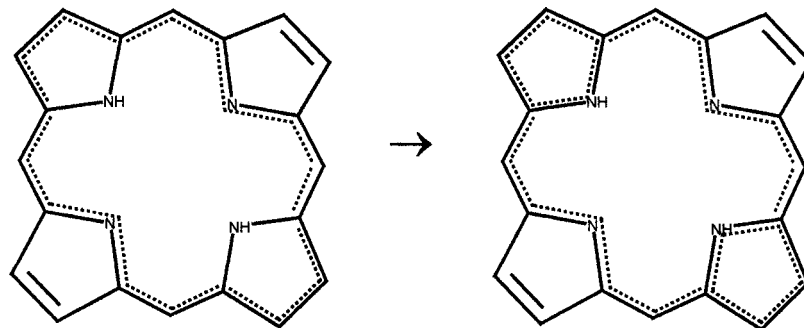
Figure 14. Two models of the π-electron system of porphyrin: (left) as a bridged [18]annulene derivative;[139] (right) as macrocyclic 22 π-electron system.[42] (Reprinted with permission from ref 42. Copyright 1998 Wiley-VCH Verlag GmbH.)
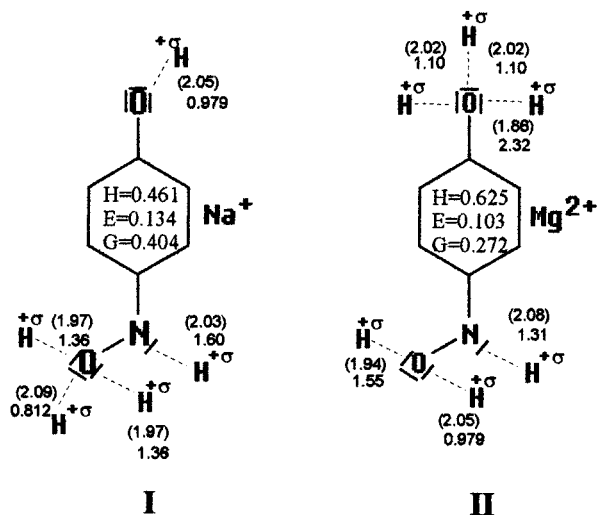

Figure 15. Interatomic distances in H-bonds (Å, in parentheses), their energies (kcal/mol) of interactions, and estimated aromaticity descriptors for the *p*-nitrosophenolate anion in two salts: sodium and magnesium, respectively. (Reprinted with permission from ref 47. Copyright 1998 Elsevier Science.)

The difference between the sodium and magnesium salts consists of the nature of the hydration sphere around the anion. In the case of the sodium salt (**I**), there is a trihydrate and the water molecules interact via the hydrogen bonding mainly with the nitroso group, whereas in the case of the magnesium salt (**II**), which exists as a hexahydrate, both basic terminals are almost equally hydrated. The energies presented in the scheme visualize that the oxygen atom in the nitroso group of **I** is much more hydrated ($E = 3.54$ kcal/mol) than the oxygen atom in the nitroso group of **II** ($E = 2.53$ kcal/mol), particularly if compared with the hydration of the oxygen atom in the phenolate group of **I** ($E = 0.98$ kcal/mol) and **II** ($E = 4.52$ kcal/mol). In consequence, the negative charge in **I** is mostly located at the nitroso oxygen, whereas in the case of **II**, it is shared with the phenolate oxygen. Thus, in **I** shorter CO and CN bond lengths are observed and hence a stronger contribution of the quinoidal structure than in **II**, leading to a larger decrease in the aromatic character in **I** as compared with **II**.

Analysis of the HOMA components shows that the main contribution to the observed decrease in aromaticity stems from the GEO term (around 70% of the total decrease) but the other part, due to EN,

points to a known fact that in quinoidal structures four bonds are lengthened and only two are shortened.

