

Crystallographic Studies of Inter- and Intramolecular Interactions Reflected in Aromatic Character of π -Electron Systems

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An old quantitative measure of aromatic character named HOMA (harmonic oscillator measure of aromaticity) is reformulated and related to the Jug and Koester concept of resonance coordinate. In its new version, the HOMA index can be used to estimate an aromatic character of π -electron systems (molecules, ions, or their fragments) built up of the following bonds: CC, CN, CO, CP, CS, NN, and NO. It is shown that even if aromatic stabilization is due to σ -electron structure inclined to maintain equal bond lengths, the aromatic character is mainly a result of π -electron properties of the system. Application of the HOMA index to benzene rings in various molecular and ionic systems showed that the aromatic character depends rather weakly on deformation from planarity whereas it may be strongly dependent on the intermolecular H-bonding net as well as on cooperative substituent interactions of push-pull type and on the topology of a mutual link between benzene rings in condensed benzenoid hydrocarbons.

INTRODUCTION

Interest in aromaticity has recently been renewed as a result of reinterpretation of its electronic background. It was found¹ that the bond length equalization of aromatic compounds is due to σ -electron bonds, which tend to maintain equal lengths, whereas π -bonds tend to have alternated bond lengths, i.e., to be localized. In other words, they act against the σ -bond trend. The observed geometry is a compromise between these two tendencies. Recently Jug and Koester² have shown that these ideas work fairly well for quite a large number of different π -electron systems, including aromatic, heteroaromatic, partially nonaromatic, and antiaromatic compounds. Ideas of this kind appeared quite frequently in the past (cf. the references cited in refs 1 and 2), but it was only after the σ/π separation of energy has been effectively applied to the problem, that there appeared decisive arguments against the classical view that aromatic stability is due to the delocalization of π -electrons. Additionally, it has been found very recently by the use of factor analysis^{3,4} that aromaticity is a multidimensional phenomenon, and energetic, geometric, and magnetic criteria of aromatic character need not say exactly the same. Even more dramatically, energetic and geometric indices of aromatic character have occurred to be (almost) orthogonal!⁴

As the problem of aromatic character is of key importance and quite precise molecular geometries are now easily accessible for many compounds (from X-ray or neutron diffraction measurements or via Cambridge Structural Data Base⁵), we intend to recall and reexamine the utility of aromaticity index HOMA⁶ based on experimental bond lengths. This was invented some 20 years ago when not too many reliable molecular geometries for π -electron compounds were available. In spite of a very recent approach⁷ giving the possibility to study local aromatic character by using an energy-related parameter of aromaticity, an advantage of the HOMA procedure in comparison with most other aromaticity indices, particularly those based on energy, is the possibility of using HOMA both for the whole molecule as well as for any fragment with the π -electron systems. Additionally, what is very important, the HOMA treatment is not limited to the hydrocarbon systems only.

As the utility of the HOMA index to study the aromatic character has already been proven,⁸⁻¹⁰ the aim of this paper

is to show its further applications. We intend to show how inter- and intramolecular interactions in the crystalline state can modify molecular geometry, and hence modify the aromatic character of molecules.

REINTERPRETATION OF HARMONIC OSCILLATOR MODEL OF AROMATICITY (HOMA)

Following the new ideas^{1,2} of the σ and π contributions to decide about the shape of molecules with π -electron systems, it is reasonable to accept that

- (i) σ -electrons tend to form bonds of equal lengths
- (ii) π -electrons tend to form bonds with alternated lengths, i.e., localized bonds
- (iii) bonds of the real molecule with a π -electron system have lengths somewhere in between (i) and (ii).

This is in full agreement with the results of Jug and Koester.² Now let us define two "ideal" structures of the π -electron molecular system. One of them, $S(\sigma)$, describes a case when σ -effects dominate over π -effects, and the structure is built up of the bonds of equal or almost equal lengths. Then the $S(\pi)$ structure describes the opposite situation where π -electron effects dominate and all bonds exhibit alternated lengths. In the extreme case the single and double bonds can be marked out with their lengths such as in the typical single and double bonds in a molecule with sp^2 -hybridized conjugated atoms. The real structure is usually somewhere in between. The problem arises with how to find the numerical measure to estimate its position along the resonance coordinate between $S(\sigma)$ and $S(\pi)$. Following Jug and Koester,² one can define the resonance coordinate r as

$$r = \sum |\Delta r(i)| = \sum [(\Delta xi)^2 + (\Delta yi)^2 + (\Delta zi)^2]^{1/2} \quad (1)$$

where $\Delta(xi)$, $\Delta(yi)$, and $\Delta(zi)$ are deviations of an i th atom from its position in an equilibrium structure $S(eq)$. We assume that in the equilibrium structure of the molecules with a fully aromatic character the bonds have their optimal lengths. For such a case the resonance coordinate may be rewritten as

$$r^2 = \sum (R_{opt} - R_{ij})^2 \quad (2)$$

where the summation runs over all bonds between the atoms bearing π -electrons to the common system, and R_{opt} stands for the bond of optimal length (see next section). It is

