

Partition of topological indices of benzenoid hydrocarbons into ring contributions

Izudin Redžepović^{a,*}, Slađana Đorđević^b, Simon Brezovnik^c, Niko Tratnik^{d,e}, Petra Žigert Pleteršek^{d,f}, Boris Furtula^b, Slavko Radenković^b

^a*State University of Novi Pazar, Novi Pazar, Serbia*

^b*Faculty of Science, University of Kragujevac, Kragujevac, Serbia*

^c*Faculty of Mechanical Engineering, University of Ljubljana, Slovenia*

^d*Faculty of Natural Sciences and Mathematics, University of Maribor, Slovenia*

^e*Institute of Mathematics, Physics, and Mechanics, Ljubljana, Slovenia*

^f*Faculty of Chemistry and Chemical Engineering, University of Maribor, Slovenia*

Abstract

This work presents a simple method for partitioning of the bond-additive and atoms-pair-additive distance-based topological indices of plane graphs into the sum of contributions of inner faces. The proposed method was applied to decompose several topological indices (Wiener, hyper-Wiener, Tratch-Stankevich-Zefirov, Balaban, and Szeged indices) into the ring contributions for a series of benzenoid systems. It was found that the employed ring partitioning scheme can provide accurate assessment of the dominant cyclic conjugation modes in the studied benzenoid hydrocarbons. Thus, the proposed method can be used as the alternative for the quantum-chemistry-based aromaticity indices which are significantly more computationally demanding.

Keywords: molecular properties; cyclic electron delocalization; quantum chemistry indices; graph indices; intramolecular distance.

*Corresponding author.
e-mail: iredzepovic@np.ac.rs

1 Introduction

Molecular descriptors are numerical representations of a molecular structure that play an important role in a great variety of cheminformatics investigations [1,2]. Among their versatile applications, the most prominent are those in QSPR/QSAR modeling, molecular similarity analysis, virtual screening, and drug discovery [3–6]. Contemporary utilization of molecular descriptors involves unveiling complex connections between chemical and biological data [7], design of surface–functionalized nanoparticles used for drug delivery [8], and the stability prediction of components found in fuel cells [9]. Due to the wide range of implementation possibilities and also the availability of various computation algorithms, a large number of molecular descriptors have been devised so far. Depending on the computational complexity, they differ in the amount of structural information they provide. Molecular descriptors are classified into several groups, usually using as a criterion the dimensionality of molecular structure from which they are calculated. Therefore, one can distinguish 1D, 2D, and 3D molecular descriptors. A special class is reserved for molecular descriptors calculated from molecular graphs, i.e., to graph indices, or as they are usually referred to, topological indices [10,11].

Topological indices are a convenient class of descriptors, since they encode a considerable amount of structural information of a molecular graph, with low computational cost. The use of these indices in chemistry–related research has proven to be quite beneficial [12,13]. Namely, one of the most common employment of topological indices is in the prediction of physicochemical properties and activities of compounds [14–16]. For example, in the paper [16] the authors have applied several weighted topological indices to model the corrosion inhibition effectiveness of various compounds. Fourches and Tropsha have developed a method to analyze and compare diverse chemical datasets applied in QSAR modeling by using simple topological indices [17]. Topological indices have also shown potential applicability in drug discovery research [18].

Generally, one may differentiate three distinct types of topological indices, i.e., degree– [19], distance– [20], and eigenvalue–based [21] indices, depending on graph parameters they consider in their definitions. In order to single out an appropriate index among a plethora of present indices, a set of several features that one index should possess has been compiled [22]. One of the most important properties of a topological index found in this list is its structure sensitivity [23,24].

The success of a topological index as a molecular descriptor relies on its ability to properly encode and interpret the information on features of molecular structure, e.g., the presence of a ring and its size. This is important since the existence of a ring in a molecule significantly influences many molecular properties. For example, some rings in a molecule may act as holes and thus influence the molecular shape. Years ago, a method for assessing the effect of a ring on the value of the graph energy has been presented [25]. Recently, this approach has been expanded to other eigenvalue-based indices [26].

It should also be noted that there are similar approaches in which one can decompose the number of π -electrons [27,28], as well as the graph energy into ring contributions [29]. In the present paper, we proposed a rather general scheme for partitioning topological indices into ring contributions. Furthermore, we investigate how the proposed methodology can have applications in chemistry. In particular, we examine the performance of the ring contributions of several distance-based topological indices as a tool to analyze cyclic electron delocalization in a series of selected benzenoid hydrocarbons: acenes (Ac_h), phenacenes (Ph_h), and fully benzenoid hydrocarbons (FB) (Figure 1).

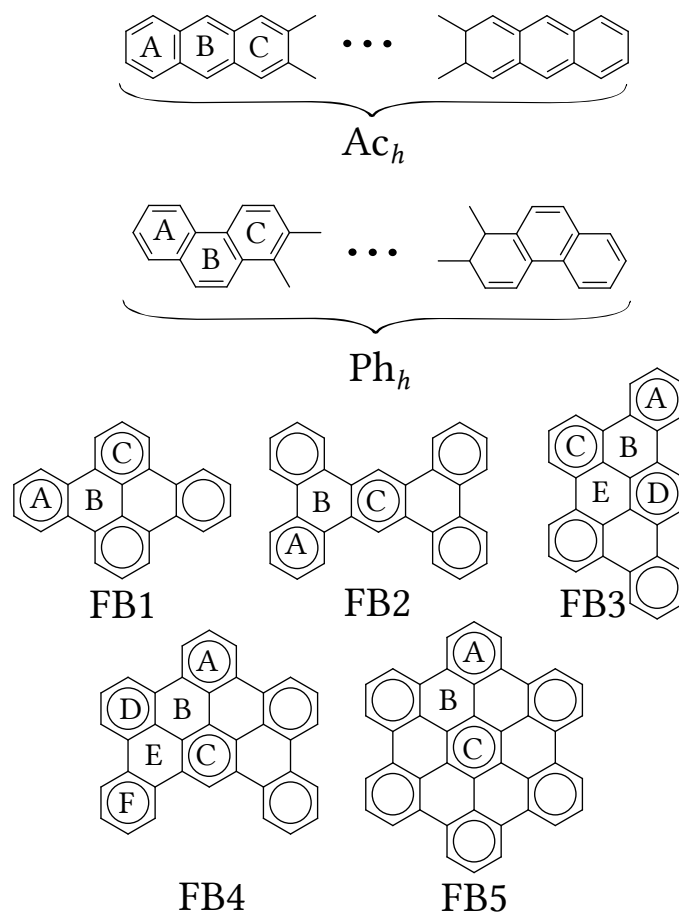


Figure 1. Investigated families of benzenoid hydrocarbons.