Another group of systems showing a significant influence of the intermolecular interactions on aromaticity are EDA complexes. These compounds crystallize well and have often been subject to thorough structural studies. A good illustration is given by tetracyanoquinodimethane (TCNQ) and its salts. HOMA for TCNQ is 0.377, whereas for its Na salt is 0.724. Evidently the quinoidal structure of TCNQ is not aromatic and acceptance of π-electrons leads to an increase in aromaticity. A rough dependence between the charge transferred to the TCNQ moiety[141,142] and the HOMA value of the ring was found.[8]

J. Aromaticity vs Deviation from Planarity

Benzene itself in the crystalline state studied at 15 K is not planar.[50] Its slight chair conformation is caused by weak intermolecular interactions in the crystal lattice. According to Kitaygorodsky,[143] the energy of interactions between two adjacent chemical species is in the range of 1−3 kcal/mol. This is sufficient to bend the ring in the crystalline benzene. Furthermore, this means that the out of plane deformation of the aromatic ring does not need much energy.[144] Indeed, it was shown that close contacts in the crystal lattice, exemplified by the studies on sodium *p*-nitrobenzoate trihydrate, cause significant deformations in the ring, which are proportional to the strength of these interactions.[145] In view of those observations, a question arises: how do distortions from planarity affect the aromaticity of the ring(s)?

Analysis of the experimental molecular geometry (X-ray) of 1,4-dichloro-2,6[5]metacyclophane[146] shows its high aromaticity (HOMA = 0.985), despite substantial distortions from the planar conformation, as shown in Figure 16. This is in line with the ^{1}H NMR signals of the ring protons but against the increased reactivity of this compound.[147]

A similar situation is observed for [5]-*p*-cyclophane,[119,148] where the HOMA is also high, 0.953, despite a substantial folding of the ring. The same results were obtained from magnetic studies of the folded benzenes.[149]

Per-substituted naphthalene derivatives are also convenient model systems to exemplify the changes in aromaticity due to the folding of the aromatic moiety. The distortions lead the moiety to a chiral conformation as shown in Figure 17.
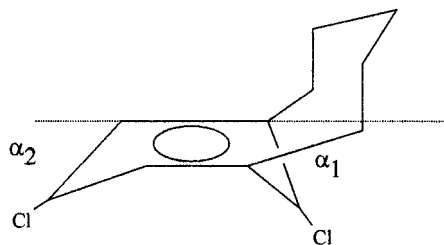
Figure 16. Scheme of [5]metacyclophane indicating folding of the ring: $\alpha_1 = 26.8°$, $\alpha_2 = 12°$.
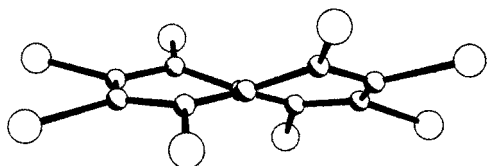

Figure 17. Projection of per-bromo-substituted naphthalene along $C_{4a}-C_{8a}$ bond.

Table 25. HOMA Values and Nonplanarity Parameters for a Few Persubstituted Derivatives of Naphthalene (octa-X-naphthalene)

X	HOMA	maximal deviation of the carbon atom from the best plane of the naphthalene moiety (in Å)
H	0.810	0.003
methyl	0.723	0.234
S–Ph	0.715	0.293
F	0.743	0.007
Cl	0.730	0.213
Br	0.431	0.427

Table 25 presents a magnitude of the deformation from planarity (as the value of the maximal deviation of carbon atoms from the least-squares plane for carbon atoms) and HOMA values. The presented results show that small folding of the naphthalene moiety does not substantially affect the aromaticity.

