CHEMISTRY
A EUROPEAN JOURNAL

DOI: 10.1002/chem.200700250

Application of AIM Parameters at Ring Critical Points for Estimation of π-Electron Delocalization in Six-Membered Aromatic and Quasi-Aromatic Rings

Marcin Palusiak*[a] **and Tadeusz M. Krygowski**[b]

Dedicated to Professor Günter Häfelinger on the occasion of his 70th birthday

Abstract: The AIM parameters at the *ring critical point* (the electron density and its Laplacian, the total electron energy density and both its components, potential and kinetic electron energy densities), have been intercorrelated with aromaticity indices: the geometry-based HOMA and the magnetism-based NICS, NICS(1), and $NICS(1)_{zz}$. A set of 33 phenylic rings having possibly a diversified aromatic character, and a set of 20 quasi-rings formed by intramolecular hydrogen and lithium bonds, have been taken into consideration. It has been found that the density of total electron energy, *H*, may serve as a new quantitative characteristic of π-electron delocalization. The dependences between *H* values and aromaticity indices are correlated ($cc_{H/\mathrm{HOMA}} = 0.99$, $cc_{H/\mathrm{NICS(1)}zz} = 0.95$).

Keywords: aromaticity • atoms in molecules theory • density functional calculations • HOMA • NICS

Introduction

A qualitative concept of aromaticity dates back to the second half of the 19th century. Kekulé defined aromatic systems as those which are similar to benzene,[1] whereas Erlenmeyer postulated those hydrocarbons with properties similar to those of benzene to be aromatic.[2] In this way a dichotomy between the structural and behavioral definition of the term was created. Recently Randić has argued that aromaticity is associated mostly with structure.[3] Nevertheless, various properties are observed which may indicate that a given system is aromatic. Recently it has been postulated that cyclic delocalized π-electron systems are typified by the following ground state properties:[4]

1) they are more stable than their olefinic analogues by an energy called "resonance energy", RE (nowadays often named aromatic stabilization energy, ASE);
2) they have bond lengths intermediate between those of typical single and double bonds;
3) when they are put in an external magnetic field a π-electron ring current is induced, leading to an increased diamagnetic susceptibility and typical diatropic chemical shifts of exocyclic protons in ^{1}H NMR spectra;
4) in addition, aromatic compounds generally undergo reactions in which the π-electron structure is conserved (the so-called aromatic substitution).[5]

Criteria (1–3) have been used for defining various quantitative measures of aromaticity, sometimes named as indices of aromaticity.

1) REs were first used to quantify the aromaticity (i.e. aromatic stability) of benzene,[6] and then of other benzenoid hydrocarbons.[7] Over the years a huge amount of work has been done by use of theoretical and experimental methods applying various models for reference states of given real molecules. The most applicable model (because it can be applied to a wide range of π-electron systems) is a model based on a bond separation reaction.[8] However, this model is not very reliable theoretically, because it does not take into account many subtle effects. The bond separation reaction belongs to a group of isodesmic (bond conserving) reactions[9] that compare potentially aromatic systems against a set of the

---

[a] Dr. M. Palusiak
Department of Crystallography and Crystal Chemistry
University of Łódź
Pomorska 149/153, 90–236 Łódź (Poland)
Fax: (+48) 42-6790447
E-mail: marcinp@uni.lodz.pl

[b] Prof. Dr. T. M. Krygowski
Department of Chemistry, Warsaw University
Pasteura 1, 02–093 Warsaw (Poland)

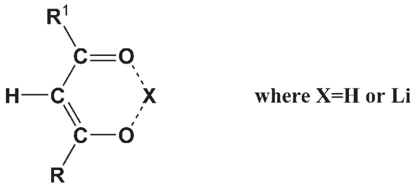
smallest prototype molecules that make up the ring structure. Another model, named the homodesmotic reaction[10] is based on a comparison of the energetic stability of the cyclic aromatic system with its linear or cyclic (but non-aromatic, i.e. devoid of π-electron delocalization) counterpart. Another approach based on σ/π separation led Maksic et al.[11] to formulate a concept of homostructural reactions which give some insight into the importance of the π-electron delocalization in relation to the stability of the system. This approach is closely related to the Shaik et al. and Jug et al.[12] analysis of the energetic relation between the σ- and π-structure of π-electron systems. A review dealing with the energetic aspects of π-electron delocalization can be found in reference [13].

2) The first quantitative approach for using bond alternation to estimate aromaticity was presented by Julg and François[14], and then refined in various ways.[15] For reviews of geometry-based indices of aromaticity see reference [16].
3) When the molecule is exposed to an external magnetic field a π-electron ring current is formatted that is associated with an anisotropy of the magnetic susceptibility, an increase of the exaltation of the magnetic susceptibility, typical ^{1}H NMR chemical shifts,[17] and the nucleus-independent chemical shift (NICS).[18] For reviews see references [17a] and [18b].

In principle aromaticity is a controversial issue for many reasons. First, the concept was originally associated with benzene: its structure,[1] or its chemical properties.[2] Moreover, at the very beginning the aromatic character of molecules was observed in planar molecules, and was thus associated with planarity of the π-electron system.[19] Presently it is well known that aromaticity does not necessarily have to be associated with planar molecules, even if the term is understood in its traditional manner (cf. points (1–4)). Good examples are *para*- and *meta*- cyclophanes,[20] pyrenophanes,[21] or per-substituted derivatives of polyacenes.[22] The planarity of aromatic molecules can be destroyed relatively easily.[23] Benzene in the crystalline state at 20 K is not planar, but has a chair conformation, due to sufficiently strong intermolecular forces in the crystal lattice.[24]

Second, as shown in many papers,[18b,22,25] monographs,[26] collections of reviews[27] and as summarized in Tetrahedron Report 520,[4] aromaticity is a collective phenomenon, and various criteria do not always give the same result.[28] Hence a variety of criteria should be used in the discussion of this term in any particular subject of investigation.[29]

Third, in many cases the term aromatic/aromaticity has been applied to systems which are far from the traditional understanding of these terms in organic chemistry,[30] hence their application to 3D systems in polyhedral boranes and related molecules,[31] metallobenzenes,[32] spherical systems such as fullerenes,[33] and many other non-traditional uses of the term.[26c] Therefore in many cases the term aromatic/aromaticity has frequently been extended by the use of various prefixes: *anti-*, *pseudo-*, *quasi-*, *homo-* and others, sometimes leading to confusion. One of the most common situations is the mixing of the terms *quasiaromaticity* and *pseudoaromaticity*. Literally the prefixes have their own meaning: *quasi: resembling, having the same but not all of the features;* and *pseudo: pretended, closely or deceptively resembling*. Both terms mentioned above were defined a long time ago.[26] Pseudoaromaticity was originally associated with the aromaticity of non-alternant π-electron hydrocarbons, such as azulene, fulvene, and others, whereas quasiaromaticity was associated with systems such as that presented in Scheme 1 (in the general case X may be a metallic ion). This is how we apply the terms *quasi*-aromaticity and *quasi*-ring when referring to the problems discussed in this paper.



Scheme 1.

Another important issue is the origin of aromaticity. Traditionally this is associated with "aromatic" stability, which is due to the π-electron delocalization.[18b,26c–d] However, for almost half of the 20th century scientists have postulated that the role of the σ-electron structure may be of importance.[12b–c,34] In the last two decades there has been lively discussion on this topic, but no final conclusion has been reached.

The quantitative characteristics of aromaticity may be considered from two points of view: as indicators describing the whole molecule (global aromaticity indices); and those which may be used locally, for individual rings (local aromaticity indices). In some cases only some fragments of a π-electron system may be considered, for example, the diatropic 18-carbon rim and paratropic 6-carbon hub in coronene[35] or its valence isomer.[36] Quantitatively these fragments may be described by a geometry-based aromaticity index, HOMA[15a,37] or by an electron density based index, FLU.[29]

The aim of this paper is to show that the Bader *Quantum Theory Atoms in Molecules*[38] (AIM) provides good tools to investigate the properties of a π-electron structure in the sense of electron density properties estimated in the ring critical point (RCP). A decade ago, Howard et al.[39] showed that $\rho(\sigma)$ and $\rho(\pi)$ values estimated in the RCP of individual rings of ten benzenoid hydrocarbons plotted against the aromaticity indices HOMA and NICS, gave rough linear relationships. Interestingly, it was not the case for Laplacians. These results encouraged us to undertake a more detailed study also employing other AIM parameters estimated in the RCP.