Benzenoid molecules have been attracting renewed attention thanks to the central role of π -conjugated molecules in the design and synthesis of new molecular spintronic materials needed for information storage and processing [30]. Thereafter, the selected families of benzenoids (Figure 1) are important both from the theoretical point of view and in materials science. Such a big interest in benzenoid molecules and their application possibilities might be attributed to cyclic electron delocalization, i.e., to the distribution of π -electrons across different rings in a molecule. It is widely accepted that cyclic electron delocalization governs unique characteristics of benzenoid molecules, such as bond length equalization, very specific energetic stabilization, magnetic, and reactivity properties. All these manifestations of cyclic electron delocalization are usually referred to as aromaticity. In this work, the ring components of the selected distance-based topological indices were compared with a set of well-established molecular-electronic indices which quantify various aspects of cyclic electron delocalization: energy effects (*ef*) [31], six center delocalization index (*SCI*) [32, 33], harmonic oscillator model of aromaticity (*HOMA*) index [34], and nucleus-independent chemical shifts (*NICS*) [35]. Namely, we show that a simple concept based on topology allows an understanding of the nature of individual rings in polycyclic benzenoid systems. In this way, we provide a basis for devising new larger benzenoid systems with specific properties.

2 Partition of topological indices

In this section, we show how a bond-additive or an atoms-pair-additive distance-based topological index of a plane graph can be partitioned into the sum of contributions of inner faces.

A graph $G = (V(G), E(G))$ is an ordered pair of a set of vertices $V(G)$ and a set of edges $E(G)$. For any two vertices $x, y \in V(G)$, we denote by $d(x, y)$ the usual shortest path distance between x and y . Moreover, a plane graph is such a drawing of a graph in the plane that its edges intersect only at their endpoints. The drawing of G divides the plane into connected regions called *faces*. One of these faces is unbounded also called the *outer face* and the remaining faces are *inner faces*.

Let G be a plane graph and let $\mathcal{F}(G)$ be the set of all inner faces of G . For any inner face F we denote by $E(F)$ the set of all the edges of G that form the boundary of F . If $e \in E(F)$, we say that F is incident to e . On the other hand, let $V(F)$ be the set of

all the vertices of G that belong to F . Moreover, for any edge $e \in E(G)$ let $k(e)$ be the number of inner faces that are incident to e . Obviously, $k(e) \in \{1, 2\}$ for any $e \in E(G)$ since every edge belongs to at most two inner faces of G . Finally, for any vertex $u \in V(G)$ let $l(u)$ be the number of inner faces that contain u . Obviously, $l(u)$ is at most the degree of u .

First, we will consider the partition of the bond-additive topological indices. Suppose that a bond-additive topological index $TI_e(G)$ is defined as

$$TI_e(G) = \sum_{e \in E(G)} \alpha(e),$$

where $\alpha : E(G) \rightarrow \mathbb{R}$ is any real-valued function. For any inner face $F \in \mathcal{F}(G)$ we define the contribution of F to topological index TI_e as

$$TI_e(F; G) = \sum_{e \in E(F)} \frac{\alpha(e)}{k(e)}. \quad (1)$$

Then, it obviously holds

$$TI_e(G) = \sum_{F \in \mathcal{F}(G)} TI_e(F; G).$$

In this paper, we investigate two bond-additive topological indices. The first one is the famous Balaban index [36, 37], which is formulated as:

$$J(G) = \frac{m}{m - n + 2} \sum_{uv \in E(G)} \frac{1}{\sqrt{w(u) \cdot w(v)}},$$

where m stands for the number of edges and n for the number of vertices of G , and for $x \in V(G)$,

$$w(x) = \sum_{y \in V(G)} d(x, y). \quad (2)$$

The second examined bond-additive topological index is Szeged index [38], defined as:

$$Sz(G) = \sum_{e \in E(G)} n_1(e|G) \cdot n_2(e|G)$$

whereas for any $e = xy \in E(G)$,

$$n_1(e|G) = |\{v \in V(G) \mid d(v, x) < d(v, y)\}|,$$

$$n_2(e|G) = |\{v \in V(G) \mid d(v, y) < d(v, x)\}|.$$

Now, we consider the partition of the atoms–pair–additive topological indices. Suppose that an atoms–pair–additive topological index $TI_v(G)$ is defined as

$$TI_v(G) = \sum_{\{u,v\} \subseteq V(G)} \beta(u,v) = \frac{1}{2} \sum_{u \in V(G)} \sum_{v \in V(G)} \beta(u,v),$$

where $\beta : V(G) \times V(G) \rightarrow \mathbb{R}$ is any symmetric real–valued function of two variables. For any $u \in V(G)$, we also define

$$\beta(u) = \sum_{v \in V(G)} \beta(u,v).$$

If $F \in \mathcal{F}(G)$ is an inner face, we define the contribution of F to topological index TI_v as

$$TI_v(F; G) = \frac{1}{2} \sum_{u \in V(F)} \frac{\beta(u)}{l(u)}. \quad (3)$$

Then, it obviously holds

$$TI_v(G) = \sum_{F \in \mathcal{F}(G)} TI_v(F; G).$$

The first investigated topological molecular descriptor of this type is Wiener index [39, 40], which is defined as:

$$W(G) = \sum_{\{u,v\} \subseteq V(G)} d(u,v).$$

Suppose that B is a benzenoid system with the set of hexagons $\mathcal{H}(B)$. For any hexagon $H \in \mathcal{H}(B)$, the contribution of H to the Wiener index is defined as

$$W(H) = W(H; B) = \frac{1}{2} \sum_{u \in V(H)} \frac{w(u)}{l(u)}.$$

Note that for any vertex $u \in V(B)$, $w(u)$ is defined in (2). Moreover, since B is a benzenoid system, $l(u)$ is at most 3 for any $u \in V(B)$.

