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To What Extent Can Aromaticity Be Defined Uniquely?[†]

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Statistical analyses of quantitative definitions of aromaticity, ASE (aromatic stabilization energies), RE (resonance energies), Λ (magnetic susceptibility exaltation), NICS, HOMA, I_5, and A_J, evaluated for a set of 75 five-membered π-electron systems: aza and phospha derivatives of furan, thiophene, pyrrole, and phosphole (aromatic systems), and a set of 30 ring-monosubstituted compounds (aromatic, nonaromatic, and antiaromatic systems) revealed statistically significant correlations among the various aromaticity criteria, provided the whole set of compounds is involved. Hence, broadly considered, the various manifestations of aromaticity are related and aromaticity can be regarded statistically as a one-dimensional phenomenon. In contrast, when comparisons are restricted to some regions or groups of compounds, e.g., aromatic compounds with ASE $>$ 5 kcal/mol or polyhetero-five-membered rings, the quality of the correlations can deteriorate or even vanish. In practical applications, energetic, geometric, and magnetic desriptors of aromaticity do not speak with the same voice. Thus, in this sense, the phenomenon of aromaticity is regarded as being statistically multidimensional.

Introduction

To what extent are the geometric, energetic, and magnetic criteria of aromaticity quantitatively related? Extensive discussions during the past decade[1−8] led to no generally agreed position on this question. Since its introduction 135 years ago,[9] the concept of aromaticity has become one of the most important in chemistry as demonstrated by some 60 000 references to "aromaticity" or "aromatic" in the scientific literature between 1981 and 2000.[10] Thus, we believe that it is appropriate to provide some general guidance for organic chemists and others who deal with aromatic compounds.

As with many other important chemical concepts (e.g., electronegativity, van der Waals radii, etc.), "aromaticity" is not a directly measurable quantity and is universally understood by convention. Moreover, it has no precise quantitative and generally accepted definition.[8,10,11] Aromaticity was originally conceived to describe the stability, type of reactivity, and structure of benzene and benzenoid derivatives. However, changes in structure are not always paralled by changes in reactivity and other physicochemical properties. By the 1960s, it was established[12−14] that, if its π-electrons are delocalized, a planar cyclic fully conjugated π-electron system is aromatic in its ground state if the following features are manifested:

(i) A system is more stable than its acyclic or cyclic olefinic or conjugated unsaturated analogues. This was previously quantified by "resonance energy"[15] and then more subtly by "aromatic stabilization energies" (ASE) on the basis of homodesmotic reactions.[16−19] Although the

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[†] This paper is dedicated to the memory of Prof. Dr. Dr. h. c. Włodzimierz Kołos (1928−1996), an outstanding Polish quantum chemist, 5 years after his passing.

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ASE is only around 3−4% of the total atomization energy of a system,[20] the energetic criterion, if well defined, is considered to be the principal one,[5,8,10b,21] since it governs the reactions and much of the chemical behavior.

(ii) The cyclic CC bond lengths tend to be intermediate between those typical for single and double bonds. Quantitative descriptors of this effect are the geometrical indices. It has been shown[10c] that among the indices based on geometry the "harmonic oscillator model of aromaticity" (HOMA) model[22−24] may be considered to be the most reliable one. It provides easily accessible information on aromaticity.

(iii) An external magnetic field induces a diatropic π ring current. Historically, the exaltation of magnetic susceptibility (Λ)[25] and characteristic proton NMR chemical shifts were important criteria frequently used in experimental work.[26] Now, the "nucleus independent chemical shift" (NICS)[21] is often considered to be a better criterion.[20,27]

The extent to which all these criteria of aromaticity agree is a question fundamental to a proper understanding of the concept of aromaticity. Until the late 1980s, it was usually assumed that they reflected aromatic character in equivalent ways. However, during the period 1989−1995, several independent applications of multidimensional statistics (principal component analysis and factor analysis)[28] demonstrated that two or three orthogonal factors were necessary to describe the variation of a range of aromaticity indices for many aromatic, nonaromatic, and anti-aromatic systems,[1−4] revealing the multidimensional character of the term. Naturally, this conclusion could depend on the reliability of the indices used and was subject to the limitations of the current methodology.

