Aromatic molecular zones and fragments

Laszlo Tarko

Center of Organic Chemistry "C.D.Nenitzescu" – Romanian Academy, 202B Spl.
Independentei, Bucharest - 6th Sector, PO Box 35-108, MC 060023
E-mail: ltarko@cco.ro

Abstract

An edge on the weighted molecular graph is aromatic if the bond order B value is within [α, β] range. A certain "non-conjugated topological path" includes minimum two adjacent "single" edges ($B < \alpha$). The topological paths that are not "non-conjugated" are "conjugated topological paths". An aromatic zone is a collection of contiguous aromatic edges. An aromatic fragment is a topological path within aromatic zone. The proposed aromaticity formula measures the aromaticity of zones and any "conjugated paths" via two variables that gauge deviations of bond orders from a reference value and of atom hybridization from sp^2 character. The aromaticity of "non-conjugated paths" is, conventionally, null. The analysis of organic/inorganic molecules, ions and radicals, including those having cyclic, non-cyclic, planar and non-planar geometries, uses a unique set of parameters. The larger the deviation from Hückel rules, the smaller (even negative) is the computed aromaticity value. The paper presents a few non-aromatic Hückel and aromatic non-Hückel structures. After geometry optimization by PM6 method, one can compute the value of some aromaticity molecular descriptors, useful in QSPR computations. The paper includes a list of some descriptors that are measurements of the aromaticity of zones and aromatic "conjugated topological paths".

Keywords: Aromaticity, non-Hückel, bond orders, PM6 method, molecular descriptors

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Introduction

The story of aromatic compounds has extended over almost two centuries, since the Faraday discovery, in 1825, of "bicarburet of hydrogen", by distilling crude oil. In 1833, Mitscherlich produced it via the distillation of benzoic acid (from gum benzoin) and lime. In 1845, Mansfield isolated the same product from coal tar.

Later chemists have observed that "bicarburet of hydrogen", now called benzene, and other unsaturated hydrocarbons, with a specific odor, present a reduced reactivity, in addition reactions, relative to alkenes and alkynes.

Specific physical and chemical properties lead to the definition of a new class of organic compounds, namely aromatic molecules. The development of experimental chemistry has made necessary to introduce into this class some molecules containing heteroatoms, ions and radicals.

Features of aromatics include:

- low reactivity in addition reactions
- high substitution / addition ratio of reactivity
- elevated energy of hydrogenation
- typical values of bond length and bond orders
- specific magnetic properties of aromatic rings

While the above properties could be considered a more or less adequate measurement of the aromatic character, modern computational chemistry has revealed its structural basis.

Hückel rules,[1] state that a certain chemical ring is aromatic if:

a) there is continuous conjugation
b) the number of electrons involved in conjugation (both π and non-participants) is $4n + 2$, n being an integer ($n = 0, 1, 2, 3 \ldots$)
c) the ring is planar

Condition "and non-participants" and condition c) have not been formulated by Hückel, but imposed based upon the observed aromaticity of some heterocycles and lack of aromaticity of non-planar annulenes. Non-cyclic structures are considered *a priori* non- aromatic.

Limitations and difficulties of the Hückel model include:

- difficulties in counting, in certain cases, of electrons that participate in conjugation, to verify fulfilling of b) condition; in fact the Hückel model does not include any procedure for counting of these electrons
- difficulties in deciding whether condition c) applies, in the absence of either experimental or theoretical information regarding molecular planarity
- some aromatic structures are non-planar
- some aromatic structures are non-cyclic
- instability of some presumably stable, aromatic molecules
- insufficient information for quantitative comparison of aromatic species
- lack of options for comparison of local values of aromaticity within a molecule

In the quantitative evaluation of aromaticity, experimentally determined or theoretically calculated, parameters currently used include: magnetic properties,[2-12] geometry,[13-18] bond orders,[19-28] isodesmic energy,[29] combustion energy,[30] (topological) resonance energy,[31-38] bond lengths[40-46] etc.

Randić is inventor of "conjugated circuits" term and uses resonance energy RE, computed for these cyclic topological paths, to evaluate the aromaticity.[33-35] Almost simultaneously, "topological resonance energy" TRE was put forward by Aihara[31] and Gutman *et al*.[32] The values of aromaticity (Randić) and TRE (Gutman) are computed using very different formulas. These two models, used in the quantitative computation of aromaticity, use the "limit" Kekulé structures, in fact non-existent. The analyzed molecule includes, *a priori*, just one aromatic zone (continuous conjugation of all edge in molecular graph).

Aihara revealed recently[78-80] some limitations of TRE algorithm:

- large positive TREs for reactive non-Kekulé hydrocarbons, such as some quino-dimethanes
- the computed TRE value for a polycyclic π-system cannot be used for correct prediction of thermodynamic or kinetic stability
- many of molecular dianions/dications of many PAHs are supposed to be aromatic due to their positive TREs; however, many of them have long been regarded as anti-aromatics because of their global paratropic π -electron current.

The Randić/Gutman models may be considered the oldest predecessors of the author’s approach.

A few years ago, Tarko and Filip proposed a non-Hückel model of aromaticity, considered a bi-dimensional property.[39] This model, named TPA (Topological Path Aromaticity), eliminates the difficulties of the Hückel model listed above.

In the TPA sense, a given topological path is aromatic if all bond order values of edges are within an "aromaticity range" and all aromatic topological paths are "aromatic zones". The TPA model computes the aromaticity for aromatic zones only and does not estimate the non-aromaticity/anti-aromaticity. In practice, these limitations prove rather unproductive.

This article proposes an improved version of the TPA model. This new version redefines the notion of “aromatic zone”, defines the "non-conjugated topological path " and "conjugated topological path" terms, defines the notion of “aromatic fragments” and proposes a unique formula in the calculation of aromaticity/non-aromaticity/anti-aromaticity. In addition, the paper presents a list of molecular descriptors that are measurements of the aromaticity of zones/fragments.

In the following sections, the new algorithm will be called TOPAZ (**TO**pological **P**aths and **A**romatic **Z**ones). The TOPAZ model is based upon concepts shown in the next paragraph.

Aromaticity is considered the property of unsaturated species to exhibit a reduced reactivity in addition reactions, relative to alkenes that include the same number of double bonds. The cause of aromaticity of unsaturated species is considered "strong conjugation" of chemical bonds. This "strong conjugation", effect of a certain spatial distribution of electrons in a minimum energy conformer, brings about the absence of double and triple bonds, i.e. those chemical bonds involved in addition reactions. In fact, the absence of double and triple bonds, within non-saturated structures, is the sign of aromaticity. The net charges and bond orders are considered the most reliable source of information on the electron spatial distribution. The bond order is considered the best criterion and sufficient for the identification of the bond type of certain chemical bond. The single bond has a bond order lower than that of an aromatic bond, while the aromatic bond one intermediate between that of single and double bonds.