The second topological index is hyper–Wiener index [41, 42], which represents a modification of the Wiener index:

$$WW(G) = \frac{1}{2} \sum_{\{u,v\} \subseteq V(G)} (d(u,v) + d(u,v)^2).$$

Finally, the last examined index is Tratch–Stankevich–Zefirov index [43, 44], which is obtained as an additional improvement of the Wiener index:

$$TSZ(G) = \sum_{\{u,v\} \subseteq V(G)} \left(\frac{1}{6} d(u,v)^3 + \frac{1}{2} d(u,v)^2 + \frac{1}{3} d(u,v) \right).$$

Note that throughout the paper,

$$TI(H) = TI(H; B).$$

These topological indices were selected since they belong to different classes of distance-based indices, i.e., to bond-additive and atoms-pair-additive indices. Such a selection enables a thorough evaluation of our partition scheme. Moreover, these indices have proved to be useful in many different fields. For example, the Balaban index has been applied to model chelation of zinc with amino acids [45], Szeged-like entropies were devised to measure network complexity [46], and a water pipeline network has been described by Wiener index [47].

3 Numerical work

The structures of the studied molecules were optimized by means of the B3LYP/6-311+G(d,p) method using the Gaussian 09 program [48]. The frequency calculations showed that the obtained optimized geometries have no imaginary vibrational frequencies. *NICS*(1) values were calculated at the same level of theory through the gauge-including atomic orbital (GIAO) method as implemented in the Gaussian 09 program. The *HOMA* index was computed for the optimized B3LYP/6-311+G(d,p) geometries. The *SCI* calculation was carried out by means of the natural atomic orbital (NAO) density matrices [49]. The energy effects (*ef*) were calculated within the chemical graph theory framework. The *ef* values are expressed in units of the HMO carbon-carbon resonance integral β and positive (negative) *ef* values indicate thermodynamic stabilization (destabilization) of a considered molecule. Calculations of *ef* and *SCI* were performed using in-house FORTRAN routines. Calculations of the contributions of rings to distance-based topological indices were performed in SageMath. Firstly, we implemented two functions α and β introduced in the previous section to obtain the contributions of edges and vertices, respectively. Secondly, each ring (inner face) was represented by the list of vertices contained in it. Next, we prepared two algorithms based on the formulas (1) and (3) to calculate the contribution of a given ring to the topological index TI_e or TI_v , respectively. The calculated values of the employed indices for all symmetry-unique rings in the studied molecules are collected in Tables 1, 2, and 3 in paper, and Tables 1S, 2S, and 3S in Supporting Information. The obtained local aromaticity indices are in very

good agreement with the results from previous studies on acenes, phenacenes [50–52], and fully benzenoid hydrocarbons [53].

Table 1. Calculated ring contributions to the topological indices of the studied acenes.

molecule	ring	$J(H)$	$Sz(H)$	$W(H)$	$WW(H)$	$TSZ(H)$
Ac ₁	A	2.0000	54.0	27.0	42.0	60.0
Ac ₂	A	0.9627	121.5	54.5	107.5	188.5
Ac ₃	A	0.5382	205.5	106.5	274.0	608.0
	B	0.6061	245.0	66.0	132.0	232.0
Ac ₄	A	0.3350	301.5	178.5	574.5	1556.5
	B	0.3974	389.0	106.0	256.0	536.0
Ac ₅	A	0.2267	409.5	270.5	1049.0	3362.0
	B	0.2688	541.0	162.0	484.0	1240.0
	C	0.2968	605.0	146.0	380.0	840.0
Ac ₆	A	0.1631	529.5	382.5	1737.5	6432.5
	B	0.1903	701.0	234.0	848.0	2600.0
	C	0.2194	829.0	202.0	608.0	1544.0
Ac ₇	A	0.1227	661.5	514.5	2680.0	11256.0
	B	0.1404	869.0	322.0	1380.0	4936.0
	C	0.1645	1061.0	274.0	972.0	2904.0
	D	0.1744	1125.0	258.0	836.0	2248.0
Ac ₈	A	0.0957	805.5	666.5	3916.5	18400.5
	B	0.1074	1045.0	426.0	2112.0	8632.0
	C	0.1261	1301.0	362.0	1504.0	5240.0
	D	0.1381	1429.0	330.0	1200.0	3608.0
Ac ₉	A	0.0766	961.5	838.5	5487.0	28514.0
	B	0.0846	1229.0	546.0	3076.0	14136.0
	C	0.0989	1549.0	466.0	2236.0	8936.0
	D	0.1101	1741.0	418.0	1732.0	5944.0
	E	0.1144	1805.0	402.0	1564.0	4968.0
Ac ₁₀	A	0.0627	1129.5	1030.5	7431.5	42324.5
	B	0.0682	1421.0	682.0	4304.0	21960.0
	C	0.0793	1805.0	586.0	3200.0	14440.0
	D	0.0889	2061.0	522.0	2464.0	9640.0
	E	0.0946	2189.0	490.0	2096.0	7304.0

Table 2. Calculated ring contributions to the topological indices of the studied phenacenes.

molecule	ring	$J(H)$	$Sz(H)$	$W(H)$	$WW(H)$	$TSZ(H)$
Ph ₃	A	0.5680	199.5	101.5	248.0	524.8
	B	0.6043	233.0	68.0	140.0	252.5
Ph ₄	A	0.3573	277.5	168.5	512.5	1323.0
	B	0.4119	373.0	104.0	244.0	494.5
Ph ₅	A	0.2414	355.5	255.5	941.0	2891.3
	B	0.2826	513.0	156.0	444.0	1084.5
	C	0.3128	593.0	140.0	348.0	736.5
Ph ₆	A	0.1729	433.5	362.5	1573.5	5617.5
	B	0.2006	653.0	224.0	772.0	2262.5
	C	0.2327	813.0	192.0	548.0	1326.5
Ph ₇	A	0.1295	511.5	489.5	2450.0	9969.8
	B	0.1479	793.0	308.0	1260.0	4332.5
	C	0.1745	1033.0	260.0	876.0	2504.5
	D	0.1855	1113.0	244.0	748.0	1916.5
Ph ₈	A	0.1005	589.5	636.5	3610.5	16496.0
	B	0.1128	933.0	408.0	1940.0	7662.5
	C	0.1334	1253.0	344.0	1364.0	4574.5
	D	0.1467	1413.0	312.0	1076.0	3094.5
Ph ₉	A	0.0802	667.5	803.5	5095.0	25824.3
	B	0.0885	1073.0	524.0	2844.0	12684.5
	C	0.1043	1473.0	444.0	2044.0	7904.5
	D	0.1167	1713.0	396.0	1564.0	5164.5
	E	0.1215	1793.0	380.0	1404.0	4272.5
Ph ₁₀	A	0.0654	745.5	990.5	6943.5	38662.5
	B	0.0712	1213.0	656.0	4004.0	19894.5
	C	0.0833	1693.0	560.0	2948.0	12926.5
	D	0.0939	2013.0	496.0	2244.0	8494.5
	E	0.1002	2173.0	464.0	1892.0	6342.5