immediately clear that the expression for r^2 is directly related to the formula for HOMA⁶ which reads as

$$\text{HOMA} = 1 - \alpha/n \sum (R_{\text{opt}} - R_{ij})^2 \quad (3)$$

where n is the number of bonds taken into summation and α is an empirical constant fixed in a way to give $\text{HOMA} = 0$ for a Kekulé structure of the typical aromatic system and equal to 1 for the system with all bonds equal to the optimal value R_{opt} . To apply the HOMA index to study the aromatic character of a given π -electron system, the following data are needed: the precise geometry of the molecule in question, i.e., its bond lengths R_{ij} ; the R_{opt} values for all types of bonds existing in the molecule in question; and the respective values of the constant α .

It was suggested in our earlier paper on HOMA⁶ that R_{opt} might be estimated by the minimization of energy of deformation $E(\text{def})$ due to the extension and compression of bonds from their observed lengths to the "optimal" lengths:

$$E(\text{def}) = -1/2(k(d) \sum [R_i - R(d)]^2 + k(s) \sum [R_i - R(s)]^2) \quad (4)$$

which finally leads to the formula

$$R_{\text{opt}} = [k(s)R(s) + k(d)R(d)]/[k(s) + k(d)] \quad (5)$$

where $k(s)$ and $k(d)$ stand for the force constants for the single and double bonds, respectively, whereas $R(s)$ and $R(d)$ are the lengths of single and double bonds, respectively. For multiatomic molecules, the force constants are not precisely defined quantities, and we accepted at that time,⁶ following the general trend¹¹ concerning the force constant values of single and double bonds, that $k(d) = 2k(s)$. This simplified eq 5 to the form

$$R_{\text{opt}} = [R(s) + 2R(d)]/3 \quad (6)$$

The physical meaning of this minimization is that the energy of extension of the typical double-bond $R(d)$ to the value of R_{opt} is equal to the energy of compression of the typical single-bond $R(s)$ to the length of R_{opt} . Equation 6 was applied many times⁸⁻¹⁰ even if the reference bond lengths $R(s)$ and $R(d)$ used in this formula changed slightly.¹⁰ In using eq 6, we have to select typical single- and double-bond lengths to be applied in it to give the value of R_{opt} . The following reasoning for this selection was accepted. In the modern definition of the resonance energy, it was assumed that the reference structures for aromatics have bond lengths as in acyclic polyenes^{12,13} or related systems for molecules with heteroatoms.^{14,15} Thus for the CC bond, there were taken single and double bonds from the gas-phase electron diffraction measurement of butadiene-1,3.¹⁶ For other bonds the closely related model structures which could resemble acyclic polyenes are either unavailable or their geometry could not be measured with sufficient precision. Table I presents the selected reference bond lengths together with the calculated R_{opt} values. It should be emphasized here that since the empirical constant α in eq 3 depends on the magnitude of the range between $R(s)$ and $R(d)$, it should be estimated for each kind of bond for which R_{opt} was estimated. The condition $\text{HOMA} = 0$ for the Kekulé structure should be understood now that $\text{HOMA} = 0$ for a system with bond lengths equal to the reference $R(s)$ and $R(d)$ bond lengths of Table I. From this condition the following formula for α constant results:

$$\alpha = 2([R(s) - R_{\text{opt}}]^2 + [R(d) - R_{\text{opt}}]^2)^{-1} \quad (7)$$

Table I. Reference Bond Lengths $R(s)$ and $R(d)$ for CC, CN, CO, CP, CS, NN, and NO, Appropriate R_{opt} Values and α Constants

type of bond	$R(s)$	$R(d)$	R_{opt} eq 6	$\alpha(\text{eq 6})$
CC ^a	1.467	1.349	1.388	257.7
CC ^b	1.524	1.334	1.397	98.89 ⁱ
CN ^c	1.465	1.269	1.334	93.52
CO ^d	1.367	1.217	1.265	157.38
CP ^e	1.814	1.640	1.698	118.91
CS ^f	1.807	1.611	1.677	94.09
NN ^g	1.420	1.254	1.309	130.33
NO ^h	1.415	1.164	1.248	57.21

^a Butadiene-1,3 [16]. ^b Ref 6. ^c $\text{H}_2\text{N}-\text{CH}_3$ and $\text{HN}=\text{CH}_2$, respectively, ref 17, pp 170 and 185. ^d HCOOH , monomer, ref 17, p 162. ^e $\text{H}_2\text{C}=\text{P}-\text{CH}_3$, ref 17, p 215. ^f $\text{S}(\text{CH}_3)_2$ and $\text{H}_2\text{C}=\text{S}$, respectively, ref 17, pp 220 and 218. ^g $(\text{CH}_3)_2\text{C}=\text{N}-\text{N}(\text{CH}_3)_2$ and $\text{H}_3\text{C}-\text{N}=\text{N}-\text{CH}_3$, respectively, ref 17, pp 177 and 185. ^h $\text{CH}_3-\text{O}-\text{N}=\text{O}$, ref 17, p 196. ⁱ This parametrization had been used in older papers,¹² and it is recommended now to use parameters CC^a. ^b See text.

