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AROMATICITY AS A MULTI-DIMENSIONAL PHENOMENON

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The classification of aromaticity criteria is studied. New aromaticity criteria are developed and discussed. A statistical analysis of such criteria is presented and compared with a similar analysis of the recent literature. It is shown that aromaticity is at least a two-dimensional phenomenon. The classification of the compounds depends on the type of criteria included in the analysis.

INTRODUCTION

Aromaticity is a concept that has often been called elusive. Since benzene is the prototype of an aromatic compound, one is inclined to look for similarities with benzene in order to assess whether a compound is aromatic or not. The quantification of this idea is the goal of theoreticians and experimentalists alike. One of the first successful schemes was the proposition of Hückel to study the π-electron system of π-electron rings. This is now manifested in the famous $4n + 2$ Hückel rule. It relates aromaticity to the stability of benzene via the π-electron system. However, one could also use reactivity as a criterion, calling a compound aromatic if it is inclined to undergo substitution and disinclined to undergo addition reactions. In the course of development, many theoretical and experimental methods were designed to give a quantitative view of the concept of aromaticity. Bergmann and Agranat[1] reviewed such theoretical and experimental means for the determination of aromaticity almost 20 years ago. Many of the criteria discussed at that time are no longer of interest. However, new criteria have been suggested since then and the end of this diversification is not in sight. The key question which has evolved now is whether the phenomenon of aromaticity can be described by a single index on a one-dimensional scale. Recently the issue has been put to test by Katritzky *et al.*[2] They selected twelve aromaticity criteria, grouped them in classes and subjected the data for sixteen six-membered and five-membered monocyclic rings to a statistical analysis. Their aim was to extract information on the number of independent ingredients for the description of aromaticity. In the following section we shall review the classification of aromaticity criteria and add several more to the list. We finally subject the data generated with eight criteria to the same statistical analysis as Katritzky *et al.* We can show that two components are involved, but that the relative emphasis depends on the selection of such criteria.

CLASSIFICATION OF AROMATICITY CRITERIA

We follow the classification of Katritzky *et al.* and group the aromaticity criteria in three classes: geometric, energetic and magnetic. The geometric criteria actually do not use geometry directly, but indirectly via bond orders. Bond orders can be approximately related to bond lengths and are more suitable than the bond lengths themselves for the comparison of heterocyclic rings.

Pozharskii[3] introduced the arithmetic mean, ΔN, of the sum of bond-order differences between pairs of bonds as a criterion for aromaticity. He used an empirical bond-order criterion by Gordy[4] which involves the bond length and two empirical parameters. A similar criterion, $I_{5,6}$, was suggested by Bird,[5] who used the sum of squares of deviations of all bond orders from the arithmetic mean in his calculation of aromaticity indices. Both criteria suffer from the result that they predict perfect aromaticity for rings without bond-order alternation. With these criteria, benzene and borazine would have the same degree of aromaticity, a prediction not supported by chemical intuition. The problems connected with the two criteria just mentioned are avoided by the ring-current criterion *RC* introduced by us.[6] The basic idea was to look for the ring bond with the lowest bond order, because this bond would be decisive for the ring current. If no π bonding is involved in one of the ring bonds of a monocyclic ring, the compound could not be classified as aromatic.

A second class of criteria involves energy considerations. Starting from the idea of resonance stabilization

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by delocalization of π electrons, Dewar *et al.*[7] defined resonance structures with localized single and double bonds as reference structures for energy calculations. Except for the π-electron energy of the structure in question, all other energies are determined empirically. Dewar's resonance energies, *DRE*, are formally related to heats of formation. The π-electron energy can be calculated by an SCF method. An alternative resonance energy, *HSRE*, was proposed by Hess and Schaad[8] on the Hückel level. Again, empirical energy increments for various types of bonds are defined and the π-electron energy is calculated explicitly. Both methods suffer from the difficulty of defining an appropriate reference structure. In addition, the Hess–Schaad resonance energy has the drawbacks of the Hückel method. Sometimes it cannot generate the correct symmetry orbitals because of the limitation of a single secular determinant for the bonding of a structure. A graph theoretical approach based on Hückel theory and π electrons was introduced independently by Gutman *et al.*[9] and Aihara.[10] In another concept, proposed by Kollmar,[11] a model wavefunction is generated for the calculation of resonance energies by localization of the π-electron system. This localization can be most easily obtained by using a separate π MO as in ethylene for each CC double bond. The π MOs can be orthogonalized among each other and to the σ MOs. The σ MOs are optimized in the framework of the model π system. The resonance energy is defined as the difference between the energy of the optimized model wavefunction and the SCF energy. Since this energy is only positive, a renormalization with reference to open-chain polyene structures is again necessary.