Table 3. Calculated ring contributions to the topological indices of the studied fully benzenoid hydrocarbons.

molecule	ring	$J(H)$	$Sz(H)$	$W(H)$	$WW(H)$	$TSZ(H)$
FB1	A	0.2379	468.0	249.0	786.5	2068.0
	B	0.2286	549.0	97.0	234.2	488.0
	C	0.2522	531.0	185.0	498.8	1126.5
FB2	A	0.1686	607.5	379.5	1423.0	4367.3
	B	0.1741	904.5	175.5	534.0	1375.5
	C	0.2143	1125.0	210.0	548.0	1200.0
FB3	A	0.1571	648.0	372.0	1365.3	4110.5
	B	0.1512	783.0	146.0	415.8	1011.3
	C	0.1690	769.5	273.0	850.4	2200.9
	D	0.1730	904.5	200.5	541.3	1219.7
	E	0.1444	769.5	116.5	297.7	647.0
FB4	A	0.1268	1062.0	361.0	1202.0	3275.3
	B	0.1053	1048.5	159.5	457.8	1110.2
	C	0.1256	1260.0	197.0	527.0	1177.2
	D	0.1201	994.5	381.5	1368.3	4049.9
	E	0.1132	1125.0	194.0	591.5	1512.9
	F	0.1210	828.0	480.0	1821.0	5574.3
FB5	A	0.0919	1314.0	469.5	1719.8	5124.3
	B	0.0783	1381.5	202.5	617.8	1573.3
	C	0.0756	1323.0	153.0	407.0	905.0

4 Discussion

Benzene and naphthalene can be formally considered members of both groups of acenes and phenacenes. It is well-known that the so-called local aromaticity indices used in this work (*ef*, *HOMA*, *SCI*, and *NICS(1)*) sometimes can provide very different quantification of the extent of electron delocalization in polycyclic molecules [54]. This is evident in the studied series of acene molecules (Table 1S). The *HOMA*, *ef*, and *SCI* agree that the extent of cyclic electron delocalization of benzene is greater than that of any of the individual rings in acenes. Contrary, the *NICS(1)* values show that some hexagons in higher acene can be even more aromatic than benzene. Another disagreement can be seen if one compares the electron delocalization of the terminal and central rings in a given acene molecule. *HOMA*, *ef*, and *SCI* predict that the terminal rings are the most aromatic, while *NICS(1)* predicts the opposite. Here it should be noted that it has been shown that for higher acenes (number of hexagons > 5), the restricted DFT approach gives a less stable solution relative to that of the unrestricted symmetry-broken formalism [55, 56]. However, the quantum-chemistry-based indices in this work were obtained

using the restricted formalism, since we were focused on the performance of the proposed topological ring indices. The calculated $W(H)$ continuously decreases when one goes from the terminal to the central ring in acene molecules. This is in agreement with the ef and SCI indices. The $WW(H)$ and $TSZ(H)$ show the same trend as the $W(H)$, while the opposite was found for the $J(H)$ and $Sz(H)$ indices. The cross-correlations between the employed indices for acenes were examined and the obtained results are collected in Table 4. It can be seen that between the $W(H)$ and SCI there is a very good correlation (Figure 1S). Reasonably good correlations were found between the $W(H)$ and ef and $HOMA$ indices.

Table 4. Correlation coefficients between employed indices for acenes.

	<i>HOMA</i>	<i>ef</i>	<i>SCI</i>	<i>NICS</i> (1)	$W(H)$	$WW(H)$	$J(H)$	$Sz(H)$	$TSZ(H)$
<i>HOMA</i>	1.0000								
<i>ef</i>	0.7041	1.0000							
<i>SCI</i>	0.8787	0.9561	1.0000						
<i>NICS</i> (1)	-0.1060	0.4851	0.2597	1.0000					
$W(H)$	0.8517	0.9601	0.9902	0.3156	1.0000				
$WW(H)$	0.7830	0.9761	0.9712	0.4307	0.9914	1.0000			
$J(H)$	0.9627	0.8426	0.9606	0.0008	0.9402	0.8876	1.0000		
$Sz(H)$	0.9688	0.8161	0.9461	-0.0485	0.9220	0.8634	0.9987	1.0000	
$TSZ(H)$	0.7219	0.9776	0.9458	0.5129	0.9735	0.9951	0.8379	0.8094	1.0000

Phenacenes are isomers of acenes with a zig-zag ring constellation. It is known that in the ground state phenacenes are more stable than the corresponding isomeric acenes. All quantum-based indices show zig-zag trends for all studied phenacenes (Table 2S). In addition, all these indices agree that the most intensive cyclic conjugation occurs in the terminal rings of phenacenes. These results are well known and can be rationalized by simple Clar-structure-based arguments. Along these lines, the $W(H)$, $WW(H)$, and $TSZ(H)$ exhibit the largest values for the terminal rings, while the $J(H)$ and $Sz(H)$ show the opposite. On the other, all ring contributions of the topological indices show continuous change along the phenacene chains and cannot reproduce the zig-zag trend found with the quantum-chemistry-based indices. The cross-correlation data show that there is reasonably good agreement between the $TSZ(H)$, $W(H)$, and $WW(H)$ and local aromaticity indices (Table 5).