The following characteristics will be applied: electron density ρ, its Laplacian, $\nabla^2\rho$, the density of the total energy H and its components; kinetic (G) and potential (V) energy densities. A comparison of these parameters with other well known aromaticity indices, HOMA[15a,37] and NICS,[18] will allow us to show how useful the AIM parameters are for describing the aromaticity of both aromatic and quasi-aromatic rings.

Methodology

All the systems analyzed are shown in Figure 1. The geometries for obtaining the wave functions were taken from previous studies.[40] Geometry optimizations were carried out using the Möller–Plesset second-order perturbation theory[41] (MP2) in conjunction with the 6–31G(2d,p) basis set.[42] The frequency analysis at the same level of theory was carried out by the authors of the above-mentioned work[40] in order to verify that the optimized geometries correspond to stationary points. No imaginary frequencies were found. For such optimized geometries the MP2/6–31G(2d,p) wave function approximations were estimated by using the Gaussian 03 set of codes[43] and detailed analysis of the electron distribution function was made on the basis of *"Atoms in Molecules" Quantum Theory* proposed by R. W. F. Bader.[38] The AIM2000 program[44] was used for topological analysis of electron density. Special attention was focused on the parameters of the *ring critical points* (RCP) found for cyclic systems present in the investigated molecules, that is, for various phenylic rings and for quasi-rings formed by fragments of molecules interacting via hydrogen bonding or Li-bonding. The following parameters of electron density function were taken into account: electron density estimated at given RCP (ρ), its Laplacian ($\nabla^2\rho$) being the sum of the three eigenvalues of the Hessian of ρ, the density of the total energy of electrons (H) and its two components, the kinetic (G) and potential (V) electron energy densities. According to definition, $G>0$ and $V<0$. The relations shown in Equations (1) and(2) are known for $\nabla^2\rho$ and the energy densities mentioned above.

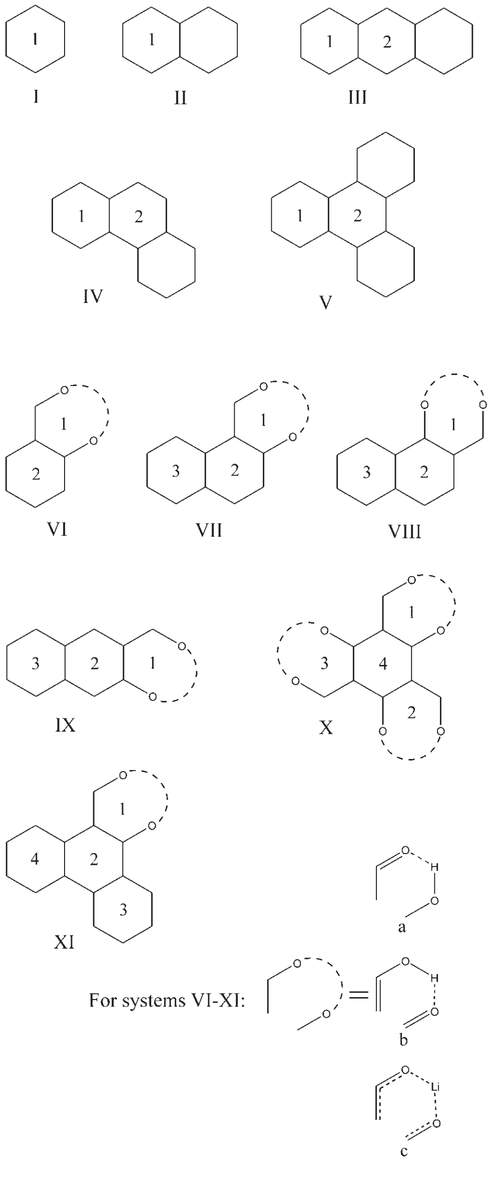


Figure 1. Scheme of the molecular systems taken into analysis.

$$\tfrac{1}{4}(\nabla^2\rho) = 2G + V \tag{1}$$

$$H = G + V \tag{2}$$

The parameters characterizing the RCPs under consideration were additionally related to well known and commonly used aromaticity indices: the geometry based HOMA[15a,37] and magnetic properties based NICS.[18]

According to its definition HOMA can be expressed by Equation (3)

$$\mathrm{HOMA} = 1-\frac{1}{n}\sum_{j=1}^{n} \alpha_i(R_{opt,i}-R_j)^2 \tag{3}$$

where n represents the total number of bonds in the molecule and α_i is a normalization constant (for C–C and C–O bonds: $R_{opt,CC}=1.388$ Å, $R_{opt,CO}=1.265$ Å, $\alpha_{C-C}=257.7$ and $\alpha_{C-O}=157.38$) fixed to give HOMA = 0 for a model non-aromatic system, for example, the Kekulé structure of benzene, and HOMA = 1 for a system with all bonds equal to the optimal value $R_{opt,i}$, assumed to be realized for fully aromatic systems.[14] The higher the HOMA value, the more "aromatic" the ring in question and, hence, the more delocalized the π electrons of the system.

As a magnetic indicator of a local aromaticity, the concept of the nucleus independent chemical shift (NICS) was used by employing the values of NICS(0),[18,45] NICS(1) and NICS(1)$_{zz}$.[46] NICS(0) is defined as the negative value of the absolute shielding computed at a ring center determined by the average of the heavy atoms' coordinates in the ring.

NICS(1) is a negative value of the absolute shielding measured 1 Å above the center of the ring, while NICS$(1)_{zz}$ is the out-of-plane component of the absolute shielding estimated in the same position as NICS(1). The GIAO method[47] at the Hartree–Fock level of theory with the 6–31++G(2d,p) basis set was applied to estimate all NICS values. Generally, the more negative the NICS value, the more aromatic the given ring.

Results and Discussion

Electron density *versus* electron energy density: The AIM-based analysis of electron density at different characteristic points, particularly at *bond critical points* (BCP), has been found to be a powerful tool in investigations of different chemical or physical phenomena.[48,49] It is well proved that the magnitude of the electron density function estimated at BCP can reflect the strength of a given bond. This relation has been found for strong bonds, covalent in nature, for example, C–C and C–O,[39,50] and for weak interactions, such as metal–ligand interactions[51] or hydrogen bonds.[52] Generally, it can be stated that the greater the value of the electron density at BCP, the stronger the bond. Also, the values of the total electron energy density (H) and its components, the kinetic (G, positive by definition) and potential (V, negative by definition) electron energy densities provide valuable information on the nature of the chemical bond. For the strongest bonds, mainly covalent in nature, the value of H is negative and relatively large in its absolute value. This is because for this kind of interaction the potential energy density, V, predominates in the sum of both components of H. In the case of the covalent bond, both interacting atoms are sharing electrons, thus creating a common electron pair, which is considerably localized in the region between these two atoms. Hence, the potential energy density estimated in BCP adopts large values, since the electrons are relatively stable energetically in the region around BCP. This is additionally accompanied by negative values of $\nabla^2\rho$, since at the BCP of the covalent bond the concentration of electron density is observed. The situation is different if one considers closed-shell interactions (e.g. ionic interactions). In this case the value of H is positive and close to zero. This results from the fact that the kinetic energy density, G, positive by definition, predominates over the negative V, since the electrons are energetically less stable in the region between two closed-shell systems. This effect is mainly connected with Pauli repulsions between two closed-shell systems. Additionally, it is accompanied by positive values of $\nabla^2\rho$ estimated at the corresponding BCP, around which the electron density is depleted. (The only known exception is the metal–metal or metal–ligand bonding with characteristics that represent a mix of shared and closed-shell interactions. In this case the value of H is usually negative and close to zero, as found for shared interactions, but with $\nabla^2\rho < 0$, as found for closed-shell interactions.[53]) More generally, it can be stated that the relatively large values of G are characteristic of those regions of molecules in which the electrons are moving faster, and relatively large values of V characterize those parts of molecules in which the electrons are more localized.[54] Relations between ρ and electron densities were nicely characterized during investigations on continua of interactions for different types of atoms.[55] This kind of analysis for the proton transfer reaction through the formation of O–H···O and N–H···O hydrogen bridges is also worth mentioning.[56] In this case the characteristics of covalent (D–H) and closed-shell (H···A) interactions in D–H···A bridges were found for ground states as well as for transition states, and the hydrogen bond parameters of the transition states were localized between typical covalent and typical closed-shell interactions. Therefore, it can be said that in the case of *bond critical points* an increase of electron density is accompanied by an increase of the magnitude of V. The magnitude of the total electron energy, H, follows the increase of the absolute values of V, which directly arise from the essential stability of electrons in the region of BCP for the strongest bonds, which are mainly covalent in nature.