The third class of aromaticity criteria currently recognized comprises the magnetic criteria. A characteristic feature of aromatic compounds is the anisotropy of the diamagnetic susceptibility, which is large compared with that of non-conjugated systems and is traced back to a ring current induced by the external magnetic field.[12] This ring current is attributed to the π-electron system, but it is not a measurable quantity, only a concept for the explanation of measurable effects. Besides the large diamagnetic susceptibility of aromatic compounds, the chemical shift of ring protons in NMR is frequently used to support the ring current concept. Katritzky[2] included nitrogen-15 chemical shifts[13] and called the criterion ^{15}N. Musher[14] suggested that these effects can be explained by a model of localized σ and π electrons. However, Gaidis and West[15] showed that a model with localized electrons gives wrong predictions for the chemical shift of inner ring protons.

The molar diamagnetic susceptibility for non-conjugated systems is an additive quantity of atomic diamagnetic susceptibility.[16] For isolated multiple bonds, correction terms must be introduced. If such an incremental system is used to calculate the diamagnetic susceptibility of aromatic compounds represented by their most stable Kekulé structure, a large difference appears between the calculated and measured values. Palmer *et al.*[17] defined the difference between measured and estimated molar susceptibilities χ_M as an aromaticity index, Λ. This magnetic exaltation can be transformed into another index ρ, which is proportional to Λ and to the number n of π electrons and inversely proportional to the square of the area s of the ring. Bulgarevich *et al.*[18] proposed aromaticity indices based on the anisotropic polarizability of the molecules. The quantity obtained is related to the number of bonds in the ring. The first of these indices is called I_1 and was included by Katritzky *et al.*[2] in their analysis.

DEVELOPMENT OF AROMATICITY CRITERIA

Valence criterion

Starting from the bond-order criterion RC^6 for ring-current effects, we may as well use an alternative criterion RC_v based on bond valence. The idea of bond valence V_{AB} was advanced by Gopinathan and Jug.[19,20] Compared with bond order, which is linear in density matrix elements, bond valence is quadratic in density matrix elements:

$$V_{AB} = \sum_{\mu,\nu} (P_{\mu_A \nu_B})^2 \qquad (3.1)$$

The matrix elements $P_{\mu\nu}$ are defined over atomic orbitals μ, ν and the first-order-reduced density operator P.

Analogous to the bond-order criterion *RC*, we define the bond-valence criterion RC_v for aromaticity in the following way. The minimum bond valence of all ring bonds in a monocyclic ring is the index of aromaticity. For polycyclic rings the *RC* criterion was also defined[6] and the analogous definition could be taken for RC_v.

We have collected values for aromaticity indices *RC* and RC_v in Table 1 for a large number of three- to six-membered rings. The wavefunctions were generated by the semi-empirical method SINDO1[21,22] for uniform comparison. From our experience we do not expect qualitative differences with *ab initio* wavefunctions. Both criteria distinguish clearly between organic six- and five-membered rings. The former are classified as more aromatic. However, within these groups there are substantial differences in the sequence. For instance, the following sequence is obtained for six-membered rings:

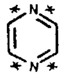
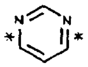
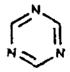
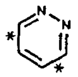
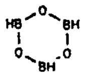
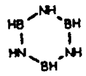
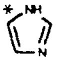
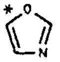
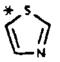
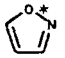
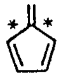
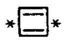
RC:

hexaazine > benzene > pentaazine > pyrazine
> tetraazine > pyridine > pyrimidine > triazine
> pyridazine;

RC_v:

benzene > hexaazine > pyridine > pyridazine
> pyrimidine = pyrazine > pentaazine > triazine
> tetraazine.