Table II. HMO Atom-Atom Polarizabilities $\pi_{r,s}$ for Benzene and Butadiene-1,3

r	s	$\pi_{r,s}$ values for		ratio of $\pi_{r,s}$ values, butadiene/benzene
		benzene	butadiene-1,3	
1	1	0.398	0.626	1.57
1	2	-0.157	-0.402	2.56
1	3	0.009	0.045	5.00
1	4	-0.102	-0.268	2.63

Table I presents the α and R_{opt} values calculated for the most popular bonds in organic compounds. Application of the α constant in calculating the HOMA index is in variance with the older use of HOMA index,^{6,8-10} where the dependence of α value on the range of $R(s)$ and $R(d)$ was not recognized. The final formula for HOMA now reads

$$\text{HOMA} = 1 - \{ \alpha(\text{CC}) \sum [R(\text{CC})_{\text{opt}} - R_i]^2 + \alpha(\text{CX}) \sum [R(\text{CX})_{\text{opt}} - R_i]^2 + \alpha(\text{CY}) \sum [R(\text{CY})_{\text{opt}} - R_i]^2 + \alpha(\text{XY}) \sum [R(\text{XY})_{\text{opt}} - R_i]^2 \} / n \quad (8)$$

where α and R are specified by the type of bonds indicated in parentheses and have the meanings as mentioned in the text, and n stands for all bonds taken into consideration. This means that the contribution of each bond is taken with the same weight in estimation of the aromatic character of a given π -electron system.

CONSEQUENCES OF EQUALIZATION OF BOND LENGTHS IN A π -ELECTRON SYSTEM

Though π -electrons do not seem to be responsible for the aromatic stability, their different behavior as compared with that in a system with alternated bond length is due to equalization of bond lengths. To illustrate this, let us look at HMO atom-atom polarizability for positions (1,4), (1,3), (1,2), and (1,1, i.e., self polarizability) in benzene and butadiene-1,3. These data are presented in Table II. For all these cases the values for butadiene-1,3 are at least 1.5 times greater (as absolute values) than the data for benzene. Evidently, this illustrates well a much greater mobility of π -electrons in butadiene-1,3 than in benzene. It might be explained by equal overlapping of each 2pz orbital with both orbitals of this type residing at both neighboring atoms in benzene, and hence a more "stiff" π -electron structure in it,

Table III. HMO Atom-Atom Polarizabilities for Para-like Position in Series of Benzenoid Hydrocarbons

naphthalene (1,4)	0.134	tetracene (1,4)	0.156
anthracene (1,4)	0.151	(5,12)	0.250
(9,10)	0.217		

as compared with the situation in butadiene-1,3. Obviously, it results in much lower reactivity of benzene and its lower transmitting abilities for substituent effect. Marino et al.¹⁸ showed that the reaction constant of the Hammett-like equation employed to ionization potentials decreased in the sequence: furan, pyrrole, thiophene, and benzene. This finding was then interpreted within the simple HMO theory, and the sequence was related to both energetical (resonance energy) and HOMA indices of aromaticity.¹⁹

Furthermore, the atom-atom polarizability $\pi_{r,s}$ for r and s representing p -type positions, taken for a few compounds of decreasing aromaticity, shows that the values of $\pi_{r,s}$ increase in this direction. Some of these data are presented in Table III. It is well-known that in a series of linear polyacenes the aromatic character decreases with an increase of the number of rings.²⁰ Moreover, central rings of anthracene and tetracene are much more reactive than terminal ones as generally shown by the Hammett–Streitwieser position constants.^{21,22}

It seems reasonable to accept that although σ -electrons are responsible for the tendency of systems to maintain bond lengths as equal as possible, the π -electron structure of these molecules accommodates to these geometrical constraints and responds in such a way as if they did not know about it, being responsible for most of the properties of the system they were claimed for.

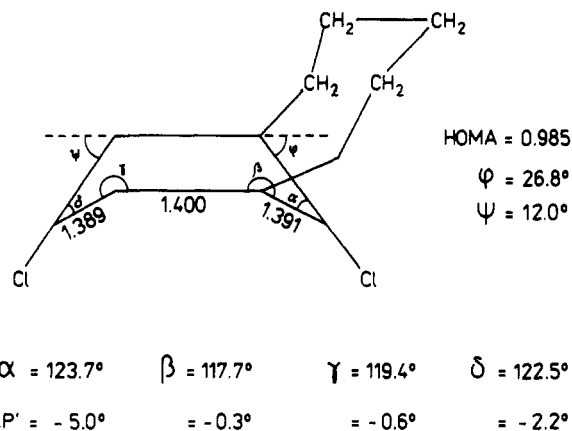
There is still an open question, if the π -electron systems in molecules or in their fragments always follow the rule that the σ -electron structure decides about their stability. It looks convincing in the case of typical aromatic systems (benzene, pyridine, or pyrimidine²) but is not so clear in the case of weakly aromatic or nonaromatic compounds for which it is difficult to define the resonance coordinate due to too many canonical structures involved in the description of the molecule. Additionally, it may be difficult to decide a priori which of them are important and which are less important. This problem undoubtedly needs further studies, both theoretical and experimental.