Methods, Formulae and Comments

A kenograph is a molecular graph whose vertices are heavy atoms, while the edges are chemical bonds.[47] In a kenograph, the vertices and edges are equivalent. In a weighted kenograph, on the other hand, they are not. For our purposes, the edges are defined by the values of bond orders. The collections of chemical bonds are identified with the edges of the kenograph. A "topological path" is the topological route that intersects each vertex only once. A path that intersects all vertices of a graph is called “hamiltonian”. A "hamiltonian" includes all the vertices of the graph, but not all the edges. Consequently, there are molecules where we can follow more than one “hamiltonian”.

The L edges located on any given group of chemical bonds of a weighted kenograph are characterized by B_i bond orders. A given chemical bond is aromatic if bond order value is within an aromaticity range.

$$B_i \in [\alpha, \beta] \tag{1}$$

where α and β are the boundaries of the aromaticity range.

Some chemical bonds are computed as "ionic"/"single" ($B < \alpha$) or "double" / "triple" ($B > \beta$). An “aromatic zone” is defined as a collection of contiguous aromatic chemical bonds. Each bond is contiguous to one or more of the bonds in the group. By definition, an aromatic zone includes only aromatic chemical bonds and is separated by other aromatic zones by non-aromatic chemical bonds. In a molecule can be present one or more aromatic zones. A unique aromatic zone may include or not all the heavy atoms of the molecule (the vertices of the kenograph). These zones may or may not include cycles.

A "non-conjugated topological path" includes two or more adjacent edges computed as "single" ($B < \alpha$), sign of "discontinuous conjugation". The topological paths that are not "non-conjugated topological paths" are defined as "conjugated topological paths". A "conjugated topological path" may be cyclic or non-cyclic, aromatic, non-aromatic or anti-aromatic.

The topological paths followed inside an aromatic zone are defined as “aromatic fragments”. All “aromatic fragments” are aromatic "conjugated topological paths". By definition, an aromatic zone may include one or more aromatic fragments. These fragments may be cyclic or non-cyclic.

Therefore, two heavy atoms linked by an aromatic bond define the simplest aromatic zone/fragment.

If the analyzed path is "non-conjugated" the aromaticity is, conventionally, null ($A = 0$).
The aromaticity of any aromatic zone or conjugated topological path is computed using formula (2).

$$A = 1000 \bullet (1 - f^2) / (1 + f^2) \tag{2}$$

where

if $f_1 / f_2 < x$ then $f = \max(f_1, f_2)$ else $f = \max(f_1, f_2, f_3)$

$f_1 = a \bullet S_1 / L$

$S_1 = \sum (B_{ref} - B_i)^2$

$f_2 = b \bullet (S_2 / L)^c$
$S_2 = |\sum (B_{ref} - B_i)|$
$f_3 = (f_1 / f_2)^d$
L is the number of edges of analyzed aromatic zone/ conjugated topological path
B_i is the computed bond order value of a certain chemical bond; $i \in [1, L]$
B_{ref} is the reference value of bond order
a, b, c, d and *x* are empirical parameters

The value B_{ref} depends upon the method used to calculate the bond orders and the reference molecule. Here the author presents the results obtained using the MOPAC2007 program[48a] and PM6 method included,[48b] with benzene as reference molecule. Therefore the calculated value of reference bond order is $B_{ref} = 1.44059$ (average of the six computed values of C-C bond orders in benzene).

The values of α, β, δ, *a, b, c, d* and *x* are not obtained using statistical methods. Starting point in seeking of these values is the value of bond order of C-C bonds in benzene, computed using PM6 method. The value of δ (accordingly α and β) is the result of aromaticity computation related to hundred of structurally diverse molecules/ions/radicals, quoted in literature as aromatic or non-aromatic/anti-aromatic. Therefore, these values are not "average" values, but "limit" values. The value of *a* and *b* force positive aromaticity value ($A > 0$) for structures quoted as "aromatic" and negative value ($A < 0$) for structures quoted as "non-aromatic". The value of *c* and bi-dimensional appearance of f function for aromatic structures, rank the analyzed species according to their quoted aromaticity (e.g. naphthalene > anthracene > phenanthrene > azulene, outer cycle in anthracene > central cycle in anthracene, thiophene > pyrrole > furan > selenofuran etc.). The value of *d* and *x* and presence of f_3 function are useful only in the computation of anti-aromaticity. The value of *d* and *x* are doubtful because of lack of quantitative data regarding to anti-aromaticity. For many cycles quoted as anti-aromatic TOPAZ computes very large value of f_1 / f_2 ratio.

For computations we use $\alpha = B_{ref} - \delta$, $\beta = B_{ref} + \delta$, $\delta = 0.390$ in formula (1) and $a = 6.57462$, $b = 1.36871$, $c = 1/3$, $d = 1/3$, $x = 3.1$ in formula (2). Thus the values of α and β are $\alpha = 1.05059$ and $\beta = 1.83059$. If other computational method (AM1, PM3, PM5, *ab-initio*, DFT) or other reference molecule is used, B_{ref}, α, β, δ, *a, b, c, d* and *x* have to be changed accordingly.

Formula (2) forces the aromaticity value within the [-1000, 1000] range. The reference molecule will always be the molecule with the maximum calculated aromaticity.

The computed value of bond orders depends on geometry of molecule and, sometimes, is very close to the boundaries of the aromaticity range [α, β]. Therefore, the computation of bond orders should be performed only after careful optimization of the geometry. Here, for geometry optimization, the software MOPAC2007 uses the key words “PM6 PULAY GNORM=0.01 SHIFT=50 GEO-OK CAMP-KING BONDS CHARGE=n MMOK”. Next, the resulting bond order values, specific for the minimum-energy conformer, were used for aromaticity calculations, using formulas (1), (2) and the last version of DESCRIPT program.[49-51] In present PM6 method includes parameters for 69 elements. In fact, capability of TOPAZ algorithm to compute aromaticity for certain thinkable chemical structure depends on ability of used quantum mechanics method to compute bond order of the included chemical bonds.

Formulas (1) and (2) reveal qualitative features of the proposed TOPAZ algorithm:

i) the model does not require the number of electrons that participate in conjugation, rather it relays upon the bond orders calculated by quantum mechanics methods

ii) single-step topological paths, i.e. those comprising a single chemical bond can be analyzed

iii) since (1) and (2) do not comprise topological or geometrical parameters, aromaticity calculations do not reject *a priori* non-cyclic and non-planar structures

iv) since (1) and (2) do not comprise atomic parameters, aromaticity calculations do not reject *a priori* inorganic (in other words without carbon atoms) structures

v) a single set of parameters is sufficient for the analysis of molecules, ions, radicals and ion-radicals since (1) and (2) do not consider explicitly upon "net charge" or "multiplicity" parameter

vi) as a result of the variability of B_i values, zones and fragments may have different aromaticity values; the collection of various edges that correspond to molecular zones/fragments, and thus have specific aromaticity assigned to them, form a molecular aromaticity map

vii) the anti-aromatic structures are a particular case of the non-aromatic structures, with large negative value of aromaticity

Function f_1 in formula (2) measures the bond order deviations from the reference value B_{ref}, while f_2 measures the deviations of chemical bonds (related to the same B_{ref} value) from the single / double alternating type, i.e. deviations from sp^2 character. Therefore, the aromaticity is considered a bi-dimensional property.