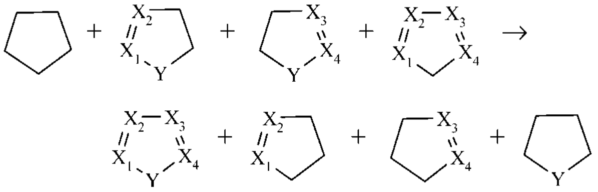
In 1995, Schleyer used precisely defined criteria, demonstrated for a limited sample (11 monoheteropentaatomic systems)[5,31] linear dependencies between the energetic, geometric, and magnetic indices, and concluded that aromaticity is a one-dimensional phenomenon.

These analyses, leading to different conclusions, were followed by many studies[6,10,29−35] claiming to demonstrate statistically that the phenomenon of aromaticity was either multi- or one-dimensional. The present paper is intended to present an authoritative assessment of all of this work.

Methodology

A comprehensive set of 75 five-membered π-electron systems: aza and phospha derivatives of furan, thiophene, pyrrole, and phosphole (aromatic systems) and a set of 30 endo-monosubstituted compounds (aromatic, nonaromatic, and antiaromatic systems) were chosen here for more extensive analysis (see eq 1 and Tables 1 and 2).

The following independent descriptors were used to quantify aromaticity: (i) aromatic stabilization energies (ASE) according to eq 1 (where (i) X_1, X_2, X_3, X_4 are (C or N) or X_1, X_2, X_3, X_4 are (C or P) and Y=O, S, NH, PH;[37] or (ii) $X_1 = X_2 = X_3 = X_4 = C$ and Y = BeH^-, B^-, BH, BH_2^-, CH^-, CH_2, CF_2, N^-, NH_2^+, Al^-, AlH, AlH_2^-, SiH^-, SiH^+, SiH_2, P^-, PH_2^+, GaH, GaH_2^-, GeH^-, GeH^+, GeH_2, As^-, AsH, AsH_2^+, Se, C=CH_2, C=O, C=S, C=Se).[36] The homodesmotic reaction scheme applied here[36] is a modification of Schleyer's isodesmotic reaction scheme.[5] Utilization of eq 1 allows a comprehensive inclusion of a variable number of heteroatoms in five-membered rings. We are aware that the ASE values derived can be slightly perturbed by additional effects, like topological charge stabilization and/or heteroatom−hereroatom interactions. These effects, however, should be diminished because of our careful formulation of the homodesmotic reactions (eq 1) as compared with other homodesmotic/isodesmotic reaction schemes.[36] Strain effects also should cancel, since all reference compounds are five-membered rings computed in their most stable conformations.



(1)

The systems with strongly positive ASEs are aromatic, while those with strongly negative ones are antiaromatic. (ii) The magnetic susceptibility exaltations (Λ, defined as a difference between the magnetic susceptibility of a given system and a reference one, without cyclic delocalization) are also based on eq 1.[38] Systems with strongly negative values of Λ are qualified as aromatic. (iii) NICS are calculated at the center of the rings and at 1 Å above the molecular plane. NICS is the negative value of absolute magnetic shieldings calculated at revealing points in or near an aromatic system.[21,35] Rings with negative NICS and NICS(1) values qualify as aromatic, and the more negative NICS, the more aromatic the rings are. Consequently, antiaromatic systems have strongly positive values of NICS. The NICS(1) values computed 1 Å above the ring centers are considered to better reflect the π-electron effects.[39] (iv) HOMA[32] (eq 2) is a geometry-based index, but cannot be applied to systems containing NS, PN, PP, PO, PS, and C−metal bonds

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[37] With the exception of the 2,3,4,5-tetraaza derivatives of furan, thiophene, pyrrole, and phosphole since one of the reference compounds (2,3,4,5-tetraazacyclopentadiene) could not be well defined.

[38] For a similar approach of calculations of exaltation of magnetic susceptibility, see, e.g., ref 31.