Since the interatomic distances, i.e., bond lengths, undoubtedly decide about overlapping between neighboring 2p_z atomic orbitals, it seems quite reasonable to use the HOMA parameter as a reliable measure of aromatic character. An additional advantage of using this model is that it is based on experimental data, which at the present are widely accessible either from X-ray or neutron diffractometric measurements or from Cambridge Structural Data Base.⁵ In variance with most other methods based on energetic characteristics of the molecule, the HOMA approach allows one to study both aromaticity of the whole system as well as of any chosen fragment with the π -electron system.

In the next section many typical examples of various π -electron systems are presented together with a few comparisons which should illustrate the advantage of using geometrical data for describing aromaticity of this kind of system.

RESULTS AND DISCUSSION

Application of the HOMA procedure to various π -electron molecules (or their fragments) will be presented so as to show how inter- and intramolecular interactions may affect their aromatic character.

**Figure 1.** Geometry of 1,4-dichloro(2,6)[5]metacyclophane,²⁷ HOMA value for the benzene ring and deviations from additivity for the bond angles in the ring (NAP values). Dihedral angle $\phi = 18.7^\circ$.

Planarity of π -Electron System as Criterion of Aromatic Character. It has long been known that aromatic systems are planar or nearly planar.²³ Benzene, the best-known aromatic compound and the one most often considered as an ideal aromatic system, in the crystal lattice is not planar but slightly folded (a small but statistically significant chair distortion from D_{6h} symmetry has recently been determined by a very accurate, low-temperature, neutron diffraction study²⁴). Most aromatic compounds studied in the crystalline state seem to be deformed from planarity as a result of crystal packing forces, but usually they may not be observed due to low precision of the measurements. Look, however, at the data for naphthalene in the next section. Distortions of this kind are easy to be realized in the crystal lattice since the force constants for bending carbon atoms out of plane in benzene ring (or in another aromatic system) are 1 order of magnitude smaller than for in-plane distortions of valence angles and 2 orders of magnitude smaller than for stretching distortions of the bond.²⁵ Much stronger distortions from planarity may be observed in the case of steric interactions, overcrowding, and chemical bonding requirements.

Distortions from Planarity Due to Chemical Bonding Requirements. Consider as an illustrative example the geometry and properties of 1,4-dichloro(2,6)[5]metacyclophane,²⁶ shown in Figure 1. NMR properties (i.e., proton chemical shifts at the benzene ring) argue for aromatic character of this compound. Reactivity, however, argues against it.²⁷ A HOMA value for this compound is 0.985, and it is very close to values for benzene itself: 0.969 for electron diffraction geometry, 0.979 for MW geometry, and 0.996 for X-ray geometry.¹⁰ A qualitative interpretation of this discrepancy was given by Bickelhaupt:²⁷ (i) reactivity is not necessarily a reliable criterion for the ground-state characteristics of molecules, and (ii) the unsymmetrical shape of the π -clouds on the two sides of the aromatic ring qualitatively shown in Figure 2²⁷ and rehybridization of the aromatic carbon atoms may contribute to these changes in reactivity.

It is well known from the simple LCAO MO considerations that the hybridization state of an atom in the molecule depends on valence angles between bonds of the atom with the adjacent atoms²⁸

$$\lambda^2 = -(\cos \phi)^{-1} \quad (9)$$

where λ is an exponent in the expression describing the hybridization state of an atom and ϕ is a bond angle in question. For π -electron systems hybridization is mostly sp^2 , hence in this case $\lambda^2 = 2$. Thus, any significant change of the bond

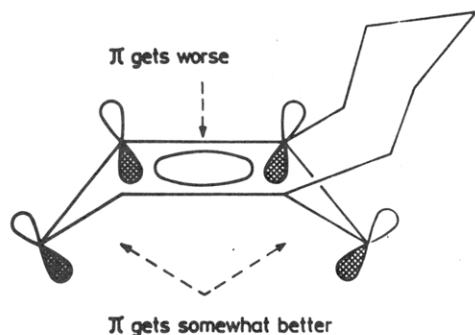


Figure 2. Scheme of distortion in π -electron overlapping in metacyclophane (as in Figure 1²⁷).