If all values of bond order are larger or smaller than B_{ref} value (i.e. the alternation of bond order values is not around of B_{ref} value) then the value of f_2 is larger. Functions f_1 and f_2 are correlated. Mathematically, if f_1 has a large value, f_2 can be either small or large. If, on the other hand, f_1 has a small value, f_2 is necessarily small. The physical meaning of this correlation is obvious: a large deviation from aromaticity may mean either a small deviation from atomic sp^2 character (up to "pure" sp^2, polyenes), or a large one (up to sp^3, alkanes). In practice, the functions f_1 or f_2 alone are insufficient for a quantitative correct description of aromaticity.

Results and Discussion

The following sections present examples of the application of the TOPAZ algorithm.

Non-aromatic (Hückel) - non-aromatic (TOPAZ) structures

The structures in Fig. 1 are non-aromatic by Hückel's definition, because the rule "4n+2" is not fulfilled, because of non-planarity or lacking of continuous conjugation. Hexatriene is non-cyclic.

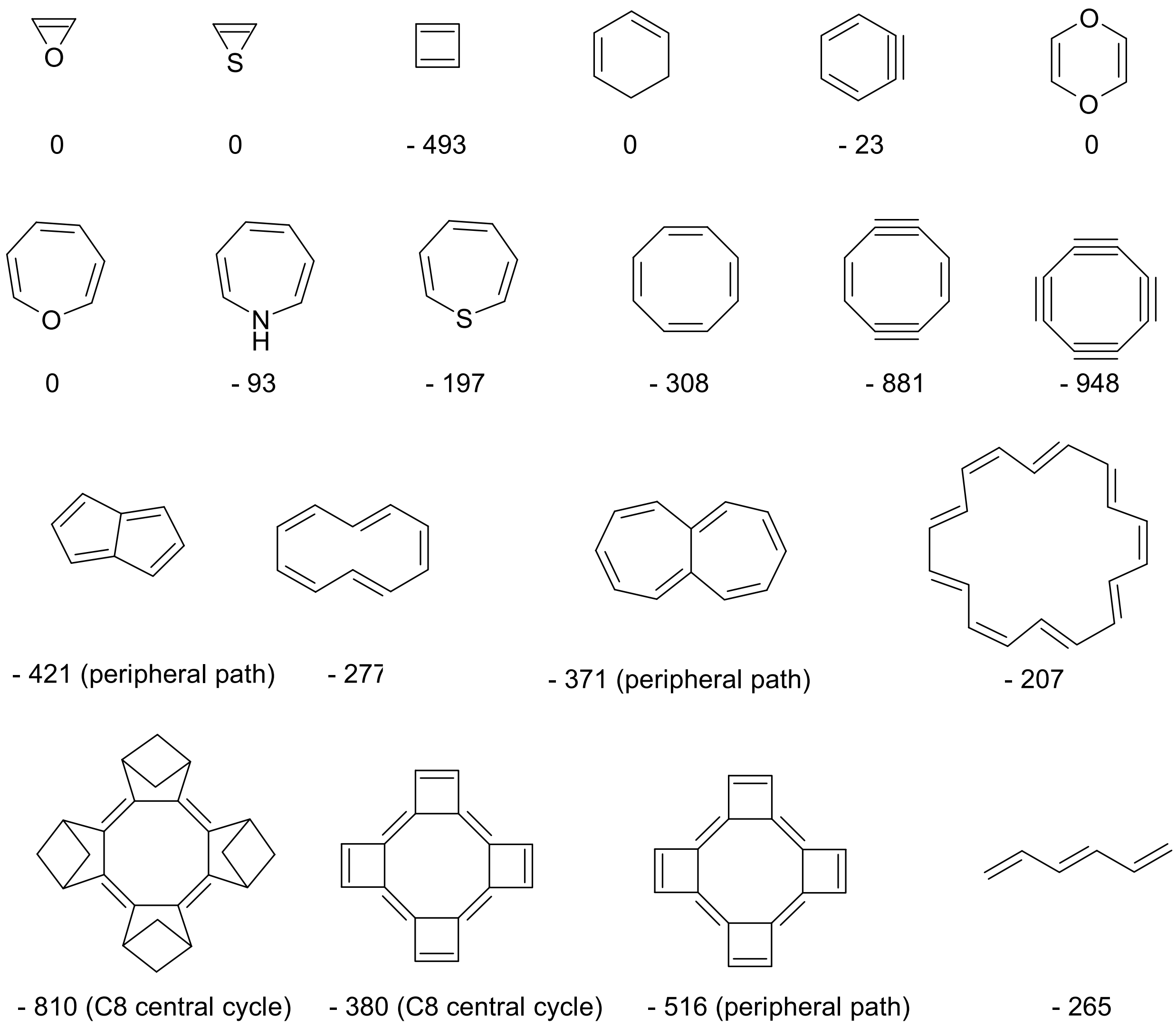

Figure 1. Non-aromatic Hückel/TOPAZ structures.

Fig. 1 presents the computed value of TOPAZ aromaticity. From the point of view of the TOPAZ, the molecules in Fig. 1 are non-aromatic because $A \leq 0$. If aromaticity is null the analyzed topological path presents "discontinuous conjugation". If $A < -350$ the analyzed cycle may be considered "anti-aromatic".

In benzyne the chemical bonds are conventionally drawn, despite of computed value of bond orders. The benzyne ring is "conjugated topological path" and contains a chemical bond computed as “double“, with a bond order ($B = 2.404$) outside the $[\alpha, \beta]$ interval. The other rings in Fig. 1 contain more than one non-aromatic bonds, computed as "single", "double" or "triple", with a bond order outside the $[\alpha, \beta]$ range.

The cycle in cyclooctatetraene is computed as non-planar. However, the central cycle C_8 in polyannelated cyclooctatetraene[77] in Fig. 1 is computed as planar.

Aromatic (Hückel) - aromatic (TOPAZ) cycles

The rings of the monocyclic species in Fig. 2 are aromatic in the Hückel definition because all the conditions of the Hückel model are, as a rule, fulfilled. From the point of view of the TOPAZ model, many cycles in Fig. 2 are aromatic because $A > 0$.

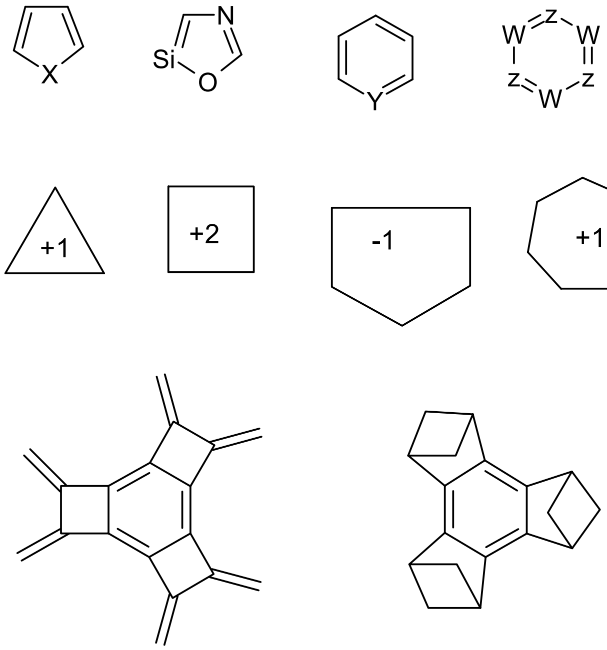

Figure 2. Aromatic Hückel/TOPAZ cycles.