In contrast to a great number of studies devoted to the application of AIM parameters to BCP, there are only a few works devoted to a systematic analysis of electron density at *ring critical point*.[39,57] It is therefore worth taking a closer look at these relations in the case when the *ring critical point* (RCP) parameters are considered.

Tables 1 and 2 contain the AIM-based parameters of ring critical points found for the systems shown in Figure 1. Reported here are the values of electron density (ρ), its Laplacian ($\nabla^2\rho$) and the density of the total energy of electrons (H) and its two components, and kinetic (G) and potential (V) electron energy densities estimated at proper RCPs. In addition, the values of the magnetism-based Schleyer's NICS(0), NICS(1), and NICS$(1)_{zz}$ and the geometry-based HOMA indices of aromaticity are also included. The analysis of mutual relations between RCP parameters for carbocyclic rings shows that there is a relation between ρ and the energy densities shown in Figure 2. These relations can be described by the use of linear regressions; however, for a large range of electron densities these regressions adopt a more complex form, as observed in the case of BCPs.[55,56,58] The values on these diagrams have been estimated for phenylic rings; however, a very similar relation can be found for quasi-rings. As seen, the greater the magnitude of electron density, the greater the absolute values of its components, G and V. This is in agreement with the observations made for BCPs. Moreover, H invariably adopts positive values, which in the case of BCPs was typical for closed-shell interactions. This should not be surprising, taking into consideration the fact that between *para*-carbon atoms there exist no classical chemical bonds, even if these atoms are partially sharing some electrons. However, if we compare the two cases, there are some general differences between the case of RCP and the case of BCP. Clearly, an increase of electron density at RCP in the phenylic ring is accompanied by an increase of the value of H. This is obviously connected with an increasing predominance of the G term over V. As mentioned

Table 1. HOMA, NICS, and parameters of the electron density function at *RCP* in phenylic rings of the systems shown in Figure 1. Values of ρ, λ, $\nabla^2\rho$, G_{RCP} and V_{RCP} are in atomic units. Values of H_{RCP} are in kcal mol^{-1} bohr^{-1}.

		HOMA	NICS(0)	NICS(1)	NICS(1)$_{zz}$	ρ	$\nabla^2\rho$	*H*	*G*	*V*
I	1	1.00	−9.635	−11.036	−32.222	0.020	0.163	5.128	0.033	−0.024
II	1	0.79	−9.753	−11.308	−31.770	0.020	0.157	5.000	0.031	−0.023
III	1	0.68	−8.141	−10.074	−27.790	0.020	0.154	4.953	0.031	−0.023
III	2	0.69	−12.901	−14.087	−38.669	0.019	0.151	4.905	0.030	−0.022
IV	1	0.86	−9.928	−11.372	−31.656	0.020	0.158	5.032	0.032	−0.023
IV	2	0.51	−6.138	−8.675	−22.028	0.019	0.148	4.813	0.029	−0.022
V	1	0.89	−8.935	−10.493	−28.738	0.020	0.159	5.054	0.032	−0.024
V	2	0.17	−1.692	−5.415	−10.569	0.018	0.136	4.557	0.027	−0.020
VIa	2	0.94	−9.861	−9.980	−26.878	0.020	0.159	5.084	0.032	−0.024
VIc	2	0.73	−6.183	−7.468	−20.213	0.019	0.153	4.928	0.031	−0.023
VIIa	2	0.69	−8.483	−9.270	−22.883	0.019	0.151	4.913	0.030	−0.022
VIIa	3	0.82	−9.680	−11.082	−31.020	0.020	0.157	5.019	0.031	−0.023
VIIc	2	0.40	−3.906	−6.120	−14.173	0.018	0.144	4.733	0.028	−0.021
VIIc	3	0.86	−9.298	−10.954	−30.491	0.020	0.158	5.029	0.032	−0.024
VIIIa	2	0.74	−8.960	−9.499	−23.952	0.019	0.151	4.927	0.030	−0.022
VIIIa	3	0.83	−9.471	−11.060	−30.630	0.020	0.158	5.028	0.031	−0.023
VIIIb	2	0.25	−0.481	−3.470	−6.590	0.018	0.142	4.699	0.028	−0.020
VIIIb	3	0.91	−9.228	−10.679	−29.391	0.020	0.160	5.066	0.032	−0.024
VIIIc	2	0.45	−4.155	−6.169	−14.839	0.019	0.145	4.736	0.029	−0.021
VIIIc	3	0.87	−9.319	−10.793	−29.859	0.020	0.159	5.040	0.032	−0.024
IXa	2	0.78	−10.584	−10.794	−27.691	0.019	0.153	4.965	0.030	−0.023
IXa	3	0.74	−8.587	−10.414	−28.883	0.020	0.156	4.998	0.031	−0.023
IXc	2	0.65	−8.234	−9.327	−23.982	0.019	0.149	4.843	0.030	−0.022
IXc	3	0.72	−6.533	−8.589	−23.628	0.020	0.155	4.969	0.031	−0.023
XIa	2	0.39	−4.939	−6.692	−13.591	0.018	0.140	4.683	0.028	−0.020
XIa	3	0.89	−9.316	−10.888	−29.815	0.020	0.160	5.063	0.032	−0.024
XIa	4	0.87	−9.420	−10.776	−29.855	0.020	0.158	5.047	0.032	−0.024
XIb	2	−0.06	2.106	−1.848	−0.129	0.017	0.132	4.460	0.026	−0.019
XIb	3	0.93	−8.612	−10.297	−27.673	0.020	0.161	5.077	0.032	−0.024
XIb	4	0.91	−8.501	−10.110	−27.734	0.020	0.160	5.073	0.032	−0.024
XIc	2	0.11	−0.681	−3.931	−6.220	0.018	0.135	4.508	0.027	−0.019
XIc	3	0.91	−8.989	−10.844	−28.874	0.020	0.161	5.064	0.032	−0.024
XIc	4	0.89	−8.797	−10.685	−29.392	0.020	0.159	5.049	0.032	−0.024

Table 2. Correlation matrix for the discussed numerical data estimated for phenylic rings. The values of $|cc|>0.9$ are in bold type.

	HOMA	NICS(0)	NICS(1)	NICS(1)$_{zz}$	ρ	$\nabla^2\rho$	*H*	*G*	*V*
HOMA	1.000								
NICS(0)	**−0.909**	1.000							
NICS(1)	−0.892	**0.985**	1.000						
NICS(1)$_{zz}$	**−0.914**	**0.975**	**0.994**	1.000					
ρ	**0.982**	−0.859	−0.865	−0.900	1.000				
$\nabla^2\rho$	**0.980**	−0.896	**−0.902**	**−0.933**	**0.990**	1.000			
H	**0.991**	−0.883	−0.874	**−0.905**	**0.990**	**0.988**	1.000		
G	**0.984**	−0.856	−0.859	−0.896	**0.999**	**0.990**	**0.994**	1.000	
V	**−0.981**	0.850	0.855	0.893	**−0.999**	**−0.989**	**−0.992**	**−1.000**	1.000

above, the predominance of *G* values are observed for those regions of molecules in which the electrons are moving faster, or in other words, in those regions of molecules in which the electrons are less localized. It can thus be expected that the analysis of *H* and its components in RCP can provide valuable information on a given ring if one considers the aromaticity of the ring, since the fundamental concepts of aromaticity are based on the phenomenon of delocalization of electrons within the ring system. (The authors are well aware of a vivid dispute on σ/π-electron contributions to the so-called aromatic stability; no decisive conclusion has been reached so far, so we follow the traditional view that the π-electron delocalization is the reason for aromatic stability.[12b,c,34,59]) There is a relation between ρ and *H* found for phenylic rings as well as for quasi-rings formed by intramolecular hydrogen bonds and Li···O interactions (see Figure 3). Clearly, there are three independent trends, corresponding to each group of the rings, illustrated by linear regressions with good correlation coefficients. The slope of the linear regression has the highest value for the data set corresponding to the phenylic rings, indicating that for these systems an increase of electron density is associated with an increase of the kinetic (*G*) component of *H* much more effectively than in the case of both types of quasi-rings. The