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Table 1. Calculated ASE (kcal/mol), Exaltations of Magnetic Susceptibility Λ, NICS, NICS 1 Å above the Ring Centers (Denoted as NICS(1)) (ppm), and HOMA for Polyhetero Five-Membered Rings (Including the Parent Systems)[a]

compound	ASE	Λ	NICS	NICS(1)	HOMA
furan	14.77	−2.90	−12.31	−9.36	0.298 (0.778)
thiophene	18.57	−7.00	−13.80	−10.79	0.891 (0.900)
pyrrole	20.57	−6.48	−14.86	−10.60	0.876 (0.895)
phosphole	3.20	−1.68	−5.43	−5.97	0.236 (0.557)
2-azafuran	17.29	−2.71	−12.36	−10.58	0.527
2-azathiophene	20.18	−7.13	−13.96	−11.66	
2-azapyrrole	23.70	−7.09	−14.75	−11.93	0.926
2-azaphosphole	3.34	−1.54	−5.65	−6.84	
3-azafuran	12.37	−1.83	−11.31	−9.45	0.332
3-azathiophene	17.43	−6.21	−13.10	−11.37	0.905
3-azapyrrole	18.78	−5.18	−13.85	−10.83	0.908
3-azaphosphole	3.01	−1.20	−3.78	−6.25	0.276
2,3-diazafuran	17.20	−1.57	−12.97	−11.99	0.443
2,3-diazathiophene	20.48	−7.75	−14.38	−13.72	
2,3-diazapyrrole	24.37	−6.67	−14.90	−13.51	0.931
2,3-diazaphosphole	2.56	−0.98	−4.13	−8.56	
2,4-diazafuran	14.23	−1.33	−11.51	−10.40	0.553
2,4-diazathiophene	18.28	−6.31	−13.47	−11.96	
2,4-diazapyrrole	21.33	−5.29	−13.66	−11.84	0.940
2,4-diazaphosphole	3.04	−1.08	−4.62	−7.16	
2,5-diazafuran	20.19	−1.58	−12.72	−12.52	0.677
2,5-diazathiophene	22.67	−7.60	−14.52	−12.96	
2,5-diazapyrrole	26.66	−7.91	−14.83	−13.61	0.960
2,5-diazaphosphole	3.14	−1.34	−5.48	−7.64	
3,4-diazafuran	7.78	−0.59	−10.74	−10.00	0.243
3,4-diazathiophene	13.69	−5.34	−13.00	−12.34	0.849
3,4-diazapyrrole	14.96	−3.50	−13.13	−11.52	0.823
3,4-diazaphosphole	1.80	−0.88	−2.94	−6.97	0.025
2,3,4-triazafuran	9.65	0.42	−12.94	−12.29	0.413
2,3,4-triazathiophene	14.72	−6.57	−15.18	−14.65	
2,3,4-triazapyrrole	18.26	−3.48	−14.79	−14.12	0.897
2,3,4-triazaphosphole	1.51	−1.27	−4.20	−8.69	
2,3,5-triazafuran	18.71	−0.12	−13.84	−13.84	0.586
2,3,5-triazathiophene	21.62	−7.85	−15.49	−14.96	
2,3,5-triazapyrrole	26.49	−6.99	−14.96	−14.64	0.960
2,3,5-triazaphosphole	2.24	−0.48	−4.92	−9.21	
2,3,4,5-tetraazafuran	-	-	−16.16	−15.34	0.500
2,3,4,5-tetraaza-thiophene	-	-	−18.40	−17.48	
2,3,4,5-tetraazapyrrole			−16.76	−16.59	0.950
2-phosphafuran	13.19	−1.60	−11.38	−9.34	
2-phosphathiophene	17.45	−7.21	−13.51	−11.40	
2-phosphapyrrole	20.31	−6.12	−13.55	−10.77	
2-phosphaphosphole	4.97	−4.91	−7.38	−7.73	
3-phosphafuran	13.50	−2.99	−11.93	−10.26	0.326
3-phosphathiophene	17.01	−8.40	−13.04	−11.59	0.854
3-phosphapyrrole	19.91	−6.85	−14.26	−11.33	0.829
3-phosphaphosphole	3.03	−2.74	−5.34	−6.90	0.378
2,3-diphosphafuran	12.23	−2.01	−11.94	−10.36	
2,3-diphosphathiophene	15.14	−8.79	−13.89	−12.24	
2,3-diphosphapyrrole	19.17	−6.70	−14.03	−11.61	
2,3-diphosphaphosphole	4.25	−5.52	−8.92	−9.17	
2,4-diphosphafuran	12.14	−1.65	−11.08	−10.14	
2,4-diphosphathiophene	16.14	−8.37	−12.90	−12.16	
2,4-diphosphapyrrole	18.85	−6.16	−12.89	−11.39	
2,4-diphosphaphosphole	6.18	−7.08	−8.50	−9.34	
2,5-diphosphafuran	12.69	−1.11	−10.25	−9.28	
2,5-diphosphathiophene	16.02	−7.91	−13.07	−11.99	
2,5-diphosphapyrrole	19.24	−6.41	−11.84	−10.85	
2,5-diphosphaphosphole	7.97	−9.75	−10.00	−10.28	
3,4-diphosphafuran	12.18	−3.33	−12.41	−11.12	
3,4-diphosphathiophene	16.75	−9.64	−13.11	−12.37	
3,4-diphosphapyrrole	19.47	−6.96	−14.45	−11.97	
3,4-diphosphaphosphole	4.11	−4.90	−6.88	−8.48	
2,3,4-triphosphafuran	11.84	−2.93	−12.73	−11.37	
2,3,4-triphosphathiophene	15.23	−10.25	−14.12	−13.21	
2,3,4-triphosphapyrrole	18.38	−6.82	−14.42	−12.35	
2,3,4-triphosphaphosphole	7.22	−11.47	−12.42	−11.75	
2,3,5-triphosphafuran	12.72	−1.19	−11.02	−10.34	
2,3,5-triphosphathiophene	14.53	−8.77	−13.60	−12.91	
2,3,5-triphosphapyrrole	17.96	−6.11	−12.42	−11.63	
2,3,5-triphosphaphosphole	8.93	−12.38	−12.32	−11.88	
2,3,4,5-tetraphosphafuran	12.30	−2.45	−13.37	−11.97	
2,3,4,5-tetraphosphathiophene	12.79	−10.57	−15.00	−14.38	
2,3,4,5-tetraphosphapyrrole	17.12	−5.98	−14.62	−12.98	
2,3,4,5-tetraphosphaphosphole	11.24	−20.82	−17.22	−14.93	