In the case of the heterocycles containing five atoms, TOPAZ calculates a high aromaticity A = 481 (X = O), A = 540 (X = NH), A = 571 (X = S) or a small aromaticity A = 216 (X = Se), A = 199 (X = Te). The silicooxazole ring includes O-CH "single" bond ($B = 0.878 < \alpha$) and exhibits a low aromaticity A = 169.

For the rings containing six atoms TOPAZ calculates a high or very high aromaticity A = 1000 (Y = CH), A = 832 (Y = N), A = 631 (Z = N; W = CH), A = 571 (Z = N; W = B), a low aromaticity A = 186 (Z = NH; W = BH), A = 125 (Z = S; W = BH) or a very low aromaticity A = 31 (Z = N; W = N), A = 9 (Z = O; W = BH). We observe that the cycle in the inorganic molecule of $B_3N_3H_6$ (borazyne) is much less aromatic than the B_3N_3 inorganic ring.

For the ionic rings in Fig. 2 we have calculated a high aromaticity A = 914 ($C_3H_3^{+1}$), A = 714 ($C_5H_5^{-1}$), A = 672 ($C_7H_7^{+1}$) or a low one A = 214 ($C_4H_4^{+2}$).

The central cycle C_6 in polyannelated benzene[76,77] in Fig. 2 exhibits a moderate aromaticity A = 522 and A = 425 (strong enough Mills-Nixon effect[82], that means alternation of C-C bonds in benzene cycle because of annelation).

Conjugated, not yet synthesized, inorganic cycle in hexazine[81] exhibits a very low aromaticity A = 31.

In the case of the inorganic cyclic ions S_xN_y, analyzed by Gimarc,[52] we have computed a diverse value of aromaticity A = 511 ($S_4N_4^{+2}$), A = 376 ($S_4N_3^{+1}$) and A = 138 ($S_3N_3^{-1}$).

For the inorganic cyclic anion N_6^{-4}, described as aromatic,[53] we have calculated a very low aromaticity A = 36.

Non-aromatic (Hückel) - aromatic (TOPAZ) cycles

The cycles in Fig. 3 are non-aromatic from the Hückel point of view because the number of electrons involved in the conjugation is different from 4n+2 and/or because of presumably discontinuous conjugation. From the point of view of the TOPAZ model, some cycles in Fig. 3 are aromatic because A > 0.

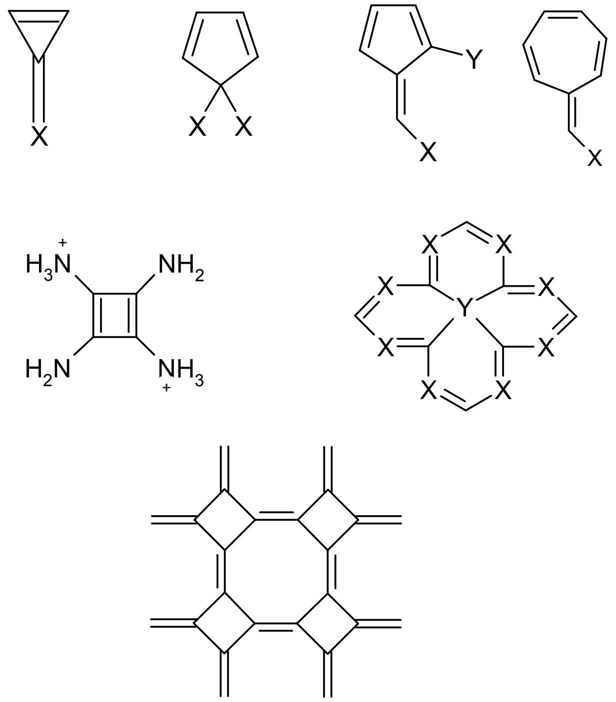

Figure 3. Non-aromatic Hückel – aromatic TOPAZ cycles.

The aromaticity of the substituted cyclopropenes (X = CH_2, NH, O, etc.) in Fig. 3 has been studied by Bachrach.[54] The algorithm proposed here calculates a small aromaticity of cycle in only one case: X = S (A = 160). For other X substituents, there is "discontinuous conjugation" (A = 0).

A few years ago, Nyulaszi asked the question "how to make cyclopentadiene cycle aromatic?" and offered a possible answer[55] with the disubstituted cyclopentadiene in Fig. 3. The TOPAZ algorithm calculates a low aromaticity for this cycle only in two situations: X = SnH_3 (A = 186) and X = $Sn(CH_3)_3$ (A = 259). For other X substituents, there is "discontinuous conjugation".

The substituted fulvene in Fig. 3 (X is NH_2; Y is CH=NH) is considered "non-classical aromatic compund".[56] For the ring in this compound TOPAZ calculates a moderate aromaticity A = 473. If X = $N(CH_3)_2$ and Y = H the ring exhibits a lower aromaticity A = 157.

The planar ring of substituted heptafulvene in Fig. 3 (X is CH=O) exhibits a very low aromaticity A = 102. For other X substituents, there is "discontinuous conjugation".

The author also asks the question "how to make cyclobutadiene cycle aromatic?". A possible answer is the cyclobutadiene dication in Fig. 3. For cycle of this dication, TOPAZ calculates a very low aromaticity A = 59. The aromaticity of the C_4 cycle in Fig. 3 is the effect of the addition of two protons in the molecule. The aromaticity of the C_4 cycle in Fig. 2 is the effect of the elimination of two electrons from the molecule.

The tetracyclic molecule in Fig. 3 (X = B or N; Y = C, Si, Ge or Sn) has a computed very non-planar geometry. The number of electrons involved in conjugation is different from 4n+2. However, the computed aromaticity of the peripheral topological cycle is positive A = 430 (X = B, Y = C), A = 369 (X = B, Y = Si), A = 427 (X = B, Y = Ge), A = 460 (X = B, Y = Sn), A = 78 (X = N, Y = C), A = 30 (X = N, Y = Si), A = 320 (X = N, Y = Ge) and A = 624 (X = N, A = Sn). All six-atom cycles C_3X_2Y are non-aromatic because the C-Y bonds are computed as "single" ("discontinuous conjugation").

The central cycle C_8 in polyannelated cyclooctatetraene in Fig. 3 is computed as planar and exhibits a low aromaticity A = 286.

The very non-planar cycle of hexa-*tert*-butyl-benzene exhibits a moderate aromaticity A = 589.

Aromatic (Hückel) - non-aromatic (TOPAZ) cycles

Many rings in Fig. 4 seem to fulfill the requirements of the Hückel model.