angle ϕ in π -electron systems from 120° may be considered as equivalent to the change in the hybridization state of the atom. The bond angle C11–C10–C1 (aliphatic) is in the above-discussed metacyclophane 114.8 , hence $\lambda^2 = 2.38$. Even if this approach is very approximate, the result shows a considerable change in hybridization from sp^2 to $sp^{2.38}$. Undoubtedly, these changes in σ -structure may be and should be reflected in π -electron structure and then in physicochemical properties due to π -electron structure. The changes of hybridization are reflected not only by exocyclic bond angles as presented above but also by deviations from additivity for bond angles inside the ring. The nonadditivity angular parameters,²⁹ which are the differences between the expected bond angles by additive substituent effect³⁰ and those which are observed, $NAP = \phi(\text{additive}) - \phi(\text{observed})$, illustrate this effect well. These values are given in Figure 1. All of them are negative since due to the nonplanarity of the ring the sum of all endocyclic angles in the ring is now less than 720° . Most of the nonadditivity is localized at positions 1 and 4. From the exocyclic bond angles it is seen that at C2 and C6 there are observed considerable deviations from sp^2 hybridization, too. Thus, these changes in bond angles, which in turn are related to changes in hybridization and in consequence in electron structure, may be very significant for reactivity, which in fact is observed.²⁷

Distortions from Planarity Due to Steric Interactions and Overcrowding. To illustrate the problem let us consider two cases in more detail: First, distortions from planarity due to spatial requirements in polycyclic, condensed benzenoid hydrocarbons and then distortions due to substituent effects which are nicely seen in octa-substituted derivatives of naphthalene.

For an illustration of the first problem, let us look at the geometry of tribenzo[*a,h,rst*]phenanthra[1,2,10-*cde*]pentaphene.³¹ Due to overcrowding it is immediately clear that this molecule is not planar. Torsion angles for most twisted parts of the aromatic moiety of the molecule depicted in Figure 3 by semicircles are $23\text{--}25^\circ$, and significant deformations in the values of bond angles are observed as well.³¹ In the same region, the lowest values of HOMA index are observed. However, the above-presented distortions from planarity are much smaller than those found in the case of the above-discussed metacyclophane. Hence it seems reasonable to take into account another explanation of this decrease of aromatic character. While looking at the geometry of benzenoid hydrocarbons, which do not have considerable steric interactions, e.g., perylene³² or coronene,³³ it is immediately clear that the way in which benzene rings are condensed has a very strong effect on the local aromatic character of benzene rings which built up these molecules. Figure 3 presents the HOMA

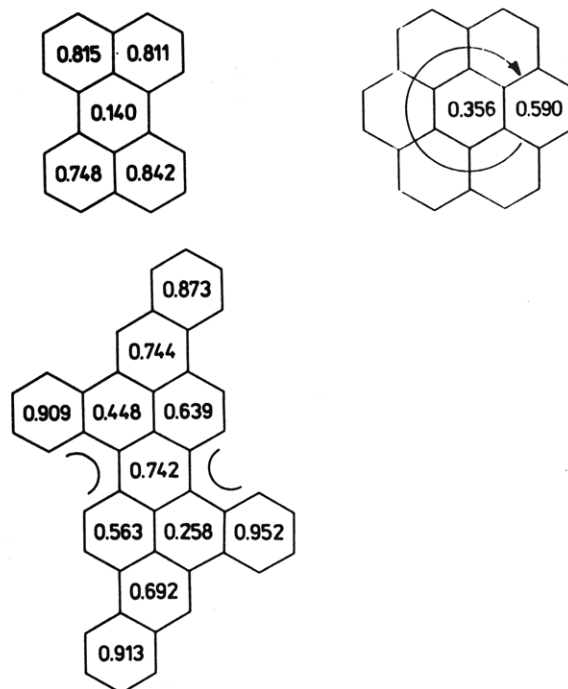


Figure 3. Local aromatic character of the individual benzene rings described by HOMA values for perylene,³² coronene,³³ and tribenzo[*a,h,rst*]phenanthra[1,2,10-*cde*]pentaphene.³¹ Semicircles depict most deformed parts of the molecules.

Table IV. HOMA Values and Nonplanarity Parameters for Few per-Substituted Derivatives of Naphthalene

octa-X-naphthalene, X =	HOMA	from the best plane of naphthalene moiety in A	
		maximal deviation of carbon atom	maximal deviation of first heavy atom of substituent
H ^a	0.810	0.003	0.019
methyl ^b	0.723	0.234	0.732
S-phenyl ^c	0.715	0.293	0.964
F ^d	0.743	0.007	0.033
Cl ^e	0.730	0.213	0.798
Br ^f	0.431	0.427	1.068

^a Ref 34. ^b Ref 35. ^c Ref 36. ^d Ref 37. ^e Ref 38. ^f Ref 39.

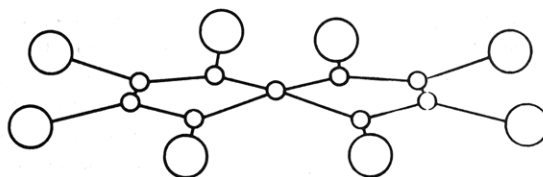


Figure 4. Projection of octa-bromonaphthalene³⁴ along the C9–C10 bond.

values for these three systems. In a further section this problem will be discussed in more detail.