The fully benzenoids are a class of benzenoid hydrocarbons that can be represented by a single Clar formula [57]. In this work, we employed a series of fully benzenoids which was used in previous work [58]. It is widely accepted that Clar aromatic sextet

Table 5. Correlation coefficients between employed indices for phenacenes.

	<i>HOMA</i>	<i>ef</i>	<i>SCI</i>	<i>NICS(1)</i>	<i>W(H)</i>	<i>WW(H)</i>	<i>J(H)</i>	<i>Sz(H)</i>	<i>TSZ(H)</i>
<i>HOMA</i>	1.0000								
<i>ef</i>	0.9879	1.0000							
<i>SCI</i>	0.9865	0.9998	1.0000						
<i>NICS(1)</i>	-0.9889	-0.9917	-0.9913	1.0000					
<i>W(H)</i>	0.5421	0.6418	0.6439	-0.6319	1.0000				
<i>WW(H)</i>	0.6696	0.7645	0.7681	-0.7450	0.9710	1.0000			
<i>J(H)</i>	-0.1164	-0.0401	-0.0431	0.0169	0.6444	0.4442	1.0000		
<i>Sz(H)</i>	-0.2982	-0.2443	-0.2489	0.2128	0.4407	0.2140	0.9694	1.0000	
<i>TSZ(H)</i>	0.7321	0.8208	0.8251	-0.7963	0.9282	0.9902	0.3159	0.0764	1.0000

theory can provide a qualitative description of the dominant modes of cyclic π -electron conjugation in benzenoid molecules. Based on the Clar formula, one can expect that the full rings (ones containing circles) have intensive cyclic electron delocalization, while the empty rings have a negligibly small extent of electron delocalization. As can be seen from the data in Table 3S, all quantum-chemistry-based indices clearly distinguished between the full and empty rings in the studied molecules. Among the topological ring indices, the *TSZ(H)*, *W(H)*, and *WW(H)* have significantly higher values for the full rings than for the empty ones, in agreement with the Clar formula. The only exception is found for ring C in FB5. On the other hand, the *TSZ(H)*, *W(H)*, and *WW(H)* similar to the *ef*, *HOMA*, and *SCI* indices, show that the aromaticity of the full rings is inversely proportional to the number of the adjacent rings. Thereafter, the ring C in FB5 is the most extreme case. A good agreement between the topological ring indices and local aromaticity measurements can be seen from the cross-correlation data (Table 6), as well as from the bar diagrams given in Figure 2.

Table 6. Correlation coefficients between employed indices for fully benzenoids.

	<i>HOMA</i>	<i>ef</i>	<i>SCI</i>	<i>NICS(1)</i>	<i>W(H)</i>	<i>WW(H)</i>	<i>J(H)</i>	<i>Sz(H)</i>	<i>TSZ(H)</i>
<i>HOMA</i>	1.0000								
<i>ef</i>	0.9177	1.0000							
<i>SCI</i>	0.9463	0.9958	1.0000						
<i>NICS(1)</i>	-0.8645	-0.6894	-0.7449	1.0000					
<i>W(H)</i>	0.6481	0.8695	0.8367	-0.4050	1.0000				
<i>WW(H)</i>	0.6345	0.8645	0.8297	-0.3766	0.9889	1.0000			
<i>J(H)</i>	0.1576	0.3131	0.2829	-0.1232	0.5525	0.4379	1.0000		
<i>Sz(H)</i>	-0.1253	-0.0501	-0.0714	0.0515	0.1600	0.0331	0.9033	1.0000	
<i>TSZ(H)</i>	0.6167	0.8500	0.8137	-0.3519	0.9704	0.9954	0.3654	-0.0401	1.0000

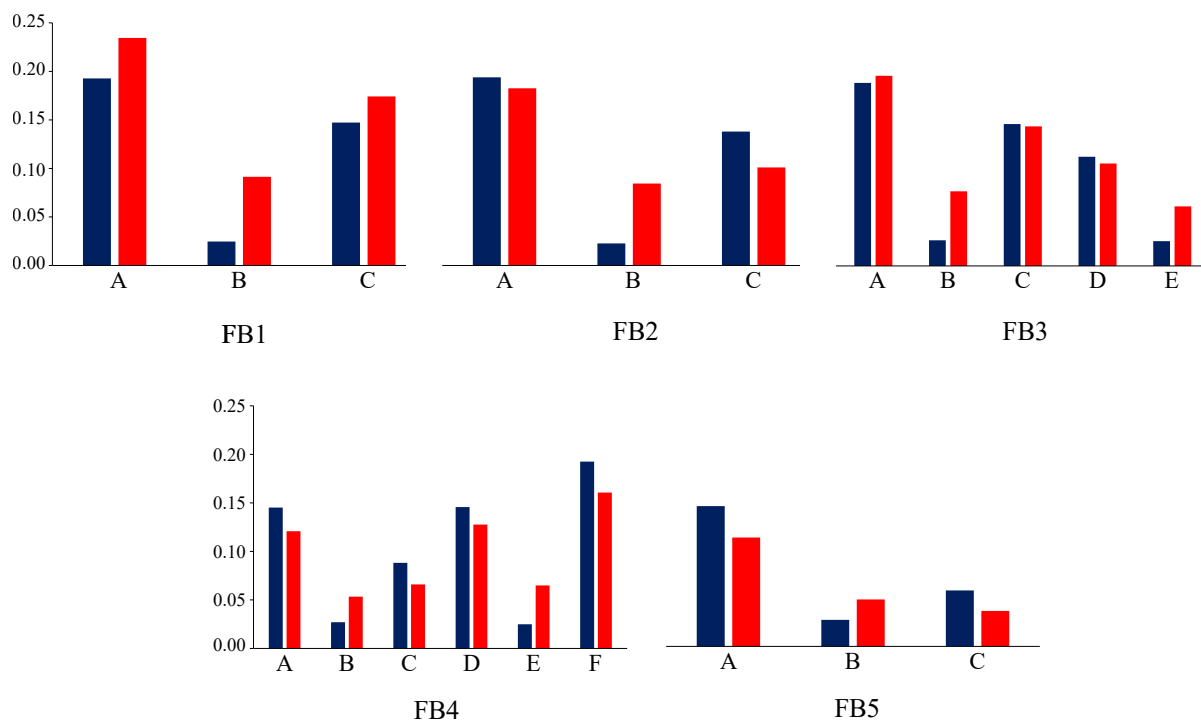


Figure 2. E_f values (navy blue) and relative Wiener index values (red) for symmetry-unique rings compared separately for fully benzenoid molecules.