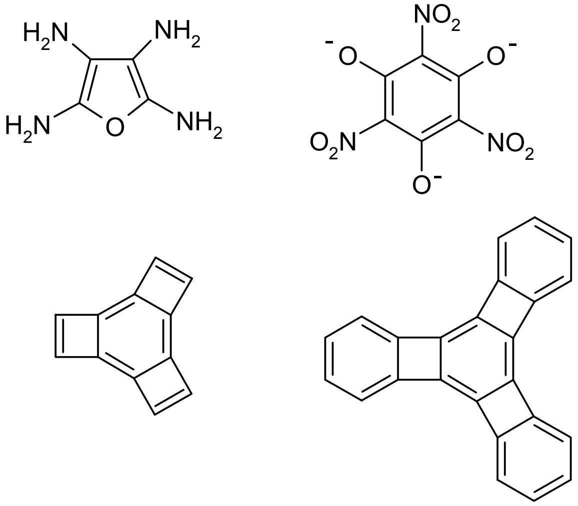

Figure 4. Aromatic Hückel – non-aromatic TOPAZ cycles.

Within some rings in Fig. 4 the algorithm we have proposed identified non-aromatic bonds, with a bond order outside the [α, β] range.

The calculations for the substituted furan ring have been done because the author has asked the question: "how to make furan cycle non-aromatic?" In tetra-amino-furan ring, the C-O bonds are “single” B = 1.007 (there is "discontinuous conjugation").

The computations for the substituted benzene ring have been done because the author has asked the question "how to make benzene cycle non-aromatic?" In the ring of the trianion, all C-C bonds are “single”, with a bond order B = 1.012 outside the [α, β] range.

The central cycle C_6 in polyannelated benzene[74–76,83] seems to be anti-aromatic (A = - 374) and low non-aromatic (A = - 16), respectively (very strong Mills-Nixon effect).

Doubtful aromatic (Hückel) - aromatic/non-aromatic (TOPAZ) cycles

The cycles in Fig. 5 are doubtful aromatic, in Hückel sense, because the number of electrons involved in conjugation is difficult to estimate (4n+2 or not 4n+2).

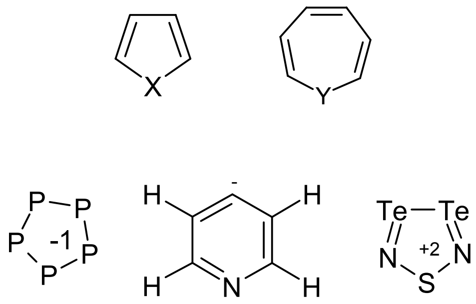

Figure 5. Doubtful aromatic cycles, in Hückel sense.

The aromaticity of phosphole and arsole (X = PH and X = AsH) is matter in dispute more than 35 years.[9, 57-60] In phosphole and arsole the chemical bonds C-X are computed as "single" (B < α). Therefore, these cycles are non-aromatic, in TOPAZ meaning ("discontinuous conjugation").

In the case of borepine ring (Y = BH) we have calculated a low aromaticity A = 196. If Y is CH_2, O, NH, S or SO_2 this cycle is computed as non-aromatic ("discontinuous conjugation").

The cycle of P_5^{-1} inorganic anion[52] exhibits a very large value of aromaticity A = 723.

For the ring of the pyridine anion in Fig. 5 TOPAZ calculated a high aromaticity A = 642, lower than the aromaticity of the pyridine cycle in Fig. 2 (A = 832).

For the ring of the $Te_2N_2S^{+2}$ inorganic dication[8] we have calculated a moderate value of aromaticity A = 441.

The computed aromaticity (A = 192) of the cycle in B/N-borazyne radicals $B_3N_3H_5$ is a bit more pronounced than the aromaticity (A = 186) of the cycle in borazyne $B_3N_3H_6$.

Aromatic zones

This chapter presents examples of “aromatic zones”, defined according to TOPAZ.

All aromatic rings in Fig. 5 represent unique cyclic aromatic zones, including all the bonds between the heavy atoms of the analyzed specie.

In naphthalene (A = 608), anthracene (A = 531), [9] helicene (A = 445), fullerene C_{60} (A = 252), indole (A = 448), for instance, the TOPAZ algorithm identifies unique polycyclic aromatic zones that include all the bonds between the heavy atoms.

Application of the TOPAZ algorithm leads to the conclusion that the aromaticity of the unique aromatic zone in naphthalene paramagnetic cation radical (A = 483) and anion radical (A = 479) is lower than that of their diamagnetic parent (A = 608), contrary to the conclusions based on application of the HOMA formula.[73] Both TOPAZ and HOMA bi-dimensional index[40-46] measure deviations of chemical bonds from the "reference value" and deviations from the single / double alternating type. However, HOMA formula uses "bond length", while TOPAZ algorithm uses "bond order".

In azulene we can identify a unique aromatic zone (A= 442), that coincides with the peripheral topological path. Similarly, in pentalene dication, we can identify a unique aromatic zone (A= 449), that is the peripheral topological path.

Unique aromatic zones, with complex shapes, that also include all bonds between the heavy atoms, are identified, for instance, in cyanuric acid (A = 219), substituted cyclopropene C_3H_2S in Fig. 3 (A = 209), thiotropone (A = 391), pyromeconic acid cation (A = 277), phenalenyl radical (A = 475), benzyl radical (A = 699) and triphenylmethane radical (A = 556).

Almost all properties of aromatic cyclic and non-cyclic structures (exception is "magnetic properties") are similar. Therefore, the application of aromaticity computation, related only to cyclic structures, seems to be rather unproductive. For about 25 years are being studied the non-cyclic, "Y-shaped", aromatic species.[62-71] TOPAZ identifies as "Y-shaped" aromatic molecules, for instance, the urea (A = 255), thiourea (A = 248) and guanidine (A = 479). In these molecules, the algorithm we have proposed here identifies a unique aromatic zone including all the heavy atoms. The unique aromatic zone in trimethylene-methane dication $(CH_2)_3C^{2+}$, the parent specie for the "Y-aromaticity" research field, exhibits a low aromaticity A = 325. The dianions CX_3^{2-} are other examples of “Y-shaped" ions, computed as aromatic. These ions result, theoretically, from the molecules with the structure of X = C $(XH)_2$, by the loss of two protons. For instance, CO_3^{2-} is formed from the carbonic acid, and $C(NH)_3^{2-}$ had guanidine as a parent compound. In these anions, the algorithm proposed here identifies a unique aromatic zone containing all the heavy atoms. The aromaticity calculated for these aromatic zones is low: A = 261 (X = CH_2), A = 212 (X = O), A = 275 (X = NH) and A = 229 (X = S). In benzene trianion in Fig. 4 we can identify three CNO_2 "Y-shaped" aromatic zones (A = 304). The unique aromatic zone, branched as double Y, in $[S\text{-}C(NH_2)\text{=}CH\text{-}C(NH_2)\text{=}S]^-$ anion, containing all the heavy atoms, exhibits a low aromaticity A = 232. The unique aromatic zone in trivinyl-methane “Y-shaped" radical exhibits a low aromaticity A = 346.