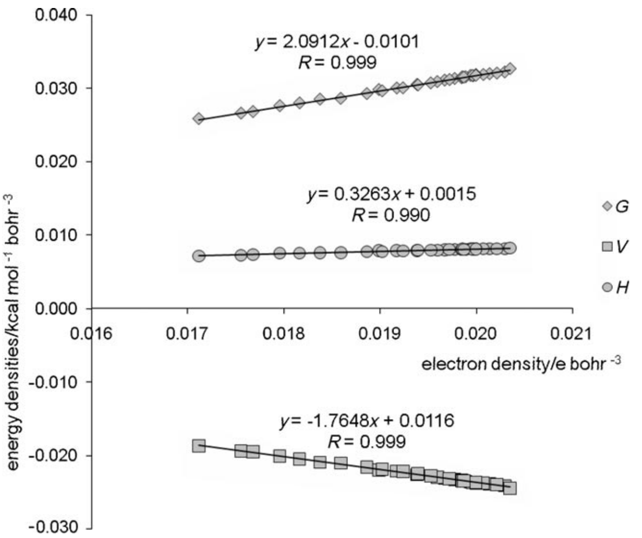


Figure 2. Total electron energy density (H) and its components, the kinetic (G) and potential (V) electron energy densities, plotted against electron density; all data estimated at *ring critical points*.

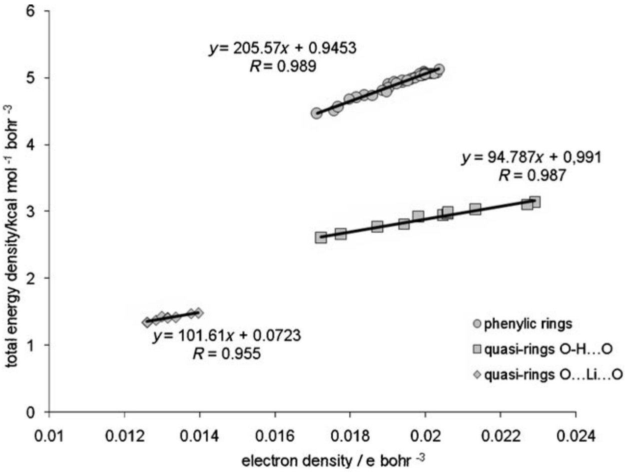


Figure 3. Interrelation between the total electron energy density (H) and the electron density, both estimated at RCPs of the phenylic and quasi-rings under discussion.

range of ρ values for phenylic rings is smaller than that for H-bridged rings, and most importantly, it is placed in the same region of the ρ axis. Therefore, if we consider only ρ, the phenylic rings and H-bridged rings are practically indistinguishable. However, the highest H values are observed for phenylic rings, and this suggests that in the center of these rings the electrons are strongly delocalized. This is in line with our conviction that these ring systems should be considered as aromatic ones. In the case of H-bridged rings the values of H are clearly lower than in phenylic rings, even if the electron density at RCP is greater than the corresponding ρ at RCP of the phenylic ring. (It is easy to imagine the case in which the electrons in two points corresponding to two different regions of molecules have the same kinetic and potential energies. If in one of these points the electron density adopts a greater magnitude, then the densities of electron energies are also greater, despite the same energetic characteristics of individual electrons). For the quasi-rings formed by Li-bonded ring systems both ρ and H have the lowest values.

In summary, it can be concluded that the physical meaning of the total electron energy density, and particularly both its components, are connected with the phenomenon of localization/delocalization of electrons. These three characteristics of electron energy densities are very strongly intercorrelated, as shown in Tables 2 and 4. In view of this we have chosen the total electron energy as the most holistic representation of electron energetic properties in the RCP. As shown in Figure 3, the total electron energy density seems to be the magnitude that is characteristic of a given kind of ring system. Therefore, it seems that the characteristics of *ring critical points* parameters, particularly of electron energy densities, should reflect some properties of the ring systems, for example, the aromaticity of a given ring. Therefore, it is worth analyzing the mutual interrelation between AIM-based parameters of RCP and aromaticity indices independent of electron density, namely, the geometry-based HOMA and the three magnetism-based NICS indices. For clarity in the subsequent discussion, phenylic rings and quasi-rings are discussed separately.

The case of phenylic rings: the relation between the densities of electron energies (*H*, *G*, and *V*) and aromaticity indices: Table 1 contains the AIM parameters of the *ring critical points* and additionally the HOMA and NICS(0), NICS(1) and NICS$(1)_{zz}$ values corresponding to these rings. Table 2 collects correlation coefficients (cc) estimated for linear regressions between all the above-discussed parameters. The most important scatter plots are shown in Figure 4, which presents the dependences of H on HOMA (4a); ρ on HOMA (4b); ρ on NICS$(1)_{zz}$ (4c); H on NICS$(1)_{zz}$ (4d) and finally HOMA on NICS$(1)_{zz}$ (4e). It should be emphasized that there are very good linear correlations for the dependences of ρ on the HOMA index as well as for the dependences of electron energy densities (H, G, and V) on HOMA. Particularly, the dependence of H on HOMA has a very high correlation coefficient. The NICS parameters correlates with ρ and electron energies densities in a much worse fashion, as shown in Figure 4c and 4d. It is interesting that the interdependence closest to linearity can be found for the NICS$(1)_{zz}$ parameter, (Table 2) in spite of the fact that the position of RCP is closest to the point of measurement of NICS(0). It is worth noting that NICS(0) may contain important contributions from local σ-bonding and that NICS$(1)_{zz}$ is considered as a magnetism-based index, in which these spurious contributions are minimized.[17a,60] However, in the case of all three NICS parameters, one point, corresponding to the inner ring of anthracene, is clearly out of place from the observed trends. This arises from the fact that the NICS value estimated for the inner ring of anthracene is overestimated. This effect is connected with the influence of ring currents present within the lateral