Table 1. Ring current criteria RC and RC_v

Molecule	RC	RC_v	Structure[a]
Hexaazine	1·792	1·426	
Cyclopropenyl cation	1·775	1·419	
Benzene	1·751	1·437	
Pentaazine	1·746	1·407	
Pyrazine	1·739	1·411	
1,2,4,5-Tetraazine	1·735	1·401	
Pyridine	1·731	1·422	
Pyrimidine	1·727	1·411	
1,3,5-Triazine	1·724	1·404	
Cyclopentadienyl anion	1·717	1·402	
Pyridazine	1·716	1·414	
Boroxole	1·545	1·052	
Borazene	1·527	1·112	
Pyrrole	1·464	1·124	
Thiophene	1·450	1·173	
Furan	1·431	1·081	
Imidazole	1·423	1·075	
1,3-Oxazole	1·393	1·042	
1,3-Thiazole	1·389	1·099	
1,2-Oxazole	1·361	1·032	
Pyrazole	1·297	1·096	
1,2,4-Triazole	1·254	1·002	
Fulvene	1·243	0·990	
Cyclopentadiene	1·228	1·003	
Cyclopentadienyl cation	1·042	0·945	
Azirene	1·031	0·945	
Oxirene	1·030	0·887	
Cyclopropenyl anion	1·016	0·911	
Cyclobutadiene	0·980	0·940	

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[a] Weakest bonds are marked with asterisks.

Whereas the sequence of molecules does not appear to be dependent on the number of heteroatoms in the ring for the *RC* index, a direct connection between number of heteroatoms and aromaticity of a compound can be seen for RC_v. Aromaticity decreases from pyridine to tetraazine and then increases to hexaazine. On the latter scale benzene is the most aromatic molecule.

For heteroaromatic five-membered rings the following sequences hold:

RC:

pyrrole > thiophene > furan > imidazole
> 1,3-oxazole > 1,3-thiazole > 1,2-oxazole
> pyrazole > 1,2,4-triazole;

RC_v:

thiophene > pyrrole > 1,3-thiazole > pyrazole
> furan > imidazole > 1,3-oxazole > 1,2-oxazole
> 1,2,4-triazole

It is apparent from these sequences that the RC_v criterion classifies heteroaromatic compounds with nitrogen as more aromatic as those with oxygen for an equal number of heteroatoms. This corresponds to the rule of thumb that a compound is the more aromatic the less the electronegativity difference between the atoms.

It seems reasonable to call those compounds with RC_v indices larger than 1·39 aromatic, between 1·39 and 1·03 moderately aromatic, between 1·03 and 0·99 non-aromatic, between 0·99 and 0·95 moderately anti-aromatic and below 0·95 anti-aromatic.

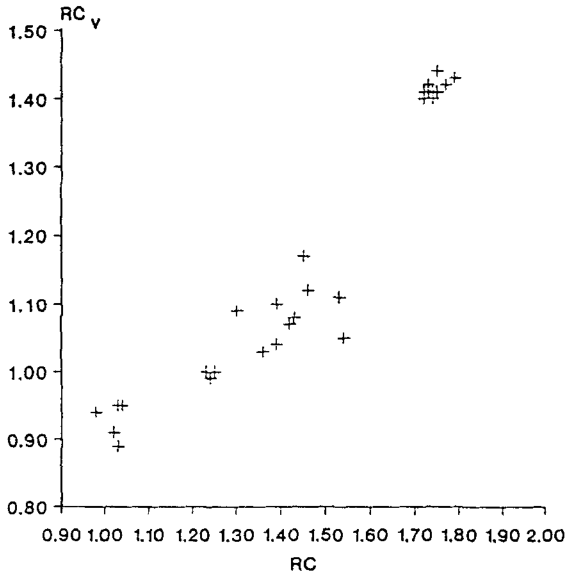

Figure 1. *RC* versus RC_v aromaticity index values for monocyclic rings

In Figure 1 we show the distribution of RC_v value versus *RC* values. To a first approximation a quadrati dependence of the form $RC_v = a + bRC^2$ is visible.