[a] Data for HOMA based on three CC bonds are given in parentheses.

for which the HOMA values cannot be estimated due to lack of parameters.

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

In eq 2, N is the number of bonds taken into the summation; α is an empirical constant fixed to give HOMA = 0 for a model nonaromatic system,[22] and HOMA = 1 for a system with all bonds equal to an optimal value R_{opt}, assumed to be realized for fully aromatic systems.[32] R_{i} stands for a running bond length.[32]

In view of the large number of systems, the highest, reasonable possible levels of theory were chosen for the computations. The geometries were computed[40] at the MP2-(fc)/6-311+G** level of theory, while the energies for calculation of ASE were corrected by the MP2(fc)/6-311+G** zero-point energies. All species corresponded to minima at the MP2(fc)/6-311+G** level, with no imaginary frequencies. CSGT calculations employing MP2(fc)/6-311+G**-optimized geometries and the HF/6-311+G** basis set were selected for the calculation of the exaltation of magnetic susceptibility. This method was chosen because it gave excellent accord of the computed magnetic susceptibilities with experimental data.[41] The GIAO/HF/6-311+G** method was used for the NICS calculations. The HOMA values also were based on molecular geometries optimized at the MP2(fc)/6-311+G** level. Tables 1 and 2 list data for quantitative measures of aromaticity for the systems considered.

Results and Discussion

How similar are the responses of the various physicochemical measures of aromaticity to structural modifications? Correlation analysis applied to the whole set of 105 five-membered π-electron systems (comprising “aromatic”, “nonaromatic”, and “antiaromatic” types) revealed significant statistical correlations[42] between the energetic, geometric, and magnetic indices of aromaticity as illustrated by Figure 1 a−d, in which Λ, NICS, NICS(1), and HOMA are plotted against ASE. Table 3 gives the corresponding matrix for the correlation coefficients. The scatter plots of Figure 1 thus confirm a general tendency toward mutual dependences among these parameters.

Such general dependence can be expected since the descriptors of aromaticity were not randomly chosen but carefully directed to known physicochemical effects generally regarded to be manifestations of aromaticity. These

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[41] For example, the magnetic susceptibility (theoretical values in brackets) for furan, thiophene, pyrrole and 3-azathiophene are −42.82 (−41.31), −57.20 (−54.90), −47.60 (−46.78), and −50.55 (−49.63), respectively.

[42] Snedecor, G. W.; Cochran, W. G. *Statistical Methods*; The Iowa State University Press: Ames, 1973; p 184.