The unique aromatic zone in $H_2N\text{-}(CH{=}CH\text{-}CH{=}CH\text{-}NH)_n\text{-}H$ includes all the bonds between the heavy atoms and exhibits a low aromaticity A = 251 (n = 1), A = 198 (n = 6), A = 192 (n = 9). Related to these values the aromaticity of these oligomers may be computed as A ~ 185.9 + 65.2 / n.

Unique aromatic zone of molecules/ions/radical in Fig. 6 includes all bonds between the heavy atoms. Therefore, Fig. 6 is able to compare TRE[32] (multiplied by 10,000) and TOPAZ computed value of aromaticity.

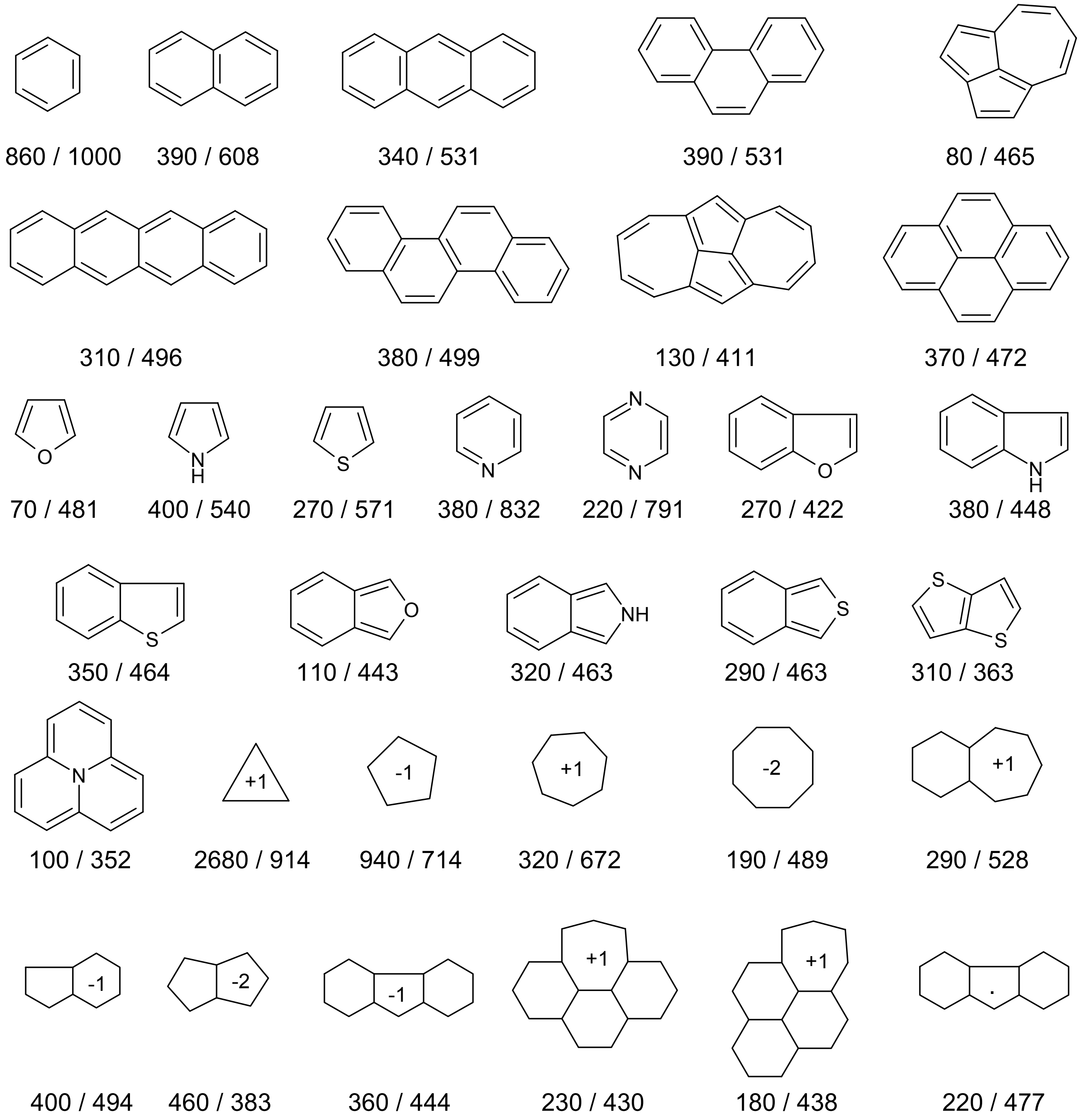

Figure 6. TRE (multiplied by 10,000) / TOPAZ value of aromaticity.

From the point of view of TOPAZ, the TRE aromaticity of azulenic PAH and 1,4-diazine seems to be underestimated. On the contrary, the aromaticity of 1,4-dithio-pentalene, cyclopropene cation, cyclopentadiene anion and pentalene dianion seems to be overestimated.

Fig. 7 presents two examples of aromatic zones included in porphorine-like organic / inorganic molecules, $C_{24}H_{16}N_8$ and B_8S_{16},[52,61] computed as planar molecules. In Fig. 7 the upper part presents the molecules (carbon atoms in black, nitrogen in blue, sulphur in yellow and boron in greenish) and the lower part presents the identified aromatic zones. Black zones are very aromatic (A ~ 791), red zones are moderate aromatic (A ~ 389) and green zone exhibits a very low aromaticity (A = 45).

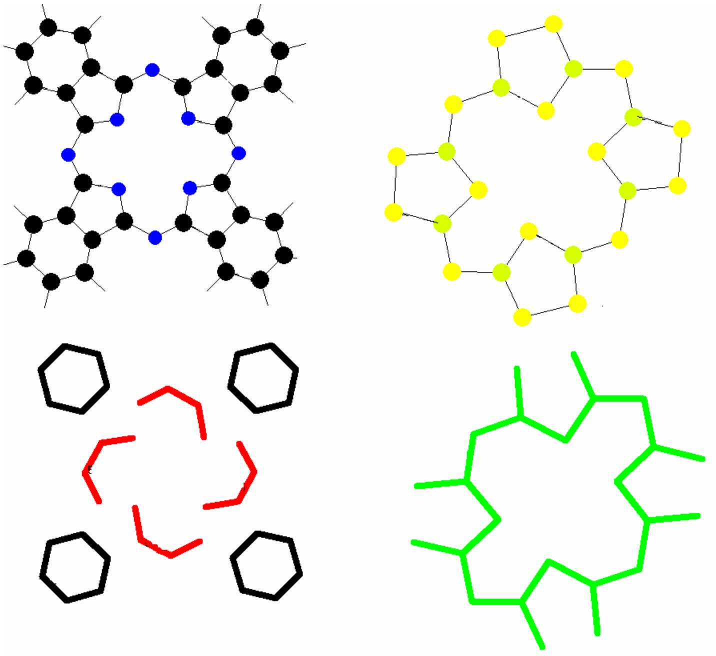

Figure 7. Aromatic zones in two porphorine-like molecules.