Susceptibility criterion

Starting from the ring-current concept, the diamagneti susceptibility of the π system perpendicular to the rin plane could be considered as a measure of aromaticit of a compound. The derivation of the component χ_z from values over MOs was given some time ago.[16] Fo some molecules, this component of the diamagneti susceptibility was calculated with SINDO wavefunctions[21,22] and compared with experimenta values. The results are given in Table 2. These result are plotted in Figure 2. The agreement between th calculated and experimental values is satisfactory. Th calculated absolute values are in general 5–10% belo the experimental values. This discrepancy betwee calculated and experimental values is mainly due t the ZDO assumption in the semi-empirical metho SINDO1. Also, the approximation of the symmetricall orthogonalized AOs[23] by Slater orbitals in th calculation of the integrals has a substantial influenc on calculated absolute values. However, for th following considerations a more accurate calculation o χ_{zz} values is not necessary, because only qualitativ conclusions about the suitability of components of th diamagnetic susceptibility tensor as aromaticit criterion are intended. Table 3 contains χ^{π}_{zz} and χ^{π}_{zz}/n values from SINDO1 calculations where n_{π} is th number of π electrons. The sequence of molecule obtained for χ^{π}_{zz}/n_{π} resembled that of the RC_v index Both criteria distinguish between two large aromati groups, namely the six- and the five-membered ring

Table 2. Calculated χ^{c}_{zz} and measured χ^{m}_{zz} *zz* component (cm mol^{-1}) of diamagnetic susceptibility

Molecule	$-10^6\ \chi^{m}_{zz}$ [a]	$-10^6\ \chi$
Fluorobenzene	736·4	639·8
Benzene	508·0	452·6
1,1,2-Trifluroethylene	413·1	357·3
Cyclopentadiene	356·9	334·0
Furan	314·0	290·0
Propene	206·6	206·3
Acetaldehyde	177·4	168·0
Acetonitrile	169·4	153·6
Difluoroacetylene	147·9	130·9
Cyclopropene	133·4	132·5
Carbon dioxide	128·6	105·8
Oxirane	125·4	125·0
Fluoromethane	71·9	74·4
Ammonia	22·0	29·1
Water	15·4	28·8

[a] From Ref. 16.

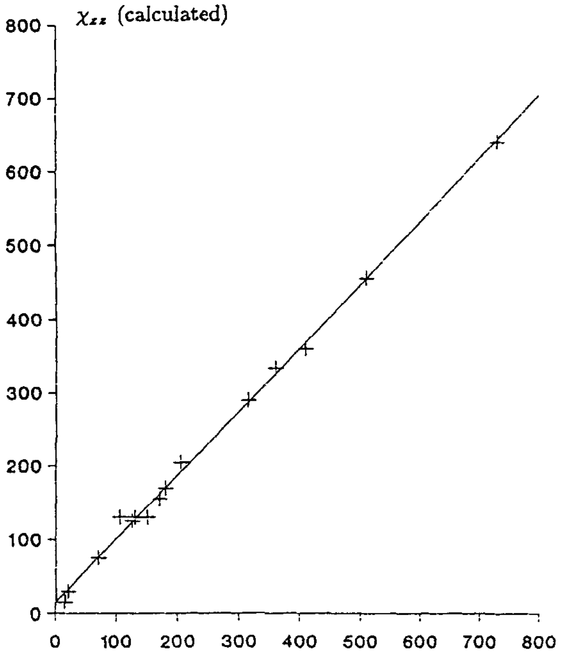

Figure 2. Calculated versus measured diamagnetic suspectibility component χ_{zz} values

Table 3. Calculated χ^{π}_{zz} and χ^{π}_{zz}/n_{π} (cm^3 mol^{-1})