Table 2. Calculated ASE (kcal/mol), Exaltations of Magnetic Susceptibility Λ, NICS, NICS 1 Å above the Ring Centers (denoted as NICS(1)) (ppm), and HOMA for Mono-Endo-Substitued Rings (C_4H_4X)[a]

X	ASE	Λ	NICS	NICS(1)	HOMA	X	ASE	Λ	NICS	NICS(1)	HOMA
BeH^-	−7.78	10.19	9.13	4.04	(−0.166)	P^-	23.12	−9.78	−13.41	−11.03	0.730 (0.859)
B^-	9.05	−13.48	−12.65	−6.92	(0.420)	PH_2^+	−8.31	4.17	−0.70	−2.56	0.047 (0.016)
BH	−22.49	16.09	17.22	9.24	(−0.595)	GaH	−9.97	13.35	6.69	3.18	(−0.300)
BH_2^-	−0.24	−0.200	0.12	−2.79	(0.281)	GaH_2^-	−0.96	3.45	1.83	−0.52	(−0.059)
CH^-	22.05	−10.15	−13.99	−10.25	0.736 (0.736)	GeH^-	4.88	−2.66	−4.29	−4.92	(0.626)
CH_2	0.00	0.00	−3.18	−4.82	−0.780 (0.306)	GeH^+	−23.92	18.48	11.33	6.90	(−0.628)
CF_2	−11.88	6.65	3.36	0.48	−1.383 (−0.287)	GeH_2	−2.97	3.74	0.35	−1.51	(0.037)
N^-	19.56	−9.43	−13.26	−11.03	0.844 (0.818)	As^-	22.21	−10.75	−12.88	−10.60	(0.877)
NH_2^+	−2.05	1.58	−5.18	−5.27	−0.308 (0.135)	AsH	1.71	−0.08	−3.93	−4.62	(0.447)
Al^-	−6.87	8.93	5.56	1.18	(0.058)	AsH_2^+	−6.55	4.12	−1.12	−2.30	(0.010)
AlH	−9.98	13.05	6.35	3.06	(−0.261)	Se	16.74	−7.43	−12.81	−10.01	(0.878)
AlH_2^-	−2.07	3.78	2.84	−0.04	(0.007)	$C{=}CH_2$	−3.06	1.01	−0.72	−3.42	−0.142 (0.280)
SiH^-	9.3	−8.92	−9.09	−7.90	(0.792)	C=O	−14.65	9.05	9.63	2.81	−1.255 (−0.326)
SiH^+	−26.58	18.60	12.42	7.66	(−0.664)	C=S	−11.96	10.48	12.6	3.46	−0.454 (0.031)
SiH_2	−4.61	4.06	1.07	−1.41	(−0.035)	C=Se	−11.44	12.44	13.49	3.79	−0.307 (0.092)

[a] Data for HOMA based on three CC bonds are given in parentheses.