Another important illustration of the steric effect which causes distortion from planarity of the benzenoid hydrocarbon may be per-substituted derivatives of naphthalene. Table IV presents the geometry and HOMA values for naphthalene and its octa-substituted derivatives with substituents like methyl group, fluorine, chlorine, and bromine. Additionally, the table contains maximal deviations of carbon atoms of the naphthalene moiety as well as the first heavy atoms of the substituent out of the best plane for carbon atoms. When we look at the HOMA values and these measures of distortion from planarity, it is immediately seen that only per-bromine

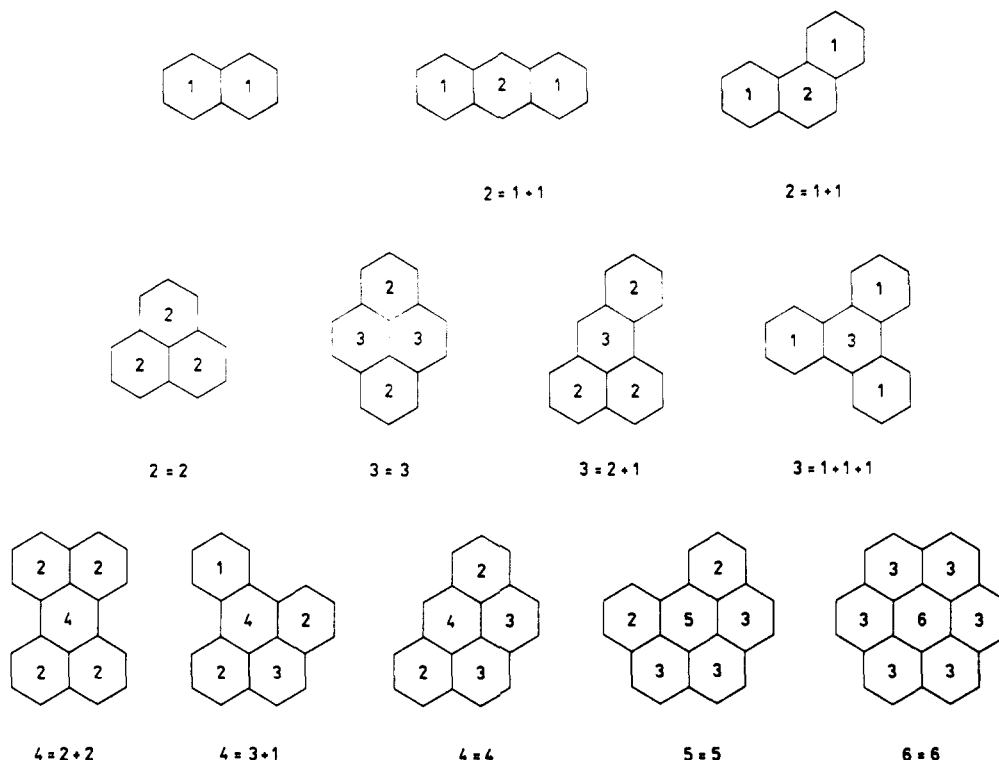


Figure 5. Classification of the ways in which individual phenylic rings may be condensed with other rings. Numbers inside the rings describe multiplicity of the ring, i.e., the number of other rings with which a given ring has a common CC bond.

derivative loses considerably its aromatic character whereas other per-substituted derivatives retain quite a lot of aromaticity, in spite of a considerable distortion from planarity. To visualize better these distortions from planarity Figure 4 presents a projection of octabromonaphthalene along the C9–C10 bond.

It may be concluded that for the range of deformation from planarity caused by F, Me, and Cl, and even by the S–Ph group, there is a smooth and practically insignificant decrease of aromatic character estimated by the values of HOMA index. The dramatic change is observed for the Br derivative. It means that the steric effect on aromatic character becomes significant somewhere in the size of substituent between S–Ph and Br.

Decrease of Aromatic Character as a Result of Topological Requirements Depending on the Way Benzene Rings Are Condensed with Each Other. It has long been known that the topology of molecules plays an important role in many of their chemical and physical properties.⁴⁰ Application of the HOMA index for estimation of a local aromatic character of an individual benzene ring condensed to other benzene rings in various ways in condensed polycyclic benzenoid hydrocarbons makes it possible to show how topological requirements act on geometry and via HOMA acts on aromaticity of the rings. In order to demonstrate this, let us look at HOMA values of individual rings condensed in various environments. Figure 5 presents schematically all possible closest environments of a given ring, whereas Figure 6 shows a few examples of practical realizations of these situations in molecules. Inside the rings in Figure 5 there are given numbers which describe multiplicity of these rings, i.e., information with how many other rings they are condensed.