Molecule	$-10^6\ \chi^{\pi}_{zz}$	$-10^6\ \chi^{\pi}_{zz}/n_{\pi}$
Benzene	60·30	10·05
Pyridine	58·02	9·67
Pyrimidine	55·68	9·28
1,3,5-Triazine	53·28	8·88
1,2,4,5-Tetraazine	51·00	8·50
Pentaazine	49·10	8·18
Hexaazine	47·16	7·86
Pyrrole	44·88	7·48
Pyrazole	44·58	7·43
Furan	43·50	7·25
Imidazole	43·02	7·17
1,3-Oxazole	42·18	7·03
1,2-Oxazole	41·88	6·98
Fulvene	40·92	6·82
Cyclopentadiene	26·92	6·73
Cyclopropene	12·60	6·30
Cyclobutadiene	24·08	6·02
Azirene	16·00	4·00
Oxirene	15·80	3·95

A decisive difference in the classification of cyclobutadiene, which appears less anti-aromatic than oxirene or azirene on the χ^{π}_{zz}/n_{π} scale. In this connection, one should consider that anti-aromatic systems have a substantial paramagnetic contribution to the susceptibility, which was not included in this calculation. The advantages of this index are that no incremental systems is needed, it is possible to consider systems which are experimentally not accessible and the calculated χ_{zz} can be compared with experiments. The disadvantages are the difficulty with the classification of anti-aromatic compounds and the lack of direct experimental observation of the aromaticity index.

STATISTICAL ANALYSIS

In a recent paper, Katritzky *et al.*[2] assembled twelve methods for aromaticity indices consisting of readily available geometric, energetic and magnetic data for the nine compounds benzene, pyridine, pyrimidine, pyrazine, thiophene, furan, pyrrole, pyrazole and imidazole and subjected them to principal component analysis (PCA). It was found that 83% of the variation of the characteristics, i.e., aromaticity indices, was explained by three principal components, of which the first, second and third PC accounted for 47%, 22% and 14%, respectively, of the variance. From the PC loadings it appeared that the twelve characteristics can be divided into three main groups. (a) The first group of five characteristics ($I_{5,6}$, ΔN, *DRE*, *HSRE*, ^{15}N) is dominated by the p_1 loadings; the p_2 loadings is small for these systems and p_3 loadings are small to moderate. It is clear that p_1 measures the so-called 'classical aromaticity.' The purest measure is given by $I_{5,6}$. (b) The second group consists of the magnetic parameters χ_{M} and Λ. These are both marked by very small p_1 components, but large positive p_2 and large negative p_3 components. This second group of characteristics includes measurements of 'magnetic aromaticity,' which is almost completely orthogonal to the classical aromaticity. (c) The remaining group of five characteristics all show moderately positive p_1 loading together with negative loadings for both p_2 and p_3 for ΔH_{F} (calculated or experimental) and positive loadings for both p_2 and p_3 for *RC*, ΔH_{a} and I_1. The characteristics in this group possess elements of both 'classical' and 'magnetic' aromaticity.

In this section we perform a similar analysis on eight methods including twelve molecules. The values for the aromaticity indices of all methods and molecules are listed in Table 4. The set consists of two geometric criteria (*RC*, RC_v), three energy criteria (*DRE*, *HSRE*, $\Delta E/E$) and three magnetic criteria ($\Lambda, \chi_{\mathrm{M}}, \chi^{\pi}/n_{\pi}$). The new criterion $\Delta E/E$ is based on distortions of equilibria to Kekulé structures.[24] ΔE is the energy difference between Kekulé structure and equilibrium structure and E is the energy of the equilibrium structure.