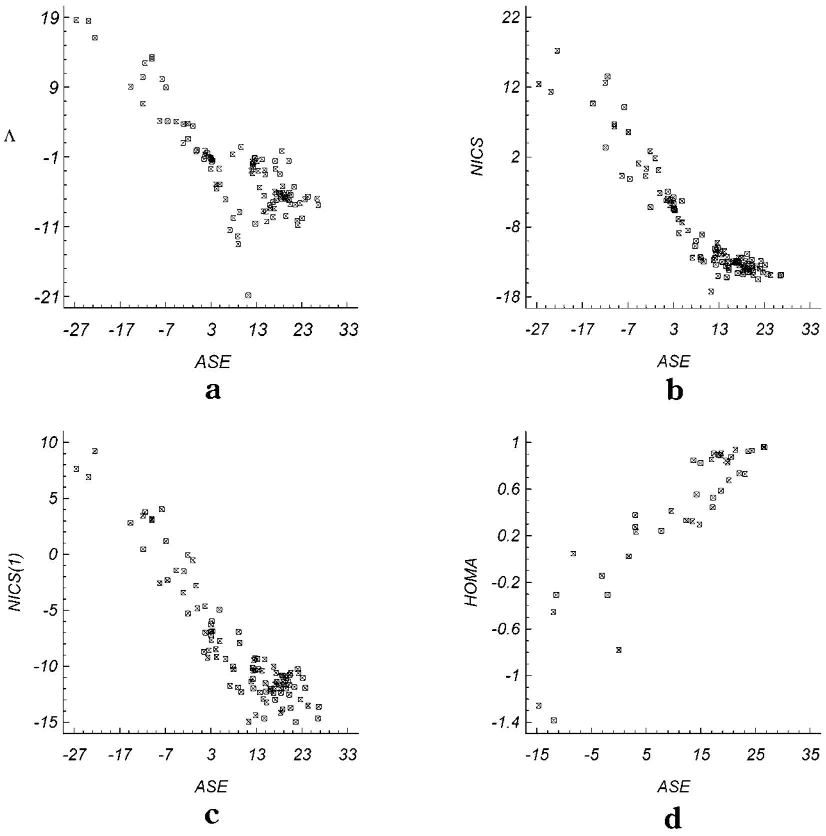

Figure 1. Dependence between Λ, NICS, NICS(1), and HOMA vs ASE for all 105 structures: (a) exaltation of magnetic susceptibility vs ASE; (b) NICS vs ASE; (c) NICS computed 1 Å above the ring centers vs ASE; (d) HOMA vs ASE.

Table 3. Correlation Coefficients for Correlation between Λ, NICS, NICS(1), HOMA, and ASE for all Compounds[a]

	ASE	Λ	NICS	NICS(1)
Λ	−0.8280 (102)			
NICS	−0.9406 (102)	0.8913 (102)		
NICS(1)	−0.9223 (102)	0.8809 (102)	0.9753 (105)	
HOMA	0.9001 (39)	−0.8269 (39)	−0.8448 (41)	−0.8556 (41)

[a] The sample size is given in parentheses.

correlations confirm the choice of the descriptors to be appropriate: the use of such descriptors to measure aromaticity makes sense, because each of these quantitative definitions of aromaticity distinguish between aromatic, nonaromatic, and antiaromatic systems in a roughly similar way.

Of equal importance from a practical point of view, however, is that when the aromaticity indices are considered separately for aromatic, antiaromatic, and nonaromatic groups of compounds, no good correlation is found. This is shown in Table 4 for the “aromatic” structures (defined as those for which ASE is greater than 5[43]); these are the systems for which the concept of aromaticity is crucial and to which it has long been applied.

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(43) The choice is somewhat conventional—note that there is no clear cut-off and thus no precise qualification system as to what is certainly aromatic.