Fig. 8 presents some examples of non-cyclic aromatic zones that are included in (or include part of) non-aromatic cycles. The aromaticity of the aromatic zones in Fig. 8 has diverse values: A = 741 (benzyne), A = 493 (2, 5-di-phospha-furan), A = 173 (tetra-amino-furan). In tropone, we identify two aromatic zones: A = 135 (the area with five aromatic bonds) and A = 47 (the area with only one aromatic bond, the carbonyl group). Thus the aromaticity map of tropone differs a lot from the map of thiotropone (unique aromatic zone A = 391).

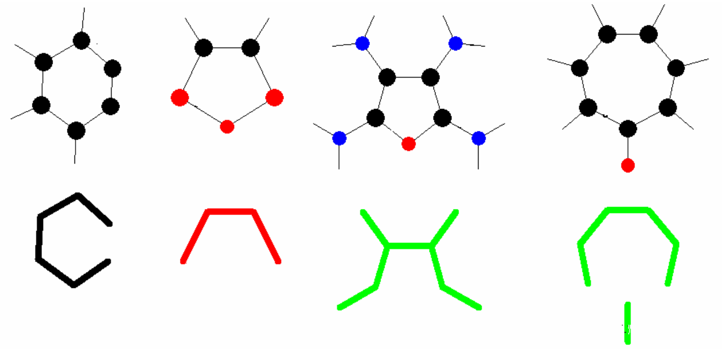

Figure 8. Non-cyclic aromatic zones related to non-aromatic cycles.

In the aromaticity maps in Fig. 7 and Fig. 8, obtained using DESCRIPT software, the non-aromatic chemical bonds are invisible.

Aromatic fragments

This chapter presents examples of "aromatic fragments", defined according to TOPAZ. In naphthalene the rings have an aromaticity (A = 600) a little different from the aromaticity of the peripheral topological path (A = 617) and of the unique aromatic zone (A = 608).

In anthracene, the outer cycles (A = 508) are more aromatic fragments than the central cycle (A = 470). The aromaticity of the peripheral topological path is a bit more pronounced (A = 585) than the aromaticity of the unique aromatic zone (A = 531).

In [9] helicene the aromaticity of the terminal rings (A = 645) is visibly higher than the aromaticity of the other rings (A = 445) and of the peripheral topological path (A = 395).

In dicyclohepta[*cd,gh*]pentalene the C_7 rings are fragments with much higher aromaticity (A = 458) than the C_5 rings (A = 346).

In C_{60} fullerene the C_6 rings are fragments with much higher aromaticity (A = 403) than the C_5 rings (A = 63). On the contrary, in C_{60}^{-6} fullerene anion, analyzed by Rabinovitz,[72] the aromaticity of C_6 rings (A = 193) and C_5 rings (A = 172) is almost equal.

A future paper will present a method for automatically identification of the aromatic fragment LATP (Longest Aromatic Topologic Path) on a random graph. In C_{60} fullerene LATP is a hamiltonian topological path and has a low aromaticity (A = 240). In polyacenes, LATP coincides with the peripheral topological path.

In Fig. 9, the upper part presents the aromaticity map in octathiadiazole. We can identify three aromatic zones: two zones (in black) with moderate aromaticity (A = 495) and one zone (in red) with low aromaticity (A = 343). The non-aromatic bonds are invisible. One may note that the ending rings are connected to the rest of the molecule by "single" bonds, invisible here, with a low bond order (B = 1.047), a bit under the limit value α. In Fig. 9 the lower part presents LATP (A = 464) in octathiadiazole (green line).

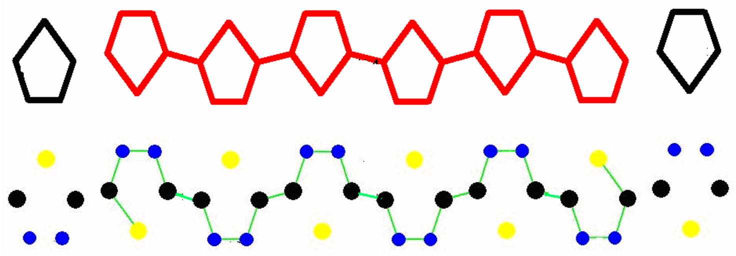

Figure 9. Aromatic zones and LATP in octathiadiazole.

In indole the six-atom ring has a much higher aromaticity (A = 579) than the five-atom heterocycle (A = 322). The peripheral topological path coincides with LATP and is a fragment with medium aromaticity (A = 459).

In thiotropone the ring does not coincide with LATP (A = 406) and is a fragment with lower aromaticity (A = 328) than the unique aromatic zone (A = 391) that includes it. In cyanuric acid, the ring coincides with LATP and is, reversely, a fragment with a higher aromaticity (A = 278) than the unique aromatic zone that includes it (A = 219).

In Table 1 we present the values of the aromaticity of some rings that are aromatic according to the NICS criterion.[2,9] Some of the cycles are, in TOPAZ sense, “aromatic zones”, others are “aromatic fragments”.

Table 1. NICS and TOPAZ values of aromaticity for some cycles

Cycle	NICS	TOPAZ	Cycle	NICS	TOPAZ
Benzene	-9.7	1000	2, 3, 4, 5-Tetraphosphathiophene	-15.0	534
Cyclopentadienyl anion	-14.3	714	Outer cycle in anthracene	-8.2	508
Tropylium cation	-7.6	672	Furan	-12.3	481
Outer cycle in phenanthrene	-10.2	663	Central cycle in anthracene	-13.3	470
Sylolyl anion $C_4H_4SiH^{-1}$	-6.7	650	3-azafuran	-11.3	451
C_6 cycle in benzocyclobutadiene	-2.5	619	2, 3, 4, 5-Tetraphosphapyrrole	-14.6	433
Each cycle in naphthalene	-9.9	600	Central cycle in phenanthrene	-6.5	375
Thiophene	-13.6	571	2, 5-diphosphafuran	-10.3	0
3-azaphosphole	-3.8	565	Phosphole	-5.3	0
Pyrrole	-15.1	540	Cyclopentadiene	-3.2	0
2, 3, 5-triphosphaphosphole	-12.3	535	Cyclohexane	-2.2	0

If A = 0 TOPAZ identified "discontinuous conjugation". In the non-aromatic cycle of 2, 5-diphosphafuran in Table 1, TOPAZ identified a non-cyclic aromatic zone P-CH-CH-P (A = 493, see Fig. 8 as well).

One may note that the NICS aromaticity values sometimes leads to results at odds with experimental data. In Table 1, according to NICS, benzene exhibits a medium aromaticity and is less aromatic than furan, pyrrole, tetra-phospha-thiophene, etc; the central ring of anthracene is more aromatic than the other two cycles; phosphole is aromatic enough; cyclohexane and cyclopentadiene exhibit a weak aromaticity.

Square correlation of NICS/TOPAZ values in Table 1 is very small ($r^2 = 0.174$).

Effect of substituent on aromaticity of substituted cycle

Figures 3, 4 and 8 present few examples related to influence of substitution on aromaticity of substituted cycle.