Recent synthesis of pyrenophanes[150] allowed us to study the dependence of the global aromaticity of the pyrene moiety on the degree of its bending and also how individual rings react to bending.[151]

K. Experimental Arguments for the Hiberty–Shaik Hypothesis of the Role of σ-Electron Structure in π-Electron Systems

Analysis of the changes in aromaticity of chrysene[152] and phenazine[109,153,154] gave interesting arguments for the Hiberty and Shaik hypothesis,[14] which claims that[14,155] "the benzene picture that emerges from (these) all-electron studies, the π-component enjoys resonance stabilization, but is also distortive and prefers a D_{3h} symmetry, and it is the resistance of the σ-frame to the distortion that restores the D_{6h} structure". A good illustration of these ideas is given by a scheme of the dependence of the σ- and π-energies on the resonance coordinate for benzene[156] presented in Figure 18.

In this case, the σ-structure dominates in the balance between trends of σ- and π-electron structures. Following this hypothesis, if the amount of π-electrons in a weakly aromatic system is decreased,
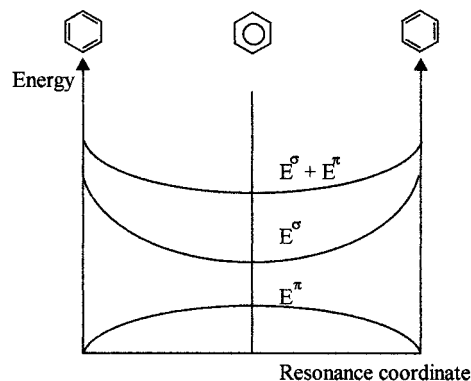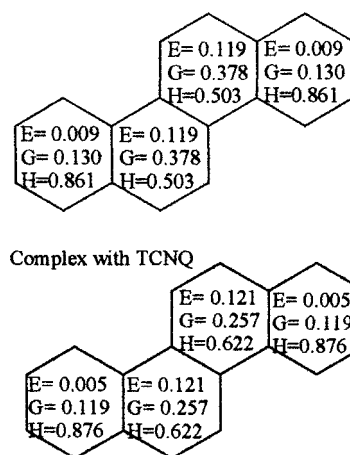

Figure 18. The σ- and π-separated energies[156] for benzene and its Kekulé structures.

Chart 6. Local Values of HOMA, EN, and GEO Terms for Chrysene and Its Moiety in EDA Complexes with TCNQ

then their distortive tendency might be decreased and the system should exhibit less bond alternation. Consequently, a higher aromaticity of the system[152] is expected. Such a situation is encountered in the case of chrysene and its EDA complexes with TCNQ and fluoranil.[152,157] Chart 6 presents HOMA values for chrysene and for its moiety in complexes with TCNQ. A similar picture is found for phenazine and its EDA complexes.[109]

It is immediately apparent that the aromaticity of the central ring increases markedly for chrysene involed in the EDA complexes. Moreover, the same is also observed for the terminal rings. Consequently, higher aromaticity is observed for the whole molecule. Looking at the EN and GEO terms for chrysene and its moiety in the EDA complex with TCNQ, it appears that the EN term for the central ring is practically the same in both cases (0.119 and 0.121) whereas the GEO term decreases from 0.378 to 0.257. TCNQ is a well-known electron-accepting system;[158] thus, in the EDA complexes it strips electrons from the chrysene moiety, enabling the σ-electrons to partially equalize the length of all CC bonds.

L. Substituent Effects on Aromaticity

This section is devoted to some special kind of interactions, due to substituents but characteristic