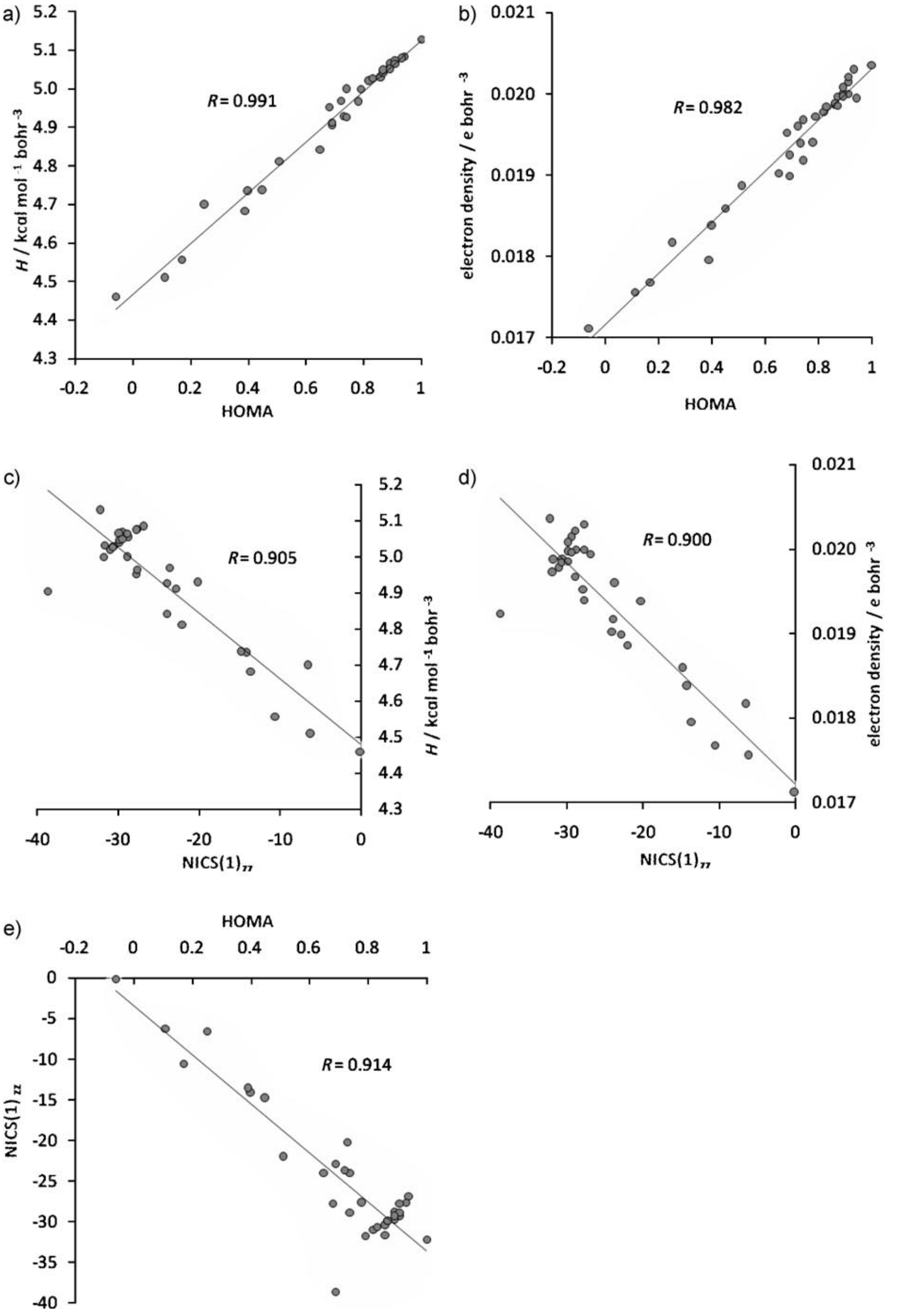


Figure 4. Mutual interrelations between HOMA, NICS(1)$_{zz}$, and electron density based parameters at RCPs of phenylic rings.

rings of this molecular system.[61] (Omitting this one point, the correlation coefficients estimated for the linear regressions are −0.929, −0.932, and −0.952 for NICS(0), NICS(1) and NICS(1)$_{zz}$, respectively). The worse correlations of NICS values may result from the fact that in general, NICS reflects the magnetic features of a molecular system perturbed in an external magnetic field, whereas both HOMA and the electron density parameters correspond to the ground state properties of the given molecular system.[17a,62]

Summarizing the observations mentioned above it can be suggested that the density of the total electron energy H (and its components, G and V) computed in the RCPs can be used for estimation of the electron delocalization effect within the phenylic ring system.

The case of quasi-rings: In Table 3 the parameters of RCPs corresponding to the appropriate quasi-rings as well as HOMA and NICS values have been collected. Tables 4 and 5 contain correlation coefficients estimated for linear regressions representing interdependences between the parameters discussed above. Selected scatter plots, that is, H against HOMA and NICS(1)$_{zz}$, are presented in the diagrams shown in Figure 5. Similarly to the case of phenylic rings, for quasi-rings all AIM-based parameters are very well intercorrelated for both Li- and H-bridged quasi-rings. However, only for hydrogen-bonded systems does the density of electron energies correlate well with HOMA, whereas the correlation for Li-bonded rings is unsatisfactory. The same can be observed for relations between H and NICS parameters. Additionally, as in the case of phenylic rings, for hydrogen-bonded rings the best correlation can be observed for NICS(1)$_{zz}$. In the case of NICS(0) there is even a lack of any direct dependence between this parameter and the H value. This can probably be explained by significant spurious contributions from the in-plane tensor components that are not related to π-electron delocalization.[62] The fact that there are some correlations for hydrogen-bonded rings, and that it is not possible to find such relations for Li-bonded systems, can be connected with the nature of the interactions in these two different chemical species. In lithium complexes the interaction between the organic moiety and the Li atom has a mainly electrostatic character with relatively low participation of the metal center in electron delocalization. The HOMA values calculated for the O-C-C-C-O sequence of atoms mainly reflect delocalization of charge surplus within this fragment of the molecule through the delocalization of π electrons. Mean-

Table 3. HOMA and NICS values and parameters of electron density function at *RCP* in quasi-rings of the systems shown in Figure 1. Values of ρ, λ, $\nabla^2\rho$, G_{RCP} and V_{RCP} are in atomic units. Values of H_{RCP} are in kcal mol^{-1} bohr $^{-1}$.

	quasi-ring	HOMA	NICS	NICS(1)	NICS(1)$_{zz}$	ρ	$\nabla^2\rho$	H	G	V
H-bonds										
VI	1 a	0.320	3.358	0.371	4.291	0.018	0.119	2.652	0.025	−0.021
VII	1 a	0.420	3.487	0.482	4.691	0.019	0.132	2.814	0.029	−0.024
VIII	1 a	0.430	3.722	0.623	5.262	0.019	0.127	2.765	0.027	−0.023
VIII	1 b	0.680	3.196	−0.033	2.573	0.023	0.160	3.134	0.035	−0.030
IX	1 a	0.170	3.781	0.800	5.735	0.017	0.115	2.600	0.025	−0.020
XI	1 a	0.490	3.721	0.616	5.257	0.020	0.141	2.938	0.030	−0.026
XI	1 b	0.680	3.120	−0.582	2.512	0.023	0.158	3.108	0.035	−0.030
X(H, H, H)	1 a,2 a,3 a	0.490	2.672	−0.012	3.459	0.020	0.137	2.914	0.030	−0.025
X(Li, H, H)	2 a	0.560	2.570	−0.069	3.122	0.021	0.142	2.965	0.031	−0.026
X(Li, H, H)	3 a	0.580	2.387	−0.162	3.042	0.021	0.119	2.983	0.031	−0.026
X(Li, Li, H)	3 a	0.620	2.350	−0.202	2.782	0.021	0.148	3.026	0.032	−0.027
Li complexes										
VI	1 c	0.630	3.645	0.444	3.194	0.013	0.070	1.337	0.015	−0.013
VII	1 c	0.730	3.517	0.918	3.978	0.014	0.078	1.475	0.017	−0.015
VII	1 c	0.760	3.933	0.669	4.105	0.013	0.072	1.378	0.016	−0.014
IX	1 c	0.430	4.142	0.842	4.646	0.013	0.070	1.342	0.015	−0.013
XI	1 c	0.820	3.634	1.345	5.885	0.014	0.079	1.479	0.017	−0.015
X(Li, H, H)	1 c	0.630	3.080	0.181	3.061	0.013	0.074	1.422	0.016	−0.014
X(Li, Li, H)	1 c	0.710	2.848	0.074	2.817	0.013	0.074	1.420	0.016	−0.014
X(Li, Li, H)	2 c	0.670	3.017	0.166	2.941	0.013	0.074	1.410	0.016	−0.014
X(Li, Li, Li)	1 c,2 c,3 c	0.730	2.841	0.077	2.747	0.013	0.075	1.417	0.017	−0.014

Table 4. Correlation matrix for the discussed numerical data estimated for H-bridged quasi-rings. In bold type are the values of $|cc| > 0.9$.

	HOMA	NICS	NICS(1)	NICS(1)$_{zz}$	ρ	$\nabla^2\rho$	H	G	V
HOMA	1.000								
NICS	−0.593	1.000							
NICS(1)	−0.831	0.778	1.000						
NICS(1)$_{zz}$	−0.851	0.802	**0.960**	1.000					
ρ	**0.961**	−0.460	−0.784	−0.807	1.000				
$\nabla^2\rho$	0.824	−0.254	−0.631	−0.660	**0.901**	1.000			
H	**0.977**	−0.555	−0.802	−0.823	**0.987**	0.859	1.000		
G	**0.965**	−0.480	−0.792	−0.815	**1.000**	0.895	**0.991**	1.000	
V	**−0.963**	0.473	0.790	0.814	**−1.000**	−0.897	**−0.989**	**−1.000**	1.000

Table 5. Correlation matrix for the discussed numerical data estimated for Li complexes. In bold type are the values of $|cc| > 0.9$.

	HOMA	NICS	NICS(1)	NICS(1)$_{zz}$	ρ	$\nabla^2\rho$	H	G	V
HOMA	1.000								
NICS	−0.331	1.000							
NICS(1)	0.139	0.745	1.000						
NICS(1)$_{zz}$	0.113	0.710	**0.960**	1.000					
ρ	0.717	−0.284	0.405	0.366	1.000				
$\nabla^2\rho$	0.710	−0.373	0.316	0.285	**0.991**	1.000			
H	0.689	−0.390	0.276	0.247	**0.955**	**0.983**	1.000		
G	0.711	−0.370	0.320	0.288	**0.993**	**1.000**	**0.979**	1.000	
V	−0.712	0.366	−0.325	−0.292	**−0.995**	**−0.999**	**−0.973**	**−1.000**	1.000

while both NICS and *H* parameters indicate Li-bonded systems as those which are characterized by relatively low electron delocalization within the ring. On the other hand, the hydrogen bonds present in hydrogen-bonded quasi-rings belong to the group of resonance assisted hydrogen bonds. These kinds of systems have been thoroughly investigated, and participation of the H-bridge in the electron delocalization effect has been well documented.[63]

Summarizing, the geometry-based HOMA correlates linearly with AIM-based parameters estimated for H-bridged quasi-rings. The magnetic-based NICS(1) and NICS(1)$_{zz}$ indices of aromaticity and AIM-based parameters follow the same trends, but with a lower precision. Therefore, it can be concluded that in this case all these parameters reflect the same property of the analyzed ring system.