While looking at these illustrative data of Figure 6 it is immediately clear that local aromatic character of the ring depends strongly on the environment, i.e., on the way in which the ring is condensed with other ones. Rings which are joined to the other ones by only one common CC bond, i.e., with

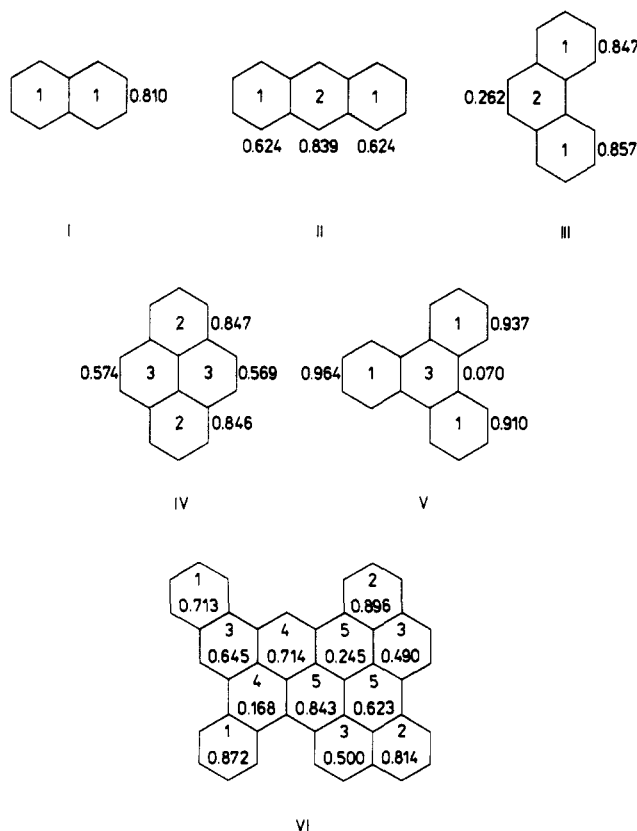


Figure 6. Few examples of condensed benzenoid hydrocarbons with HOMA values inside the ring together with its multiplicity (in parentheses). References for the geometry of these molecules are I,³⁴ II,⁴² III,⁴¹ IV,⁴³ V,⁴⁴ and VI.⁴⁵

multiplicity equal to 1 (type 1 in Figure 5), have their HOMA values decreased from the ideal state, i.e., from the value for benzene, by 0.1–0.2 unit. There are three possible ways to realize a benzene ring with two other rings condensed to it: $2 = 1 + 1$, linear or angular, and $2 = 2$. The simplest examples

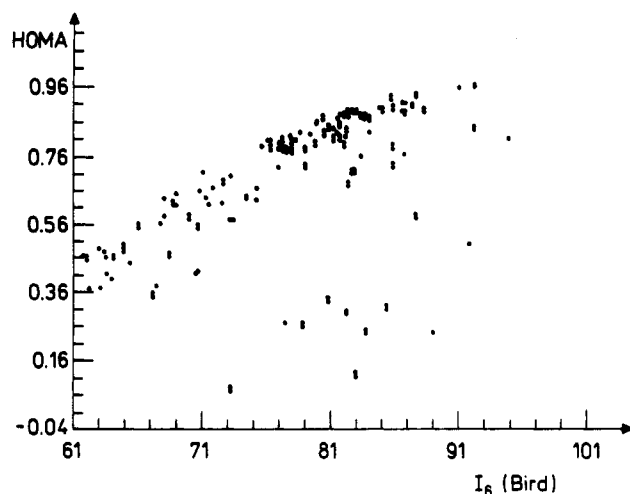


Figure 7. Scatter plot for HOMA values and I_6 values for 124 phenylic rings.

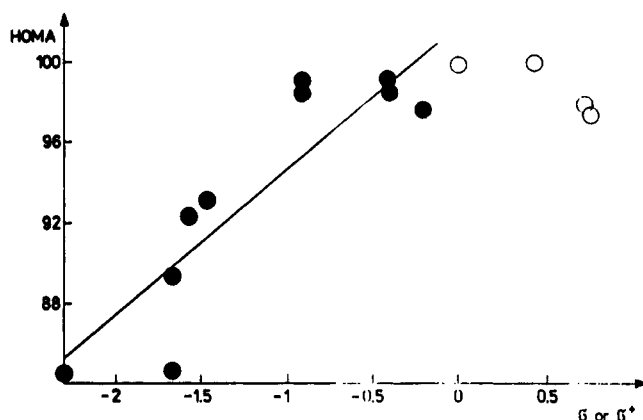


Figure 8. Scatter plot of HOMA values for para-substituted nitrobenzenes against substituent constants.

are anthracene, phenanthrene, and pyrene. While looking at HOMA values for benzene rings in these three cases it is seen that only in the case of phenanthrene does the central ring have a much decreased value of $\text{HOMA} = 0.262$, whereas for the other two cases HOMA values do not differ much from that in naphthalene. The situation becomes more difficult when we consider some more complicated systems (e.g., VI). The problem of dependence of the local aromatic character of the ring on its environment is very complex and requires deeper studies based on more numerous sets of data. Preliminary studies on using another geometry-based aromaticity index, I_6 ,^{46,47} applied to 124 phenylic rings in benzenoid hydrocarbons of which geometries were retrieved from CSDbase⁵ show that for more than 90% of these data this index correlates well with HOMA values, as it is shown in Figure 7. More detailed study of this problem is in progress.⁴⁸