Chart 7. HOMA, EN, and GEO Terms Estimated from the Experimental Geometry for Naphthalene, Phenanthrene, and Triphenylene
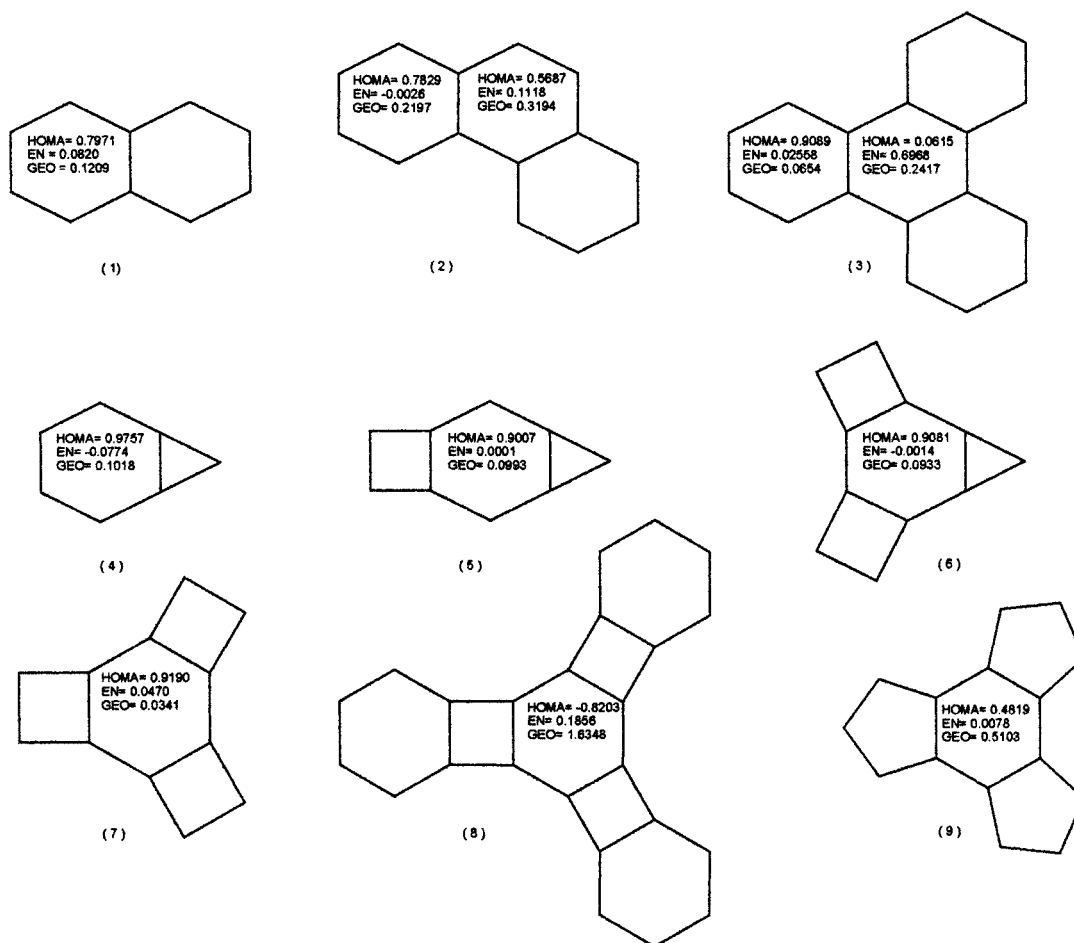
of the π-electron systems and not related to typical substituent effects, usually associated with Hammett-type plots or similar problems. The latter kind of substituent effects on aromaticity are presented and discussed throughout the whole review.

1. Bond Localization Due to the Anneleation of Small Rings to Benzene

The bond length alternation in benzene anneleated to small rings has long been observed and originally attributed to the so-called Mills–Nixon effect.[159] However, recent studies oppose using the Mills–Nixon effect for these kinds of phenomena.[160–163] Stanger suggested the name strain-induced bond localization (SIBL)[161] and mentioned three approaches which can be helpful in understanding the observed phenomena: (a) a classical π-electron effect which relies on the π-electron count in the small anneleated ring;[164,165] (b) localization due to the rehybridization caused by the strained atoms—the bonds with the wider bond angles would have a lower π-character and following the Bent–Walsh rule should form shorter bonds to the adjacent atom;[166] finally, (c) a combination of σ- and π-electron effects.[167,168] Undoubtedly increasing the bond localization means that the system becomes less aromatic, and Chart 7 presents a few typical examples. It is apparent that anneleating benzene by another benzene (naphtha-

lene) or by two benzenes in an angular manner (phenanthrene) leads to an increase in bond alternation. However, in the case of smaller rings, the effect is usually much more conspicuous.