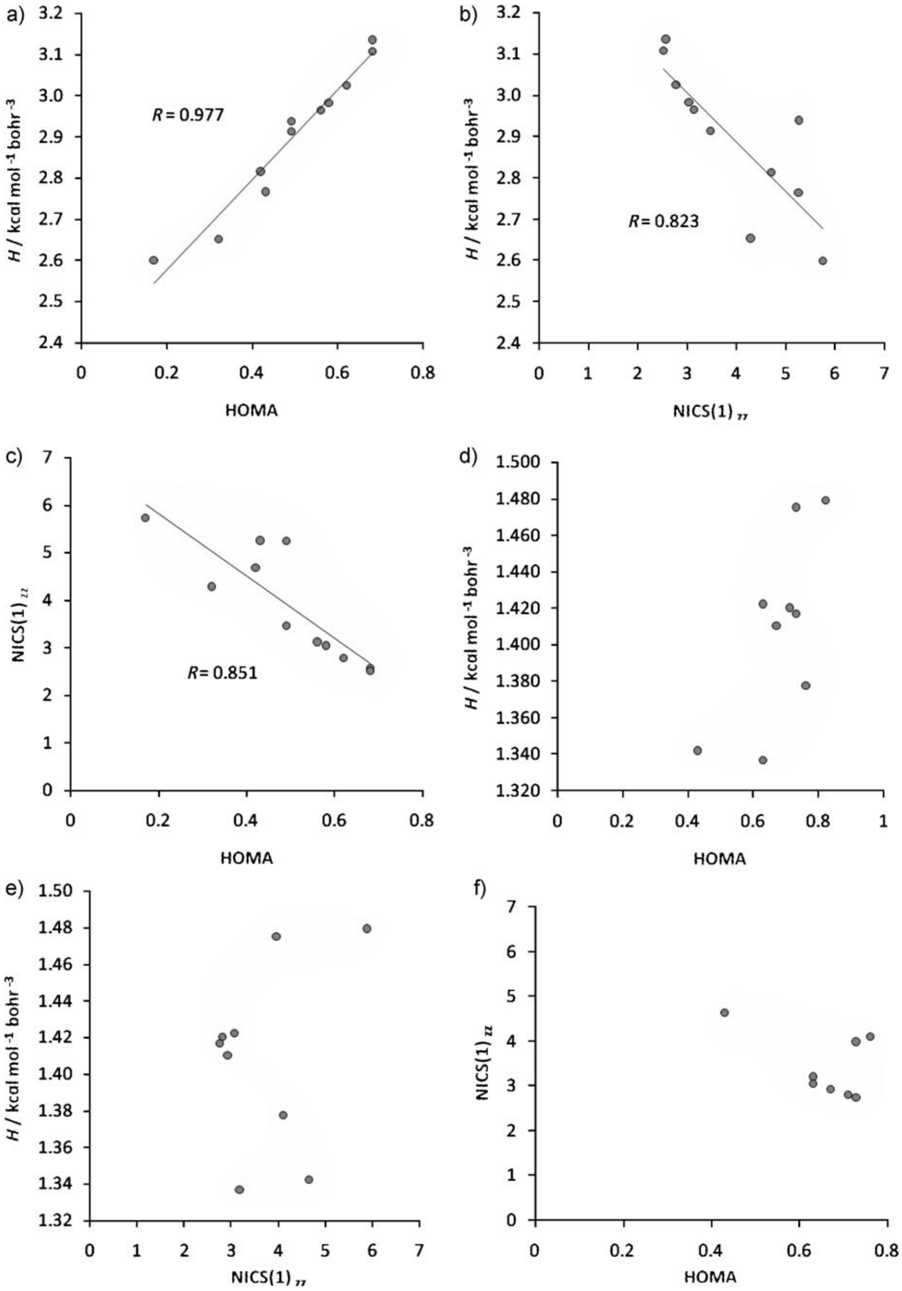


Figure 5. Mutual interrelations between HOMA, NICS(1)$_{zz}$, and electron density based parameters at RCPs of hydrogen-bonded quasi-rings (a, b, c) and Li complexes (d, e, f).

Conclusion

For carbocyclic and quasi-rings the density of the total electron energy, (*H*), its kinetic (*G*) and potential (*V*) components as well as electron density in RCPs are intercorrelated well. In the case of carbocyclic rings and hydrogen-bonded quasi-rings, *H*, *G*, and *V* correlate with the geometry-based aromaticity index HOMA and magnetism-based aromaticity index NICS(1)$_{zz}$. Particularly good correlations are found for *H*. Thus the density of the total electron energy, (*H*), computed in the RCP may serve as a new and easily estimated quantitative characteristic of π-electron delocalization.

Acknowledgements

M. P. gratefully acknowledges the Foundation for Polish Science for a postdoctoral fellowship. Authors thank the Warsaw Supercomputing

Center (ICM) for a generous allotment of computer time (Computational Grants No. G11–5 and G29–5).

---

[1] A. Kekulé, *Bull. Soc. Chim. France* **1865**, *3*, 98.

[2] E. Erlenmayer, *Liebigs Ann.* **1866**, *137*, 327.

[3] M. Randić, *Chem. Rev.* **2003**, *103*, 3449.

[4] T. M. Krygowski, M. K. Cyrañski, G. Häfelinger, A. R. Katritzky, *Tetrahedron* **2000**, *56*, 1783.

[5] R. Taylor, *Electrophilic Aromatic Substitution*, Wiley, New York, **1990**.

[6] a) L. Pauling, J. Sherman, *J. Chem. Phys.* **1933**, *1*, 362; b) G. B. Kistiakowski, J. R. Ruhoff, H. A. Smith, W. E. Vaughan, *J. Am. Chem. Soc.* **1936**, *58*, 146.

[7] G. W. Wheland, *The theory of resonance and its application to organic chemistry*, Wiley, New York, **1944**.

[8] W. J. Hehre, L. Radom, P. von R. Schleyer, J. A. Pople, *Ab-initio Molecular Orbital Theory*, Wiley, New York, **1986**, p. 371.

[9] a) W. J. Hehre, R. Ditchfield, L. Radom, J. A. Pople, *J. Am. Chem. Soc.* **1970**, *92*, 4796; b) L. Radom, W. J. Hehre, J. A. Pople, *J. Am. Chem. Soc.* **1971**, *93*, 289; c) P. George, M. Trachtman, C. W. Bock, A. M. Brett, *J. Chem. Soc.* **1977**, *6*, 1222.

[10] a) W. J. Hehre, R. T. McIver, J. A. Pople, P. v .R. Schleyer, *J. Am. Chem. Soc.* **1974**, *96*, 7162; b) L. J. Radom, *J. Chem. Soc. Chem. Commun.* **1974**, 403; c) P. George, M. Trachtman, C. W. Bock, A. M. Brett, *Theor. Chim. Acta* **1975**, *38*, 121; d) P. George, M. Trachtman, C. W. Bock, A. M. Brett, *J. Chem. Soc.* **1977**, *8*, 1036.

[11] a) Z. B. Maksić, D. Barjić, T. Müller, *J. Phys. Chem. A* **2006**, *110*, 10135; b) D. Barjić, B. Kovačević, Z. B. Maksić, T. Müller, *J. Phys. Chem. A* **2005**, *109*, 10594.

[12] a) S. S. Shaik, P. C. Hiberty, G. Ohanessian, J. M. Lefour, *J. Org. Chem.* **1985**, *50*, 4657; b) K. Jug, P. C. Hiberty, S. S. Shaik, *Chem. Rev.* **2001**, *101*, 1477; c) K. Jug, A. M. Köster, *J. Am. Chem. Soc.* **1990**, *112*, 6772.