5 Conclusions

In this work, we proposed a general scheme of how distance-based topological indices can be partitioned into the sum of contributions of inner faces. This methodology was applied to calculate ring contributions of J , Sz , W , WW , and TSZ for benzenoid molecular graphs. We found that the proposed ring partitioning can be used to qualitatively and quantitatively analyze cyclic electron delocalization in benzenoid hydrocarbons. In particular, the $TSZ(H)$, $W(H)$, and $WW(H)$ ring indices were found to be in good agreement with the so-called local aromaticity indices obtained in *ab initio* quantum chemical calculations. This finding can provide a basis for a deeper understanding of the relation between the topology of a given polycyclic molecule and the modes of cyclic π -electron delocalization in it. Being far less computationally demanding than the quantum-chemistry-based aromaticity indices, the proposed ring partition of topological indices can find applications in future QSAR/QSPR studies.

Acknowledgments

The authors B.F., S.R., S.Đ., and I.R. have been supported by the Serbian Ministry of Education, Science, and Technological Development (Grant No. 451-03-68/2022-14/200122). I.R. gratefully acknowledges the financial support of the State University of Novi Pazar. N. T. and P. Ž. P. were co-financed by the Slovenian Research Agency (core funding No. P1-0297). The research was a part of a bilateral project between Slovenia and Serbia co-founded by the Slovenian Research Agency (Grant No. BI-RS/20-21-001).

Data availability

The data used in this study are available from the corresponding author upon request.

Conflict of interest

The authors declare no conflicts of interest.

ORCID

Izudin Redžepović 0000-0003-4956-0407

Slađana Đorđević 0000-0003-0194-3927

Simon Brezovnik 0000-0001-6584-6435

Niko Tratnik 0000-0002-5564-049X

Petra Žigert Pleteršek 0000-0001-6653-9840

Boris Furtula 0000-0002-5056-6892

Slavko Radenković 0000-0002-1928-5494

References

- [1] R. Todeschini, and V. Consonni, *Molecular Descriptors for Chemoinformatics* (Weinheim, Germany: Wiley-VCH, 2009).
- [2] H. Hong, Q. Xie, W. Ge, F. Qian, H. Fang, L. Shi, Z. Su, R. Perkins, and W. Tong, "Mold², Molecular Descriptors from 2D Structures for Chemoinformatics and

- Toxicoinformatics*, " Journal of Chemical Information and Modeling 48, no. 7 (2008): 1337–1344, doi: 10.1021/ci800038f.
- [3] L. Xue, and J. Bajorath, "Molecular descriptors in chemoinformatics, computational combinatorial chemistry, and virtual screening," *Combinatorial Chemistry & High Throughput Screening* 3, no. 5 (2000): 363–372, doi: 10.2174/1386207003331454.
- [4] P. Willett, "Similarity-based virtual screening using 2D fingerprints," *Drug Discovery Today* 11, no. 23–24 (2006): 1046–1053, doi: 10.1016/j.drudis.2006.10.005.
- [5] D. C. Kombo, K. Tallapragada, R. Jain, J. Chewing, A. A. Mazurov, J. D. Speake, T. A. Hauser, and S. Toler, "3D Molecular Descriptors Important for Clinical Success," *Journal of Chemical Information and Modeling* 53, no. 2 (2013): 327–342, doi: 10.1021/ci300445e.
- [6] F. Grisoni, V. Consonni, and R. Todeschini, "Impact of Molecular Descriptors on Computational Models," in *Computational Chemogenomics*, ed. J.B. Brown (New York: Humana, 2018), 171–209, doi: 10.1007/978-1-4939-8639-2_5.
- [7] A. Fernández-Torras, A. Comajuncosa-Creus, M. Duran-Frigola, and P. Aloy, "Connecting Chemistry and Biology Through Molecular Descriptors," *Current Opinion in Chemical Biology* 66, (2022): 102090, doi: 10.1016/j.cbpa.2021.09.001.
- [8] S. Bhattacharjee, "Molecular Descriptors as a Facile Tool toward Designing Surface-Functionalized Nanoparticles for Drug Delivery," *Molecular Pharmaceutics* 19, no. 4 (2022): 1168–1175, doi: 10.1021/acs.molpharmaceut.1c00940.
- [9] S. T. Wetthasinghe, C. Li, H. Lin, T. Zhu, C. Tang, V. Rassolov, Q. Wang, and S. Garashchuk, "Correlation between the Stability of Substituted Cobaltocenium and Molecular Descriptors," *The Journal of Physical Chemistry A* 126, no. 1 (2022): 80–87, doi: 10.1021/acs.jpca.1c10603.
- [10] I. Gutman, "Degree-Based Topological Indices," *Croatica Chemica Acta* 86, no. 4 (2013): 351–361, doi: 10.5562/cca2294.
- [11] I. Gutman, *Selected Theorems in Chemical Graph Theory* (Kragujevac, Serbia: University of Kragujevac, 2017).