Table 4. Aromaticity indices for five- and six-membered rings with different methods

Molecule	RC	RC_v	$-10^6\ \chi^{\pi}_{zz}/n_\pi$ (cm^3 mol^{-1})	DRE(eV)	$HSRE(\beta)$	$\Delta E/E \times 10^{-4}$	$-10^6\ \Lambda$(cm^3 mol^{-1})	$-10^6\ \chi$ (cm^3 mol^{-1})
Benzene	1·751	1·437	10·05	22·6	0·390	6·8	13·7	54·8
Pyridine	1·731	1·422	9·67	23·1	0·348	6·2	13·4	49·2
Pyrimidine	1·727	1·411	9·28	20·2	0·297	5·7		43·1
1,3,5-Triazine	1·724	1·404	8·88			6·2		37·9
Pentaazine	1·746	1·407	8·18			1·7		
Hexaazine	1·792	1·426	7·86			0·3		
Pyrrole	1·464	1·124	7·48	5·3	0·233	3·8	10·2	47·6
Furan	1·431	1·081	7·25	4·3	0·044	2·7	8·9	43·1
Pyrazole	1·297	1·096	7·43		0·330	3·7	6·6	42·6
Imidazole	1·423	1·075	7·17	15·4	0·251	3·0		44·3
1,2-Oxazole	1·361	1·032	6·98			2·4		37·5
1,3-Oxazole	1·393	1·042	7·03			2·2		39·2

The first two principal components p_1 and p_2 for all methods are listed in Table 5. These two components comprise 75% of the variance of all variables. The location of these methods in the two-dimensional p_1 and p_2 plane is depicted in Figure 3. The first components can be attributed to the geometric criteria RC and RC_v and the second component to the energy criteria. Hence these criteria are orthogonal to each other. In contrast to Katritzky *et al.* results, Λ and χ_M are not orthogonal to the energy criteria.

Table 5. Factor analysis

Variable	Factor 1	Factor 2
RC	0·9602	0·1427
RC_v	0·9122	0·2592
χ^{π}_{zz}/n_π	0·7677	0·5837
DRE	0·3072	0·6775
$HSRE$	0·3316	0·8381
$\Delta E/E$	0·1613	0·8914
Λ	0·6401	0·4570
χ	0·5104	0·3695

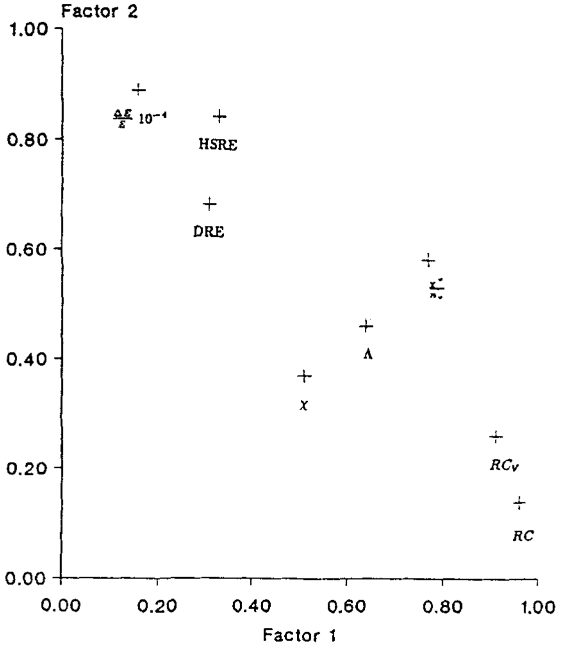

Figure 3. Various aromaticity criteria in two-dimensional factor space

If one wishes to represent aromaticity as a two-dimensional criterion, one could choose, e.g., RC as magnetic criterion and $\Delta E/E$ as energy criterion. Of course, other options of previous methods such as DRE or $HSRE$ as energy criterion and the new RC_v as magnetic criterion are also possible. It is essential that these criteria are close to the two factor axes to supply complementary information. Figure 3 shows how well this condition is fulfilled for the various criteria.

CONCLUSION

It is clear from both the analyses by Katritzky *et al.* and those by us that aromaticity is at least a two-dimensional phenomenon. Energetic and magnetic criteria appear to be dominant. However, the results of a statistical analysis of energy criteria depends on the methods and compounds included. We do not obtain the same orthogonality as Katritzky *et al.* One should therefore be careful in assessing an absolute meaning of this quantity orthogonality.

ACKNOWLEDGEMENTS

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