While looking at benzene rings which are anneleated to small rings, an important fact should be taken into account. The bond lengths calculated as the shortest distance between two adjacent atoms may not be a good picture of the bonding. In such cases the bonds are bent and an adequate description is a bond path.[75] Figure 19 presents the problem
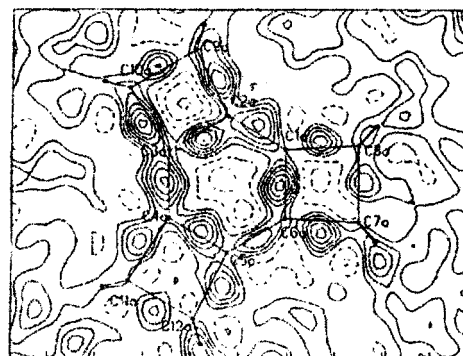

Figure 19. X–X electron densities for 1,2,3,4,5,6,-hexahydrotricyclobuta[a,c,e]benzene.[183] (Reprinted with permission from ref 183. Copyright 1994 Wiley-VCH Verlag GmbH.)

clearly showing that the maximum charge density is located outside of the shortest distance between the atoms nuclei. Thus, for these kinds of molecules, the resulting geometry-based aromaticity indices should be considered with caution.

2. Angular Group-Induced Bond Alternation (AGIBA)

Very recently it has been shown that open substituents can also induce bond alternation in aromatic rings, provided the attached groups are angular as for instance in the nitroso or methoxy group.[169−173] The effect has also been observed experimentally for ring systems with equalized bond lengths such as boraxine[174] and borazine,[175] which despite the bond length equalization are not considered to be aromatic.[176]

The observed phenomenon is schematically presented in Figure 20: the double-bonded groups
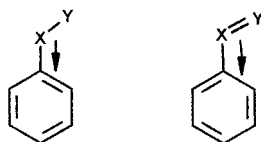

Figure 20. Scheme of the AGIBA effect. (Reprinted with permission from ref 173. Copyright 1997 Elsevier Science.)

−X=Y cause a lengthening of the cis bond and a shortening of the trans one, whereas the −X−Y groups act in the opposite way, they elongate the trans bonds and shorten the cis ones. For the type of substituent, the effect is named as angular group-induced bond alternation (AGIBA).

From an energetic point of view, the observed effect is very small. The differences in total energy for *cis*- and *trans*-*p*-dinitrosobenzene and *p*-dimethoxybenzene computed at the B3LYP/6-311G** level[177] are −0.14 and −0.17 kcal/mol, respectively. In both cases the cis conformers show a marked AGIBA effect with a difference in ipso-ortho bond lengths of 0.0089 and 0.0102 Å, respectively, whereas the trans conformers exhibit only 0.0022 and 0.0036 Å, respectively. The total energy decomposition scheme of Bader,[75] applied to determine separately the energies of substituents and rings, led to an increase of this difference for *p*-dinitrosobenzene up to 0.76 kcal/mol, when only the ring is taken into account. Figure 21 presents the HOMA, EN, and GEO values for all four cases calculated from the optimized geometry (HF/6-311G**).[178] Additionally, the weights of two canonical structures are given (calculated by use of the HOSE model[77,78]). For a benzene ring (without AGIBA effect), the contributions are equal to each other (50%). In the case with angularly-substituted benzenes (AGIBA substituents), one of the structures dominates as shown in the figures.

An interesting point in AGIBA-affected systems is that when the angular group is bent toward the ring, the effect is enhanced.[169,170,173] Since the enhancement of the AGIBA effect is nearly additive,[173] these effects are nicely observed for symmetrically trisubstituted benzenes.[171] Table 26 shows how canonical structure weights and aromaticity depend on the bending of the substituent toward the ring. Even if the changes in HOMA values are not dramatic, the ratio of the Kekulé structure contributions indicates substantial

weight of the structure:

67.42 %   50.0%   38.36%   50.0%
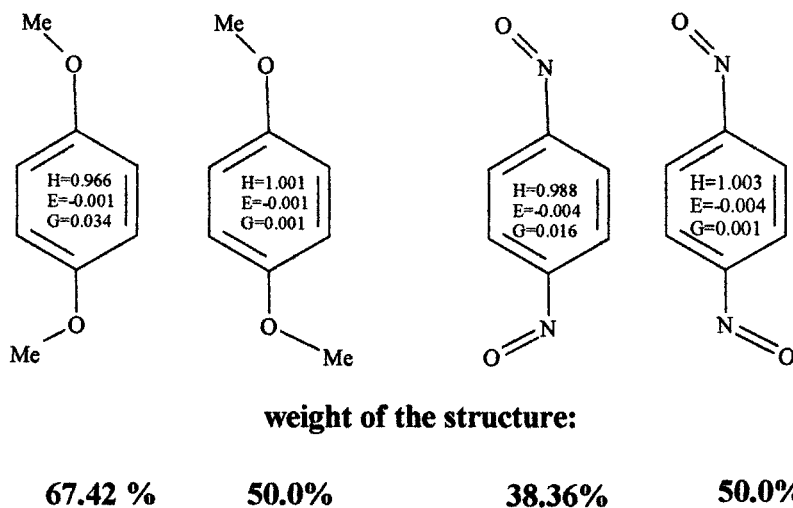
Figure 21. Aromaticity and canonical structure weights of the phenyl ring for two conformers of *p*-dimethoxy- and *p*-dinitrosobenzene. (Reprinted with permission from ref 47. Copyright 1998 Elsevier Science.)

Table 26. Aromaticity Indices and the Kekulé Structure Weights (Figure 22) of 1,3,5-Tridiazobenzene with Varying CNN Angle Based on HF/6-31G*

CNN angle(χ)	128°	124°	120°	116°	112°
HOMA	H = 0.994	H = 0.971	H = 0.929	H = 0.866	H = 0.779
	E = 0.000	E = 0.000	E = −0.001	E = 0.000	E = 0.001
	G = 0.006	G = 0.029	G = 0.072	G = 0.134	G = 0.220
canonical stucture K1	57.63%	66.53%	74.72%	81.95%	88.21%
canonical stucture K2	42.37%	33.47%	25.28%	18.05%	11.79%

[a] The Kekulé structure of the ring K1 is shown in Figure 22. Structure K2 depicts the opposite one.

Chart 8. Aromaticity Indices for Anthracene and Its 1-, 2-, and 9-CH$_2^+$ Derivatives
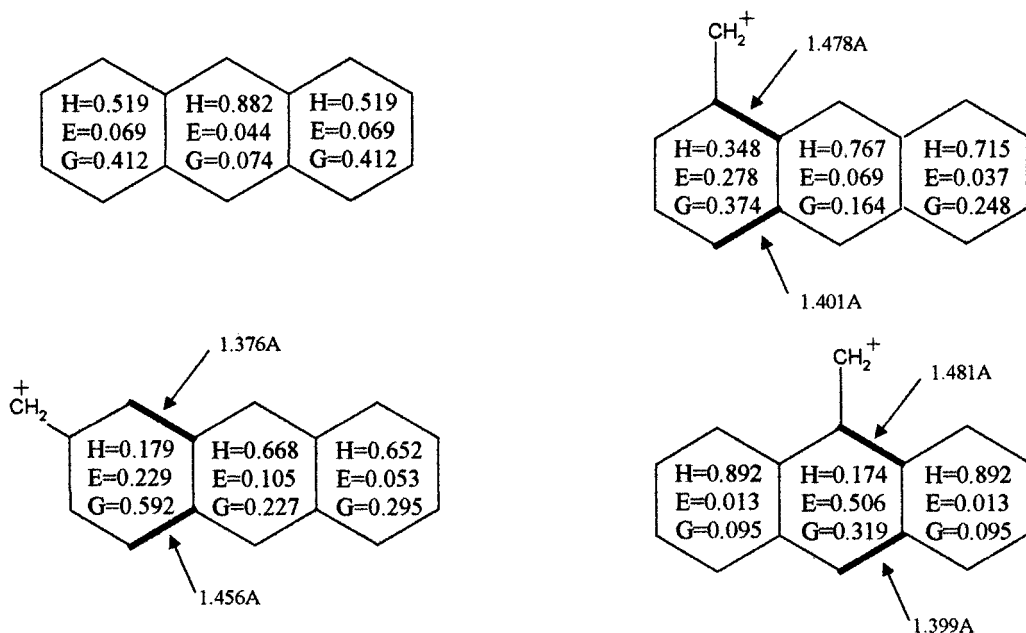
changes in electron structures. The changes in aromaticity are solely due to the increase in bond length alternation (GEO term).