- [12] O. Ivanciuc, "Chemical Graphs, Molecular Matrices and Topological Indices in Chemoinformatics and Quantitative Structure–Activity Relationships," *Current Computer–Aided Drug Design* 9, no. 2 (2013): 153–163, doi: 10.2174/1573409911309020002.
- [13] R. Zanni, M. Galvez–Llompарт, R. García–Domenech, and J. Galvez, "Latest Advances in Molecular Topology Applications for Drug Discovery," *Expert Opinion on Drug Discovery* 10, no. 9 (2015): 945–957, doi: 10.1517/17460441.2015.1062751.
- [14] I. Redžepović, and B. Furtula, "Predictive Potential of Eigenvalue–based Topological Molecular Descriptors," *Journal of Computer–Aided Molecular Design* 34, no. 9 (2020): 975–982, doi: 10.1007/s10822-020-00320-2.
- [15] I. Redžepović, "Chemical Applicability of Sombor Indices," *Journal of the Serbian Chemical Society* 86, no. 5 (2021): 445–457, doi: 10.2298/JSC201215006R.
- [16] N. Tratnik, S. Radenković, I. Redžepović, M. Finšgar, and P. Ž. Pleteršek, "Predicting Corrosion Inhibition Effectiveness by Molecular Descriptors of Weighted Chemical Graphs," *Croatica Chemica Acta* 94, no. 3 (2021): 177–184, doi: 10.5562/cca3873.
- [17] D. Fourches, and A. Tropsha, "Using Graph Indices for the Analysis and Comparison of Chemical Datasets," *Molecular Informatics* 32, (2013): 827–842, doi: 10.1002/minf.201300076.
- [18] E. Estrada, and E. Uriarte, "Recent Advances on the Role of Topological Indices in Drug Discovery Research," *Current Medicinal Chemistry* 8, no. 13 (2001): 1573–1588, doi: 10.2174/0929867013371923.
- [19] Y. Ma, S. Cao, Y. Shi, I. Gutman, M. Dehmer, and B. Furtula, "From the Connectivity Index to Various Randić–Type Descriptors," *MATCH Communications in Mathematical and in Computer Chemistry* 80, no. 1 (2018): 85–106.
- [20] K. Xu, M. Liu, K. Ch. Das, I. Gutman, and B. Furtula, "A Survey on Graphs Extremal with Respect to Distance–Based Topological Indices," *MATCH Communications in Mathematical and in Computer Chemistry* 71, no. 3 (2014): 461–508.

- [21] I. Gutman, and H. S. Ramane, "Research on Graph Energies in 2019," MATCH Communications in Mathematical and in Computer Chemistry 84, no. 2 (2020): 277–292.
- [22] M. Randić, "Generalized Molecular Descriptors," Journal of Mathematical Chemistry 7, (1991): 155–168, doi: 10.1007/BF01200821.
- [23] M. Rakić, and B. Furtula, "A Novel Method for Measuring the Structure Sensitivity of Molecular Descriptors," Journal of Chemometrics 33, no. 7 (2019): e3138, doi: 10.1002/cem.3138.
- [24] I. Redžepović, and B. Furtula, "Comparative Study on Structural Sensitivity of Eigenvalue-Based Molecular Descriptors," Journal of Mathematical Chemistry 59, (2021): 476–487, doi: 10.1007/s10910-020-01202-6.
- [25] S. Bosanac, and I. Gutman, "Effect of a Ring on the Stability of Polycyclic Conjugated Molecules," Zeitschrift für Naturforschung A 32a, (1977): 10–12, doi: 10.1515/zna-1977-0104.
- [26] I. Redžepović, S. Radenković, and B. Furtula, "Effect of a Ring onto Values of Eigenvalue-Based Molecular Descriptors," Symmetry 13, (2021): 1515, doi: 10.3390/sym13081515.
- [27] M. Randić, and A. T. Balaban, "Partitioning of π -Electrons in Rings of Polycyclic conjugated Hydrocarbons. Part 1: Catacondensed Benzenoids," Polycyclic Aromatic Compounds 24, no. 3 (2004): 173–193. doi: 10.1080/10406630490432792
- [28] A. T. Balaban, and M. Randić, "Partitioning of π -Electrons in Rings of Polycyclic Benzenoid Hydrocarbons. 2. Catacondensed Coronoids," Journal of Chemical Information and Computer Sciences 44, no. 1 (2004): 50–59. doi: 10.1021/ci034164l
- [29] B. Furtula, I. Gutman, and N. Turković, "Relation Between Electron and Energy Contents of Hexagons in Catacondensed Benzenoid Hydrocarbons," Indian Journal of Chemistry 44A, (2005): 9–12. <http://nopr.niscpr.res.in/handle/123456789/18042>
- [30] A. Narita, X. Wang, X. Feng, and K. Müllen, "New Advances in Nanographene Chemistry," Chemical Society Reviews 44, (2015): 6616–6643. doi: 10.1039/C5CS00183H

- [31] I. Gutman, and S. Bosanac, "*Quantitative Approach to Hückel Rule the Relations Between the Cycles of a Molecular Graph and the Thermodynamic Stability of a Conjugated Molecule*," *Tetrahedron* 33, no. 14 (1977): 1809–1812. doi: 10.1016/0040-4020(77)84063-5
- [32] M. Giambiagi, M. S. Giambiagi, C. D. S. Silva, and A. P. Figueiredo, "*Multicenter Bond Indices as a Measure of Aromaticity*," *Physical Chemistry Chemical Physics* 2, (2000): 3381–3392. doi: 10.1039/B002009P
- [33] P. Bultinck, R. Ponec, and S. Van Damme, "*Multicenter Bond Indices as a New Measure of Aromaticity in Polycyclic Aromatic Hydrocarbons*," *Journal of Physical Organic Chemistry* 18, no. 8 (2005): 706–718. doi: 10.1002/poc.922
- [34] T. M. Krygowski, "*Crystallographic Studies of Inter- and Intramolecular Interactions Reflected in Aromatic Character of π -Electron Systems*," *Journal of Chemical Information and Computer Sciences* 33, no. 1 (1993): 70–78. doi: 10.1021/ci00011a011
- [35] P. R. Schleyer, C. Maerker, A. Dransfeld, H. Jiao, and N. J. R. E. Hommes, "*Nucleus-Independent Chemical Shifts: A Simple and Efficient Aromaticity Probe*," *Journal of the American Chemical Society* 118, no. 26 (1996): 6317–6318.
- [36] A. T. Balaban, "*Highly Discriminating Distance-Based Topological Index*," *Chemical Physics Letters* 89, no. 5 (1982): 399–404, doi: 10.1016/0009-2614(82)80009-2.
- [37] M. Knor, R. Škrekovski, and A. Tepoh, "*Mathematical Aspects of Balaban Index*," *MATCH Communications in Mathematical and in Computer Chemistry* 79, no. 3 (2018): 685–716.
- [38] I. Gutman, and A. A. Dobrynin, "*The Szeged Index – A Success Story*," *Graph Theory Notes New York* 34, (1998): 37–44.
- [39] H. Wiener, "*Structural Determination of Paraffin Boiling Points*," *Journal of the American Chemical Society* 69, no. 1 (1947): 17–20, doi: 10.1021/ja01193a005.
- [40] S. Nikolić, and N. Trinajstić, "*The Wiener Index: Development and Applications*," *Croatica Chemica Acta* 68, no. 1 (1995): 105–129.
- [41] M. Randić, "*Novel Molecular Descriptor for Structure-Property Studies*," *Chemical Physics Letters* 211, no. 4–5 (1993): 478–483, doi: 10.1016/0009-2614(93)87094-J.