[13] M. K. Cyrañski, *Chem. Rev.* **2005**, *105*, 3773.

[14] A. Julg, P. François, *Theor. Chim. Acta* **1967**, *7*, 249.

[15] a) J. Kruszewski, T. M. Krygowski, *Tetrahedron Lett.* **1972**, *13*, 3839; b) C. W. Bird, *Tetrahedron* **1985**, *41*, 1409; c) T. M. Krygowski, *J. Chem. Inf. Comput. Sci.* **1993**, *33*, 70; d) T. M. Krygowski, M. K. Cyrañski, *Tetrahedron* **1996**, *52*, 1713.

[16] T. M. Krygowski, M. K. Cyrañski, *Chem. Rev.* **2001**, *101*, 1385.

[17] a) T. Heine, C. Corminboeuf, G. Seifert, *Chem. Rev.* **2005**, *105*, 3889; b) P. Lazzaretti, *Prog. Nucl. Magn. Reson. Spectrosc.* **2000**, *36*, 1; c) F. Sondheimer, *Pure Appl. Chem.* **1963**, *7*, 363; d) M. J. S. Dewar, *Tetrahedron, Tetrahedron Suppl.* **1996**, *8*, 75; e) J. A. Elvidge, L. M. Jackman, *J. Chem. Soc.* **1961**, 859.

[18] a) P. von R. Schleyer, H. Jiao, *Pure Appl. Chem.* **1996**, *68*, 209; b) Z. Chen, C. S. Wannere, C. Corminboeuf, R. Puchta, P. von R. Schleyer, *Chem. Rev.* **2005**, *105*, 3842.

[19] For historical outline see: a) E. Müller, *Neuere Anschauungen der organischen Chemie*, Springer, Berlin **1957**, Chapter B.III; Polish edition p. 421; b) C. K. Ingold, *Structure and mechanism in organic chemistry*, Cornell University Press, Ithaca **1953**, Chapter IV, Russian edition, p. 129.

[20] a) L. W. Jenneskens, J. C. Klammer, H. J. R. de Boer, W. H. de Wolf, F. Bickelhoupt, C. H. Stam, *Angew. Chem.* **1984**, *96*, 236; *Angew. Chem. Int. Ed. Engl.* **1984**, *23*, 238; b) F. Bickelhoupt, *Pure Appl. Chem.* **1990**, *62*, 373; c) F. Dijkstra, J. H. van Lenthe, Int. *J. Quant. Chem.* **1999**, *74*, 213; d) B. Ma, H. M. Sulzbach, R. B. Remington, H. F. Schaefer III *J. Am. Chem. Soc.* **1995**, *117*, 8392.

[21] a) G. J. Bodwell, D. O. Miller, R. Vermeij, *J. Org. Chem.* **2001**, *66*, 2093; b) G. J. Bodwell, J. N. Bridson, M. K. Cyrañski, J. W. J. Kennedy, T. M. Krygowski, M. R. Mannion, D. O. Miller, *J. Org. Chem.* **2003**, *68*, 2089.

[22] R. A. Pascal Jr. , *Chem. Rev.* **2006**, *106*, 4809.

[23] a) F. A. L. Anet, I. Yavari, *Tetrahedron* **1978**, *34*, 2879; b) K. B. Lipkowitz, M. A. Peterson, *J. Comput. Chem.* **1993**, *14*, 121; c) F. Dijkstra, J. H. v. Lenthe, *Int. J. Quant. Chem.* **1999**, *74*, 213.

[24] G. A. Jeffrey, J. R. Ruble, R. K. McMullan, J. A. Pople, Proc. Royal Soc. , London **1987**, 47.

[25] a) A. Soncini, E. Steiner, P. W. Fowler, R. W. A. Havenith, L. W. Jenneskens, *Chem. Eur. J.* **2003**, *9*, 2974; b) F. De Proft, P. W. Fowler, R. W. A. Havenith, P. v. R. Schleyer, G. Van Lier, P. Geerlings, *Chem. Eur. J.* **2004**, *10*, 940; c) M. Torrent-Sucarrat, J. M. Luis, M. Sola, *Chem. Eur. J.* **2005**, *11*, 6024; d) A. Stanger, *Chem. Eur. J.* **2006**, *12*, 2745; e) A. Stanger, *J. Org. Chem.* **2006**, *71*, 883; f) B. Hajgato, M. S. Deleuze, K. Ohno, *Chem. Eur. J.* **2006**, *12*, 5757; g) P. Bultinck, S. Fias, R. Ponec, *Chem. Eur. J.* **2006**, *12*, 8813.

[26] a) D. Lloyd, D. R. Marshall, *Chem. Ind.* **1964**, 1760; b) D. Lloyd, D. R. Marshall, *Quasi - Aromatic Compounds Examples of Regenerative, or Meneidic Systems. in Aromaticity, Pseudo - Aromaticity, Anti - Aromaticity, Proceedings of an International Symposium*, Jerusalem, 31.03–3.04 **1970**, (Eds.: E. D. Bergmann, B. Pullman) The Israel Academy of Sciences and Humanities: Jerusalem, **1971**; c) P. J. Garrat, *Aromaticity*, McGraw - Hill, **1986**; d) V. I. Minkin, M. N. Glukhovtsev, N. Ya. Simkin, *Aromaticity and Antiaromaticity - Electronic and Structural Aspects*, Wiley, New York, **1994**.

[27] a) Topical issue of *Chem. Rev.* **2001**, *101*, entitled “ *Aromaticity*”; b) Partially topical issue of *Chem. Rev.* **2005**, 105, entitled *“Delocalization - Pi and Sigma”*.

[28] a) A. R. Katritzky, P. Barczyñski, G. Mussumura, D. Pisano, M. Szafran, *J. Am. Chem. Soc.* **1989**, *111*, 7; b) K. Jug, A. Koester, *J. Phys. Org. Chem.* **1991**, *4*, 163; c) T. M. Krygowski, A. Ciesielski, C. W. Bird, A. Kotschy, *J. Chem. Inf. Comput. Sci.* **1995**, *35*, 203; d) M. K. Cyrañski, T. M. Krygowski, A. R. Katritzky, P. v. R. Schleyer, *J. Org. Chem.* **2002**, *67*, 1333.

[29] E. Matito, M. Duran, M. Solá, *J. Chem. Phys.* **2005**, *122*, 014109.

[30] M. B. Smith, J. March, *March’s Advances Organic Chemistry*, 5th Edition, Wiley, New York, **2001**, p. 48.

[31] For review see: R. V. Williams, *Chem. Rev.* **2001**, *101*, 1119.

[32] For review see: J. R. Bleeke, *Chem. Rev.* **2001**, *101*, 1205.

[33] For review see: R. V. Williams, *Chem. Rev.* **2001**, *101*, 1185.

[34] a) H. C. Longuet - Higgins, L. Salem, *Proc. Royal Soc. London* **1959**, A251, 172; b) C. A. Coulson, W. T. Dixon, *Tetrahedron* **1962**, *17*, 215; c) N. D. Epiotis, *New J. Chem.* **1984**, *8*, 11; d) S. S. Shaik, P. C. Hiberty, *J. Phys. Chem.* **1988**, *92*, 5086; e) S. S. Shaik, A. Shurki, D. Danovich, P. C. Hiberty, *J. Mol. Struct.* **1997**, *155*, 398; f) Z. B. Maksić, D. Barić, I. Petjanek, *J. Phys. Chem. A* **2000**, *104*, 10873.

[35] P. W. Fowler, E. Steiner, *J. Phys. Chem.* A **1997**, *101*, 1409.

[36] A. Ciesielski, M. K. Cyrañski, T. M. Krygowski, W. P. Fowler, M. Lillington, *J. Org. Chem.* **2006**, *71*, 6840.

[37] T. M. Krygowski, *J. Chem. Inf. Comput. Sci.* **1993**, *33*, 70.

[38] R. F. W. Bader, *Atoms in Molecules: A Quantum Theory*, Oxford University Press, New York, **1990**.

[39] S. T. Howard, T. M. Krygowski, *Can. J. Chem.* **1997**, *75*, 1174.

[40] T. M. Krygowski, J. E. Zachara, B. Osmiałowski, R. Gawinecki, *J. Org. Chem.* **2006**, *71*, 7678.