Figure 22. Scheme of one of the Kekulé structures (K1) of 1,3,5-triazobenzene.

3. Charged Substituents in Benzenoid Systems

Systematic studies on CH$_2^+$-substituted benzenoid hydrocarbons[179] carried out by use of ab initio HF/6-31G*-optimized geometries revealed a substantial influence of the position of substitution on the aromatic character of the substituted ring and other rings of the system in question. If the CH$_2^+$ group is attached to the ring in the benzenoid hydrocarbon in such a way that the induction of the 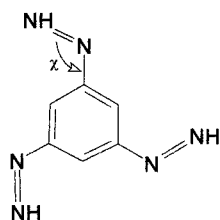quinoidal structure onto the further fragments of the molecule proceeds via a short CC bond, then the induced quinoidal structure has strong π-bond localization. If this is done via a long CC bond, then the localization is much weaker. Consequently, in the first case the decrease in aromaticity is greater whereas in the second case weaker. The case of anthracene is a good illustration. Chart 8 presents anthracene and 1-, 2-, and 9-CH$_2^+$-substituted an-

thracene derivatives as well as the values of HOMA, EN, and GEO.

1-CH$_2^+$ and 2-CH$_2^+$ anthracenes differ from each other dramatically. The substituted ring in the 1-CH$_2^+$ derivative has a less aromatic character (HOMA = 0.348) than in the parent molecule (0.519), but the ring in the 2-CH$_2^+$ derivative is much more dearomatized (HOMA = 0.179). Two other rings in the case of 2- CH$_2^+$ derivatives are much less aromatic (HOMA = 0.668 and 0.652) than in the case of the 1-CH$_2^+$ derivative (HOMA = 0.767 and 0.715). The CC bond, via which the quinoidal structure may propagate over the whole molecule, is equal to 1.401 Å in the case of the 1-CH$_2^+$ derivative as compared with the value of 1.375 Å in the case of the 2-CH$_2^+$ derivative (both bonds marked in bold lines in Chart 8).

These local characteristics of aromaticity are also well seen in the HOMA values for the whole molecule. 1-Derivatives and 9-derivatives have HOMA values nearly the same as an unsubstituted system, only the 2-derivative is strongly dearomatized. This is due to a possibility of a long-range quinoidal structure (Figure 23) which cannot be realized in other derivatives.

The least effect of CH$_2^+$ on the adjacent rings is observed in the case of 9-derivatives. The substituted ring is of low aromaticity (HOMA = 0.174), but the other two are markedly more aromatic, even more so than in the parent compound (HOMA = 0.892). This observation is in line with the well-known fact that 9-hydroxyanthracene easily tautomerizes to its
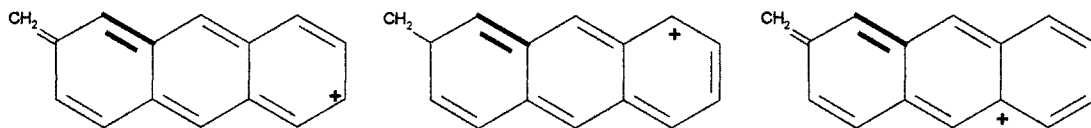

Figure 23. Selection of quinoidal canonical structures showing the long-range transmission of the CH$_2^+$ substituent effect.
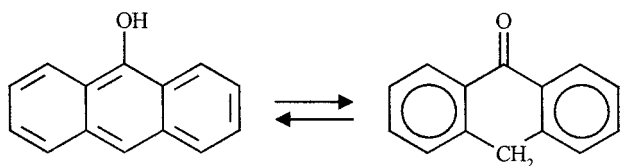
Figure 24. Tautomerism of 9-hydroxyanthracene.

keto form,[97] leaving two other rings highly aromatic, Figure 24.