- [42] I. Gutman, "*Relation Between Hyper–Wiener and Wiener Index*," Chemical Physics Letters 364, no. 3–4 (2002): 352–356, doi: 10.1016/S0009-2614(02)01343-X.
- [43] S. S. Tratch, M. I. Stankevitch, and N. S. Zefirov, "*Combinatorial Models and Algorithms in Chemistry. The Expanded Wiener Number—A Novel Topological Index*," Journal of Computational Chemistry 11, no. 8 (1990): 899–908, doi: 10.1002/jcc.540110802.
- [44] H. Shabani, A. R. Ashrafi, I. Gutman, and B. Furtula, "*On Extensions of Wiener Index*," MATCH Communications in Mathematical and in Computer Chemistry 69, (2013): 589–596.
- [45] A. V. Marukhlenko, M. A. Morozova, A. M. J. Mbarga, N. V. Antipova, A. V. Syroeshkin, I. V. Podoprigora, and T. V. Maksimova, "*Chelation of Zinc with Biogenic Amino Acids: Description of Properties Using Balaban Index, Assessment of Biological Activity on Spirostomum Ambiguum Cellular Biosensor, Influence on Biofilms and Direct Antibacterial Action*," Pharmaceuticals 15, (2022): 979, doi: 10.3390/ph15080979.
- [46] M. Dehmer, F. Emmert–Streib, N. Tratnik, and P. Žigert Pleteršek, "*Szeged–like Entropies of Graphs*," Applied Mathematics and Computation 431, (2022): 127325, doi: 10.1016/j.amc.2022.127325.
- [47] J. Dinar, Z. Hussain, S. Zaman, and S. Ur Rehman, "*Wiener Index for an Intuitionistic Fuzzy Fraph and its Application in Water Pipeline Network*," Ain Shams Engineering Journal 14, (2023): 101826, doi: 10.1016/j.asej.2022.101826.
- [48] M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, G. Scalmani, V. Barone, B. Mennucci, G. A. Petersson, H. Nakatsuji, M. Caricato, X. Li, H. P. Hratchian, A. F. Izmaylov, J. Bloino, G. Zheng, J. L. Sonnenberg, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, T. Vreven, J. A. Montgomery, J. E. Peralta, F. Ogliaro, M. Bearpark, J. J. Heyd, E. Brothers, K. N. Kudin, V. N. Staroverov, R. Kobayashi, J. Normand, K. Raghavachari, A. Rendell, J. C. Burant, S. S. Iyengar, J. Tomasi, M. Cossi, N. Rega, J. M. Millam, M. Klene, J. E. Knox, 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, R. L. Martin, K. Morokuma, V. G. Zakrzewski, G. A. Voth, P. Salvador, J. J. Dannenberg, S. Dapprich, A. D. Daniels, Farkas, J. B. Foresman, J. V. Ortiz, J. Cioslowski, D. J. Fox, Gaussian 09, Revision B.01, Gaussian Inc., Wallingford, CT 2009.
- [49] J. P. Foster, and F. Weinhold, "*Natural Hybrid Orbitals*," Journal of the American Chemical Society 102, no. 24 (1980): 7211–7218. doi: 10.1021/ja00544a007
- [50] G. Portella, J. Poater, J. M. Bofill, P. Alemany, and M. Solà, "*Local Aromaticity of [n]Acenes, [n]Phenacenes, and [n]Helicenes (n = 1 – 9)*," The Journal of Organic Chemistry 70, no. 7 (2005): 2509–2521, doi: 10.1021/jo0480388.
- [51] D. W. Szczepanik, M. Solà, T. M. Krygowski, H. Szatyłowicz, M. Andrzejak, B. Pawełek, J. Dominikowska, M. Kukułka, and K. Dyduch, "*Aromaticity of Acenes: The Model of Migrating π -Circuits*," Physical Chemistry Chemical Physics 20, (2018): 13430–13436, doi: 10.1039/C8CP01108G.
- [52] R. Pino-Rios, R. Báez-Grez, and M. Solà, "*Acenes and Phenacenes in Their Lowest-Lying Triplet States. Does Kinked Remain More Stable Than Straight?*," Physical Chemistry Chemical Physics 23, (2021): 13574–13582, doi: 10.1039/D1CP01441B.
- [53] M. Antić, B. Furtula, and S. Radenković, "*Aromaticity of Nonplanar Fully Benzenoid Hydrocarbons*," The Journal of Physical Chemistry A 121, no. 18 (2017): 3616–3626, doi: 10.1021/acs.jpca.7b02521.
- [54] P. Bultinck, "*Critical Analysis of the Local Aromaticity Concept in Polyaromatic Hydrocarbons*," Faraday Discussions 135, (2007): 347–365. doi: 10.1039/B609640A
- [55] M. Bendikov, H. M. Duong, K. Starkey, K. N. Houk, E. A. Carter, and F. Wudl, "*Oligoacenes: Theoretical Prediction of Open-Shell Singlet Diradical Ground States*" Journal of the American Chemical Society 126, no. 24 (2004): 7416–7417. doi: 10.1021/ja048919w
- [56] M. Bendikov, H. M. Duong, K. Starkey, K. N. Houk, E. A. Carter, and F. Wudl, "*Oligoacenes: Theoretical Prediction of Open-Shell Singlet Diradical Ground States*" Journal of the American Chemical Society 126, no. 33 (2004): 10493. doi: 10.1021/ja045878v

- [57] E. Clar, *The Aromatic Sextet*; John Wiley Sons Ltd: London, 1972.
- [58] I. Gutman, B. Furtula, S. Jeremić, and N. Turković, "*Electron Content of Rings of Fully Benzenoid Hydrocarbons*," *Journal of the Serbian Chemical Society* 70, no. 10 (2005): 1199–1204. doi: 10.2298/JSC0510199G