The unique aromatic zone in cyanuric acid (A = 219) is much less aromatic than the unique aromatic zone of a *sim*-triazine (A = 631). This is other example of a high decrease of aromaticity due to the presence of certain substituents grafted on the ring. The following paragraphs present other, more detailed, examples.

In Table 2, we present the values of the aromaticity of the benzene ring substituted with X. A high conjugation can bring the computed value of the bond order $B_{C\text{-}X}$ of the C-X chemical bond inside the [α, β] range.

Table 2. TOPAZ aromaticity of cycle in monosubstituted benzenes (molecules/ions)

Substituent X	Aromaticity of cycle	Bond order $B_{C\text{-}X}$	Substituent X	Aromaticity of cycle	Bond order $B_{C\text{-}X}$
H	1000	0.965	SCH_3	821	1.031
I	896	0.973	COOH	820	0.944
$C(CH_3)_3$	889	0.980	CHO	813	0.971
SO_3^-	878	0.682	$COOCH_3$	808	0.964
Br	874	0.978	NH_3^+	800	0.921
CH_3	869	1.010	NO_2	784	0.898
COO^-	864	0.818	$N{=}N\text{-}C_6H_5$	781	1.023
C_6H_5	861	1.009	SO_3H	779	0.827
CF_3	852	0.963	COCl	778	0.981
Cl	845	0.997	NCO	759	0.960
$CONH_2$	835	0.952	OH	715	1.039
$CH{=}CH_2$	832	1.039	OCH_3	702	1.044
SH	832	1.033	$N(CH_3)_2$	699	1.086
F	831	0.973	NH_2	647	1.136
CN	823	1.018	S^-	520	1.153
$COCH_3$	821	0.954	O^-	436	1.489

The insufficiently conjugated ring with the substituent ($B_{C\text{-}X} < \alpha$) is an "aromatic zone". The sufficiently conjugated ring with the substituent ($\alpha \le B_{C\text{-}X} \le \beta$) is an "aromatic fragment". One can notice that in the five species with the lowest ring aromaticity the computed value of the bond order $B_{C\text{-}X}$ is the highest.

The Fig. 10 and Table 3 present the aromaticity of some cycles from the point of view of HOMA and TOPAZ indices. The value of Espinosa bi-dimensional HOMA index for these cycles is quoted in literature.[46]

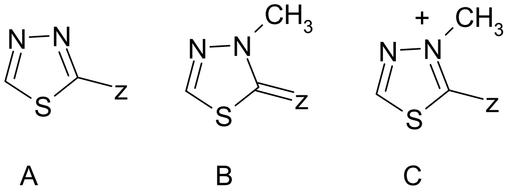

Figure 10. Substituted heterocycles related to Table 3.

Table 3. HOMA and TOPAZ aromaticity of cycle in Fig. 10 structures

Structure in Fig. 10	Z	HOMA	TOPAZ	Structure in Fig. 10	Z	HOMA	TOPAZ
A	H	0.689	538	C	OCH_3	0.675	309
C	H	0.800	509	C	NH_2	0.643	268
C	$CH(CN)_2$	0.802	474	C	$NHCH_3$	0.634	248
A	SCH_3	0.618	460	B	S	0.556	220
C	Cl	0.771	406	B	$C(CN)_2$	0.592	0
C	SH	0.725	379	B	NH	0.362	0
C	SCH_3	0.714	357	B	O	0.348	0
C	OH	0.686	318	B	NCH_3	0.327	0

Cycle in many B structures in Fig. 10 presents "discontinuous conjugation". For these cycles TOPAZ aromaticity is null. HOMA algorithm does not include something similar with condition of "continuous conjugation". Consequently, there are many TOPAZ non-aromatic rings that are aromatic from the point of view of HOMA[44,46] (cycle in many B structures in Table 3, cycle in substituted fulvene in Fig. 3 (X=CHO, Y = H), heptafulvene etc.).

Square correlation of HOMA/TOPAZ values in Table 3 is high enough ($r^2 = 0.770$).

Aromaticity molecular descriptors

After the identification on a molecular map of aromatic zones and fragments, one can calculate certain feature of these zones/fragments (number, size, proportions, aromaticity, etc.) This means the computation of some molecular aromaticity descriptors.

Here follows the list of the aromaticity descriptors that can be calculated with the DESCRIPT software, that uses the parameters of formula (2).

- number of the aromatic bonds
- percent of the aromatic bonds
- minimum aromaticity of the aromatic bonds
- average aromaticity of the aromatic bonds
- maximum aromaticity of the aromatic bonds
- number of the aromatic zones
- total mass of the aromatic zones
- mass percent of the aromatic zones
- average mass of the aromatic zones
- variation coefficient of mass in the aromatic zones
- mass percent of the largest aromatic zone
- mass percent of the most aromatic zone
- average aromaticity of the aromatic zones
- variation coefficient of aromaticity in the aromatic zones
- weighted aromaticity of the analyzed molecule
- weighted aromaticity of the largest aromatic zone
- weighted aromaticity of the most aromatic zone
- function of bond number and aromaticity in the largest aromatic zone
- topological length of LATP
- LATP length / Bond number ratio
- aromaticity of LATP
- root of LATP length • LATP aromaticity product
- LATP length / Bond number • LATP aromaticity

By statistical studies, one can measure the intensity of the cause-effect connection between descriptors, respectively between certain descriptors and various macroscopic properties. For instance, the presence of a large aromatic zone in the molecules of a certain compound/material seems to be associated with certain optical (color) or electrical (conductivity) properties. This type of statistical studies can result in a QSPR (Quantitative Structure Property Relationship).

Conclusions

The following conclusions emerge following the TOPAZ analysis of a very large number of species of diverse structural types.

Organic/inorganic aromatic molecules/ions/radicals can be viewed, from an aromaticity point of view, as a collection of zones and fragments, each with a specific, local, aromaticity.

Regarding zones/fragments as a collection of contiguous edges on the weighted molecular graph, provides an adequate, qualitative and quantitative description of aromaticity.

Aromaticity is the result of strong conjugation of chemical bonds. Qualitatively, all bond order values in a given zone/fragment are within [α, β] range. Quantitatively, a formula computes aromaticity, via two variables that gauge deviations of bond orders from a reference value and of atom hybridization from sp^2 character. Some conjugated topological paths are aromatic, despite of presence of few "single" or "double" bonds.

The Hückel cyclic, planar and 4n+2 π electrons molecular features are no longer viewed as necessary for aromaticity. Rather, they are a particular case of aromatic species with moderate to high aromaticity. Deviations from the Hückel rules are inversely correlated with the degree of aromaticity. Non-aromatic species that obey Hückel's rules and aromatic non-Hückel structures have been identified. The aromaticity of cyclic structures is a particular case of the aromaticity of zones/fragments. The anti-aromatic structures are a particular case of cyclic non-aromatic structures.

The development of a new class of molecular descriptors has emerged. They describe the aromaticity of molecular zones and fragments. The predictive value of these descriptors can be verified within a statistical QSPR approach.

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