Depending on the position of substitution, the CC bond between CH_2^+ and the benzenoid hydrocarbon varies strongly in length. The changes are related to the total atomic charge at the CH_2^+ group, $Q(CH_2^+)$, estimated by Mulliken population analysis,[180] which in turn depends on the Hammett−Streitwieser position constants.[181]

The analysis of HOMA, EN, and GEO terms made for individual rings and the whole moieties of CH_2^+-substituted naphthalene, anthracene, phenanthrene, and pyrene molecules allowed us to draw the following conclusions. If a single substituent able to form a double bond is attached to the benzenoid hydrocarbon in a position which permits the formation of the quinoidal structure along a larger part of the π-electron system, then it acts as a dearomatizing factor for this fragment and consequently may do this for the whole system. In all cases, a decrease in aromaticity is associated with an increase in the geometric term. The magnitude of the π-electron localization via the formation of the quinoidal structures depends on the accepting power of the substituent, which leads to the changes in bond lengths, which causes this induction. The shorter this bond, the greater localization is observed.

IV. Conclusions

The molecular geometry of cyclic π-electron systems is an important and readily accessible source of information from which corresponding aromaticity indices may be easily obtained. Unlike other indices, the geometry-based aromaticity indices are applicable to both local and the global π-electron systems. They can even be applied to noncyclic systems, and their values then have an interpretation as measures of π-electron delocalization.

Molecules with too much strained rings (containing three- or four-member rings) should not be treated by geometry-based aromaticity indices, since their bonds are not straight links between the atoms but rather banana-shaped "bond paths" of which the lengths are not easily accessible and which differ in length from the direct links (cf. Figure 19).

Among geometry-based indices, the HOMA index works most effectively; not only does it measure the decrease in aromaticity due to an increase in bond alternation (the GEO term), but it also estimates the decrease due to bond elongation (the EN term).

In most cases, HOMA correlates well with magnetic indices, such as NICS and the magnetic susceptibility exaltation, and this is well observed in a large sample of five-membered hetero-π-electron systems, which consists more than 100 systems

ranging from strongly antiaromatic to typically aromatic systems.[95]

V. Acronyms

HOMA	harmonic oscillator model of aromaticity
AGIBA	angular group-induced bond alternation
NMR	nuclear magnetic resonance
SE	stabilization energy
ASE	aromatic stabilization energy
NICS	nucleus-independent chemical shift
CSD	Cambridge Structural Database
ED	(gas-phase) electron diffraction
MW	microwave (measurement of molecular geometry)
A_J	Julg's index of aromaticity
BAC	bond alternation coefficient
I_5, I_6	Bird's aromaticity indices of five- and six-membered rings (with heteroatoms)
EN	term measuring the decrease of aromaticity estimated by HOMA due to bond elongation
GEO	term measuring the decrease of aromaticity estimated by HOMA due to bond alternation
REC	ring energy content
MEC	molecule energy content
HOSE	harmonic oscillator stabilization energy
DE	(Hückel's) delocalization energy
TCNQ	tetracyanoquinodimethane
EDA	electron donor−acceptor (complexes)
HMO	Hückel molecular orbital (theory)
REPE	resonance energy per electron (π)
GAV	(Cohen and Benson's) group additivity values
PBD	polysubstituted benzene derivatives
DFT	density functional theory
SIBL	strain-induced bond localization

VI. Acknowledgments

VII. References

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