Dependence of Aromatic Character of Benzene Ring on Substituent Effect. Benzene derivatives are very convenient systems to study for substituent effects on the aromatic character of the ring, since the unsubstituted benzene is considered to be the most aromatic π -electron system. We have estimated HOMA values for 11 para-substituted nitrobenzene derivatives for which precise geometry is available. The HOMA values for these compounds are in the range 0.844–0.999 and when they are plotted against the Hammett-type substituent constants σ or σ^+ one obtains a graph as in Figure 8. It is apparent that for electron-donating substituents ($\sigma < 0.0$) there is observed a rough linear dependence

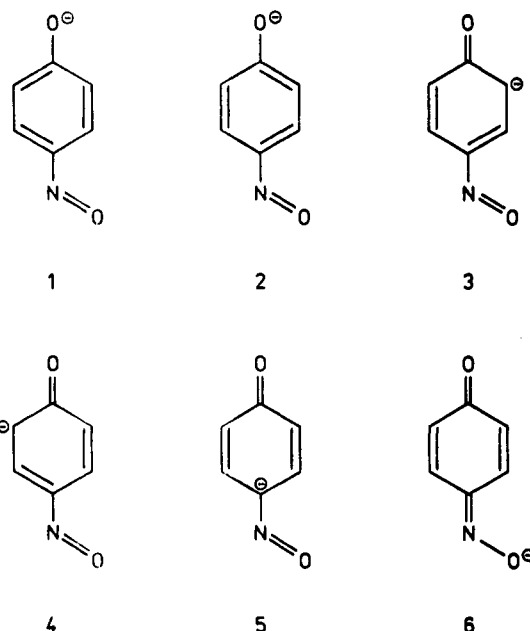


Figure 9. Scheme of canonical structures for *p*-nitrosophenolate and nitrophenolate anions. For *p*-nitrophenolate anion, NO should be replaced by NO_2 group.

of HOMA on σ of the form:

$$\text{HOMA} = 1.01(2) + 0.07(1) \sigma (\text{or } \sigma^+) \quad (10)$$

with correlation coefficient $r = 0.892$ for $n = 11$ (in a few cases there were two independent molecules in the crystal lattice, hence the total number of points in Figure 8 is $n = 14$). The σ^+ -constants are applied in those cases when we expect π -electron cooperative effect between the electron-accepting nitro group and electron-donating substituents. It should be mentioned, however, that looking at points for weakly electron-donating and electron-accepting character (empty circles) no significant dependence is observed. This finding may be related to the analysis of canonical structure weights estimated for these molecules⁴⁹ by use of the HOSE model.⁵⁰ All canonical structure weights describing the electron-donating effect of the substituent, i.e., weights 3–6 of the scheme in Figure 9, depend fairly well on substituent constants,⁴⁹ but the variation of canonical structure weights 5+6 is in the range 20–39%, as compared with 24.4–37.4% for weights of 3+4. This means that shortening of both central bond lengths in the ring as a result of substituent cooperative interactions may be considered as a main cause of the decrease of aromatic character observed with an increase of the π -electron cooperative effects between the substituents.

Another striking example is given by 2,4,6-triphenylpyrylium derivatives substituted in the phenyl ring in the para position (Figure 10). The HOMA values for the pyrylium ring for six derivatives (X = nitro, carboxy, methyl, hydroxy, *N,N*-dimethylamino, and unsubstituted) plotted against substituent constants gave the regression

$$\text{HOMA} = 0.52(1) + 0.11(2) \sigma (\text{or } \sigma^+) \quad (11)$$

with a correlation coefficient $r = 0.960$. Comparison of slopes in eqs 10 and 11 shows that the aromatic character of the pyrylium ring is more sensitive than that in the benzene ring, despite a much longer distance between the substituent and the site of changes in question. This may be rationalized in terms of two effects:

- (i) The pyrylium ring is significantly less aromatic than the phenylic one and, therefore, its π -electron system

as more favorable and hence most H-bonds are associated with this terminal. In consequence, at the oxygen atom of the nitroso group concentrated most of the negative charge of the anion, and this in turn induced the strongly indicated quinoid structure **6** (Figure 9). This structure, together with **5** gives rise to strongly localized double bonds along the long axis of the anion and is responsible for the decreased aromatic character of the phenylic ring in the sodium salt. A closer look at Table V supports this rationalization convincingly.

CONCLUSIONS

(i) Index HOMA is based on experimental bond lengths and hence represents both σ - and π -contributions to the shape of molecule.

(ii) Aromatic character of benzene ring immersed in various chemical environments measured by values of HOMA depends evidently on (a) intramolecular interactions due to topology or substituent effects and (b) intermolecular interactions as, e.g., intermolecular H-bonding.

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