[41] a) M. Head-Gordon, J. A. Pople, M. J. Frisch, *Chem. Phys. Lett.* **1988**, *153*, 503; b) M. J. Frisch, M. Head-Gordon, J. A. Pople, *Chem. Phys. Lett.* **1990**, *166*, 275; c) M. J. Frisch, M. Head-Gordon, J. A. Pople, *Chem. Phys. Lett.* **1990**, *166*, 281; d) M. Head-Gordon, T. Head-Gordon, *Chem. Phys. Lett.* **1994**, *220*, 122; e) S. Saebo, J. Almlöf, *Chem. Phys. Lett.* **1989**, *154*, 83.

[42] a) R. Ditchfield, W. J. Hehre, J. A. Pople, *J. Chem. Phys.* **1971**, *54*, 724; b) W. J. Hehre, R. Ditchfield, J. A. Pople, *J. Chem. Phys.* **1972**, *56*, 2257; c) P. C. Hariharan, J. A. Pople, *Mol. Phys.* **1974**, *27*, 209; d) V. A. Rassolov, M. A. Ratner, J. A. Pople, P. C. Redfern, L. A. Curtiss, *J. Comput. Chem.* **2001**, *22*, 976.

[43] Gaussian 03, Revision C.02, M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, J. A. Montgomery, Jr., T. Vreven, K. N. Kudin, J. C. Burant, J. M. Millam, S. S. Iyengar, J. Tomasi, V. Barone, B. Mennucci, M. Cossi, G. Scalmani, N. Rega, G. A. Petersson, H. Nakatsuji, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, M. Klene, X. Li, J. E. Knox, H. P. Hratchian, J. B. Cross, V. Bakken, C. Adamo, J. Jaramillo, R. Gomperts, R. E.

Stratmann, O. Yazyev, A. J. Austin, R. Cammi, C. Pomelli, J. W. Ochterski, P. Y. Ayala, K. Morokuma, G. A. Voth, P. Salvador, J. J. Dannenberg, V. G. Zakrzewski, S. Dapprich, A. D. Daniels, M. C. Strain, O. Farkas, D. K. Malick, A. D. Rabuck, K. Raghavachari, J. B. Foresman, J. V. Ortiz, Q. Cui, A. G. Baboul, S. Clifford, J. Cioslowski, B. B. Stefanov, G. Liu, A. Liashenko, P. Piskorz, I. Komaromi, R. L. Martin, D. J. Fox, T. Keith, M. A. Al-Laham, C. Y. Peng, A. Nanayakkara, M. Challacombe, P. M. W. Gill, B. Johnson, W. Chen, M. W. Wong, C. Gonzalez, and J. A. Pople, Gaussian, Inc., Wallingford CT, **2004**.

[44] AIM2000 designed by F. Biegler-König, University of Applied Sciences, Bielefeld, Germany.

[45] P. von R. Schleyer, C. Maerker, A. Dransfeld, H. Jiao, N. J. R. van E. Hommes, *J. Am. Chem. Soc.* **1996**, *118*, 6317.

[46] C. Corminboeuf, T. Heine, G. Seifert, P. von R. Schleyer, J. Weber, *Phys. Chem. Chem. Phys.* **2004**, *6*, 273.

[47] a) R. McWeeny, *Phys. Rev.* **1962**, *126*, 1028; b) R. Ditchfield, *Mol. Phys.* **1974**, *27*, 789; c) J. L. Dodds, R. McWeeny, A. Sadlej, *J. Mol. Phys.* **1980**, *41*, 1419; d) K. Wolinski, J. F. Hilton, P. Pulay, *J. Am. Chem. Soc.* **1990**, *112*, 8251.

[48] a) R. W. F. Bader, *Monatsh. Chem.* **2005**, *136*, 819; b) C. F. Matta, R. F. W. Bader, *J. Phys. Chem.* A **2006**, *110*, 6365; c) P. L. A. Popelier *Quantum chemical topology: On bonds and potentials.* Springer Berlin/Heidelberg **2005**, 115/2005, 1.

[49] For some criticism of AIM Quantum Theory see: a) A. M. Pendás, M. A. Blanco, E. Francisco, *Chem. Phys. Lett.* **2006**, *417*, 16; b) J. Poater, M. Solá, F. M. Bickelhaupt, *Chem. Eur. J.* **2006**, *12*, 2902; c) A. Kovacs, C. Esterhuysen, G. Frenking, *Chem. Eur. J.* **2005**, *11*, 1813; d) R. G. Parr, P. W. Ayers, R. F. Nalewajski, *J. Phys. Chem.* A **2005**, *109*, 3957. For response to this criticism (in corresponding order) see: e) R. F. W. Bader, *Chem. Phys. Lett.* **2006**, *426*, 226; f) R. W. F. Bader, *Chem. Eur. J.* **2006**, *12*, 2896; g) R. W. F. Bader, *Chem. Eur. J.* **2006**, *12*, 7769; h) C. F. Matta, R. W. F. Bader, *J. Phys. Chem. A* **2006**, *110*, 6365.

[50] S. E. O'Brien, P. L. A. Popelier, *Can. J. Chem.* **1999**, *77*, 28.

[51] a) R. W. F. Bader, C. F. Matta, *Organometallics* **2004**, *23*, 6253; b) I. Vidal, S. Melchor, I. Alkorta, J. Elguero, M. R. Sundberg, J. A. Dobado, *Organometallics* **2006**, *25*, 5638.

[52] a) L. Sobczyk, S. J. Grabowski, T. M. Krygowski, *Chem. Rev.* **2005**, *105*, 3513; b) L. González, O. Mó, M. Yáñez, J. Elguero, *J. Mol. Struct.* **1996**, *371*, 1; c) E. Espinosa, M. Souhassou, H. Lachekar, C. Lecomte, *Acta Crystallogr.* B **1999**, *55*, 563; d) S. J. Grabowski, *J. Phys. Chem.* A **2000**, *104*, 5551.

[53] R. W. F. Bader, C. F. Matta, *Inorg. Chem.* **2001**, *40*, 5603.

[54] P. L. A. Popelier, *Atoms in molecule. An introduction.* Prentice Hall, Pearson Education Ltd. **2000**.

[55] P. M. Dominiak, A. Makal, P. R. Mallinson, K. Trzcinska, J. Eilmes, E. Grech, M. Chruszcz, W. Minor, K. Wo niak, *Chem. Eur. J.* **2006**, *12*, 1941.

[56] S. J. Grabowski, M. Małecka, *J. Phys. Chem.* A **2006**, *110*, 11847.

[57] a) S. J. Grabowski, *J. Phys. Org. Chem.* **2003**, *17*, 18; b) S. J. Grabowski, *Monatsh. Chem.* **2003**, *133*, 1373; c) M. Palusiak, S. J. Grabowski, *J. Chem. Res.* **2004**, *2004/7*, 492.

[58] S. J. Grabowski, A. T. Dubis, M. Palusiak, J. Leszczyñski, *J. Phys. Chem.* B **2006**, *110*, 5875.

[59] a) S. S. Shaik, P. C. Hiberty, *J. Am. Chem. Soc.* **1985**, *107*, 3089.

[60] a) P. von R. Schleyer, M. Manoharan, Z. X. Wang, B. Kiran, H. J. Jiao, R. Puchta, N. J. R. van E. Hommes, *Org. Lett.* **2001**, *3*, 2465; b) C. Corminboeuf, T. Heine, G. Seifert, P. von R. Schleyer, J. Weber, *Phys. Chem. Chem. Phys.* **2004**, *6*, 273.

[61] a) M. K. Cyrañski, B. Stêpieñ, T. M. Krygowski, *Tetrahedron* **2000**, *56*, 9663; b) E. Steiner, P. W. Fowler, A. Soncini, L. W. Jenneskens, *Faraday Discuss.* **2007**, *135*, 309; c) P. Bultink, *Faraday Discuss.* **2007**, *135*, 347.

[62] P. Lazzeretti, *Phys. Chem. Chem. Phys.* **2004**, *6*, 217.

[63] a) G. Gilli, F. Bellucci, V. Ferretti, V. Bertolasi, *J. Am. Chem. Soc.* **1989**, *111*, 1023; b) G. Gilli, V. Bertolasi, *The Chemistry of Enols; Report*, Wiley, Chichester, **1990**, Chapter 13; c) M. Palusiak, S. Sìmon, M. Solá, *J. Org. Chem.* **2006**, *71*, 5241.

Received: February 12, 2007
Revised: April 23, 2007