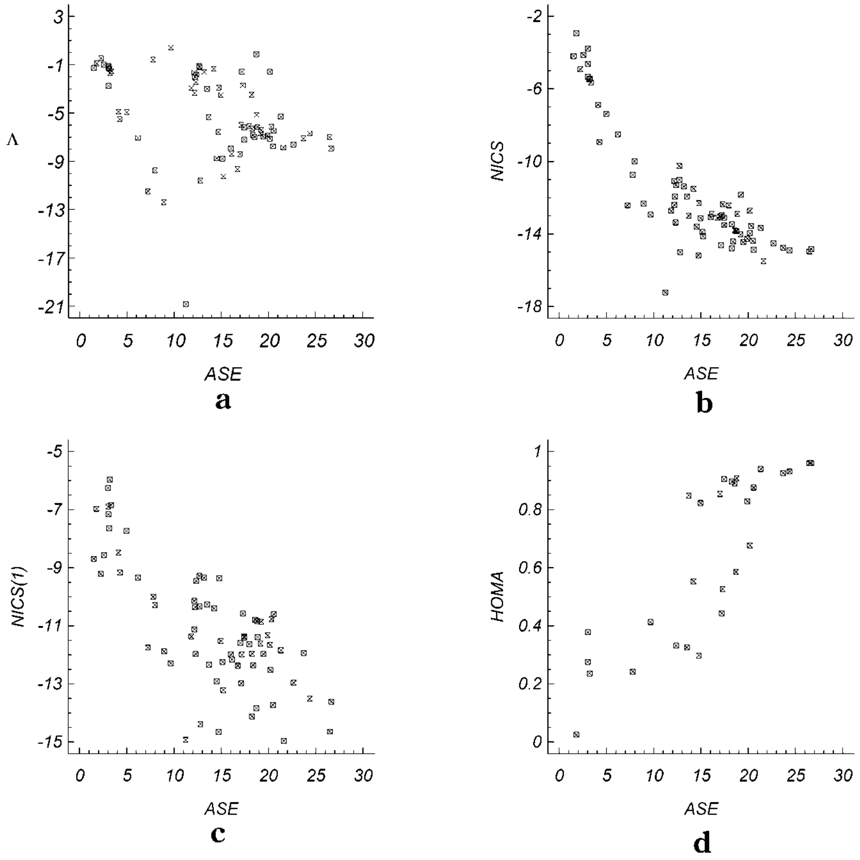

Figure 2. Dependence between Λ, NICS, NICS(1), and HOMA vs ASE for all aza and phospha derivatives of furan, thiophene, pyrrole, and phosphole (including parent systems): (a) exaltation of magnetic susceptibility vs ASE (correlation coefficient: −0.3447; 72 data); (b) NICS vs ASE (correlation coefficient: −0.8588; 72 data); (c) NICS computed 1 Å above the ring centers vs ASE (correlation coefficient: −0.7456; 72 data); (d) HOMA vs ASE (correlation coefficient: 0.8360; 28 data).

Table 4. Correlation Coefficients for Correlation between Λ, NICS, NICS(1), HOMA, and ASE for all Compounds of ASE>5[a]

	ASE	Λ	NICS	NICS(1)
Λ	−0.0625 (66)			
NICS	−0.6107 (66)	0.3827 (66)		
NICS(1)	−0.4052 (66)	0.2069 (66)	0.7605 (66)	
HOMA	0.7328 (27)	−0.6999 (27)	−0.8093 (27)	−0.5163 (27)

[a] The sample size is given in parentheses.

This lack of correlations holds both for aza-five- and for the phospha-five-membered rings when these subgroups are considered either separately or together (for the latter case, see Figure 2), although it is possible to find families of compounds (e.g., mono-endo-substituted rings) where the correlations are significantly better.[5,36]

Conclusions

We draw two general conclusions from the above data. On one hand: energetic, geometric, and magnetic indices of aromaticity all allow a rough division of conjugated cyclic compounds into three major groups: aromatic, nonaromatic, and antiaromatic. In this sense they contain similar information and show significant collinearity. Hence, various manifestations of aromaticity are related, at least to some extent[36] and from a philosophical point of view aromaticity as an abstract idea can be regarded as a one-dimensional phenomenon.[36]

On the other hand: practically within any one of these three main groups, and in particular for the group of aromatic structures, which are of major practical importance to experimental chemists, the indices are not correlated. In practical applications energetic, geometric and magnetic descriptors of aromaticity (even if optimally chosen) do not speak with the same voice. Thus, in this sense the phenomenon of aromaticity can be regarded essentially as being statistically multidimensional. Therefore, M.K.C., T.M.K., and A.R.K. stress again here[10b] that fully aromatic systems are those cyclic π-electron systems that follow all the main aromatic criteria, including special chemical behavior toward retaining the type of π-electron structure.[44] Those that follow only some, but not all of the features should be considered only as partly aromatic.[10b] Alternatively, one of us (PRS) considers that the special behavior associated with induced ring currents in aromatic compounds is most closely related to the cyclic electron delocalization which characterizes such species.[20,27] This important proposal is, however, often underappreciated by many experimental chemists. Only one of the latest editions of many advanced organic chemistry textbooks mentions “magnetic susceptibility”,[20] but NICS is becoming even now widely used.[45] Following E. D. Bergmann,[11] “...classification and theory are not ends in themselves. If they generate new experimental work, new compounds, new methods − they are good; if they are sterile − they are bad.” The next few years will

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(44) Lloyd, D.; Marshall, D. R. *Angew. Chem., Int. Ed. Engl.* **1972**, *11*, 404.

(45) Patchkovskii, S.; Thiel,W. *J. Mol. Model.* **2000**, *6*, 67−75.

validate a proper understanding of the aromaticity concept and its impact on the development of organic chemistry and related fields of research.

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Supporting Information Available: The Cartesian coordinates, absolute electronic energies at MP2(fc)/6-311+G**, zero-point vibrational energies ZPE at MP2(fc)/6-311+G**, and magnetic susceptibilities calculated with use of CSGT method at HF/6-311+G** for molecules used in eq 1. This material is available free of charge via the Internet at http://pubs.acs.org.

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