

# Topological, Spectroscopic and Energetic Properties of Cycloparaphenylene Series

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## Abstract

Carbon nanorings are macrocyclic aromatic hydrocarbons that represent the segments of carbon nanotubes and have received considerable attention due to their novel nanoelectronic and photophysical capabilities. The cycloparaphenylene (CPP), a carbon nanoring with a ring-like structure comprising of only benzene units, has been the subject matter of several studies. The carbon nanoring structures bearing polycyclic aromatic hydrocarbons such as hexabenzocoronene and pyrene molecules are also found to exhibit exciting characteristics and applications. This in turn evolves a wide range of novel chemical structures whose behaviour and attributes are to be studied and explored. Molecular descriptors help us to study such novel nanostructures by providing a greater understanding of their unique properties, whereas such characterization remains challenging due to their ring-shaped arrangement. In this study, we investigate cycloparaphenylene series and show that such structures are not bounded by the partial cube family. We also derive the exact analytic expressions of degree, distance and closeness-related descriptors. We have also computed the thermodynamic and kinetic stabilities of the three structures using the graph spectra, resonance energies, HOMO-LUMO gaps and Kekulé counts obtained from the graph spectra and combinatorial methods whereas the CPPhbc[5] structure is thermodynamically more stable, the CPPyr[9] is kinetically more stable. Furthermore, we have employed combinatorial generating function methods to compute the NMR and ESR spectra of the title compounds.

**Keywords:** Cycloparaphenylenes; topological indices; cut method; energetics; NMR and ESR spectra.

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# 1 Introduction

Carbon is an exceptional element with diverse forms and unique properties that have attracted the attention of researchers for centuries [1–3]. Even after the discovery of graphite and diamond, it continues to fascinate the scientists with much more interesting class of new allotropes namely fullerene [4], graphene [5] and carbon nanotubes (CNTs) [6]. As a crucial element for all fabricated components [3,7], they serve as game-changing elements in the electronic and optoelectronic industries with their encouraging properties and revolutionary applications. Carbon and its allotrope-based nanocomposites have captured practically every sector of research and technological progress due to their unique bonding properties. Carbon nanotubes are tubular carbon structures comprising of one or more seamless cylindrical shells of graphitic sheets with nearly 0.34 nm adjacent shell separation [6], that possess high strength [8], exceptional field emission [9] and mechanical properties [10]. They are categorized as single (SWCNT) [11,12], double (DWCNT) [6,13], and multi-walled (MWCNT) carbon nanotubes [6] based on the number of concentric walls of CNT as this parameter plays a significant role in estimating various attributes of the structure. As these nanomaterials possess unique electric properties [14], they are used as active semiconductor materials [15] and key elements in electronic devices such as transistors [16], logic circuits [15] and so on. Apart from their electrical application, numerous studies were made to attain magnetic CNTs [17,18], resulting in the successful preparation of one-dimensional magnetic tubes [19] and thus covering the fields of wearable electronics [20], nanofluidic devices [21], and even as capsules for magnetic enabled drug delivery [19]. In spite of several challenges, these nanomaterials are also employed in various biomedical [22] and biosensing [23] applications.

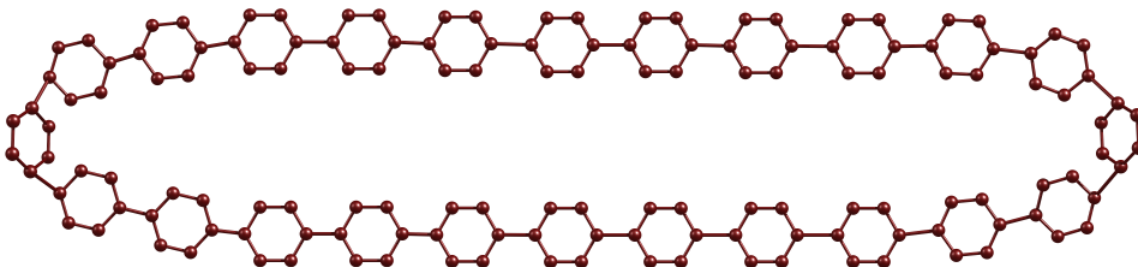


Figure 1: Cycloparaphenylene structure CPP[24]

Carbon nanorings (CNRs) are  $\pi$ -conjugated molecular structures representing the fragments of carbon nanotubes with diameter ranging from 300 nm to 500 nm and width ranging from 5 nm to 15 nm that are utilized as templates for the construction of nanostructures. The design and synthesis of these macrocyclic architectures continues to claim their own recognition for many decades, as they represent significant progress in the study of synthetic chemistry and nanoscience. Cycloparaphenylene (CPP) is

one of the most studied CNR, with simple curved structure comprising of  $n$  benzene units that are bonded at their para positions to form a ring as shown in Figure 1. It was theoretically hypothesized and examined for more than half a century because of its unique structural properties [24, 25] and its successful synthesis [26–28] have led to the synthesis of several variants of CPPs [29, 30] and its related derivatives [31–36], owing to its potential role in the fields of electronics, material science, and supramolecular chemistry [37–41]. The strong host-guest interactions of CPPs [42–44] enables the exploitation of a family of new novel carbon materials and thus accelerates the study of numerous functionalized and hetero-atom-subbed CPPs [45–47]. Furthermore, the successful synthesis of the chiral CNR by Omachi et al. [48] have led to the exploration of a unique chiral nanoring (a CPP chiral CNR bearing anthracene) with excitation energies that grows as a function of its size [49]. Furthermore, these extended crown structures have arisen the interest of synthetic chemists [50, 51]. Recently an exciting possibility of inserting twisted  $\text{Au}_2$  (diphosphine) corners into cycloparaphenylenes has been considered [52]. The topological techniques developed here can provide considerable insights into such twisted structures of cycloparaphenylene derivatives especially when comparing the topological properties with and without  $\text{Au}_2$  insertions.

Pyrene is a fluorescent probe that can be linked covalently to protein side chains as sulfhydryl groups. The appearance of a broad, unstructured band at longer wavelengths (ranging from 425 to 550 nm, centered around 460 nm) when two pyrene rings are nearly  $10\text{\AA}$  from each other, seems to be a remarkable feature of pyrene fluorescence emission that can be utilized for protein conformational analysis [53, 54]. Cycloparaphenylene-2,7-pyrenylene (CPPyr) depicted in Figure 2, is the first pyrene-containing carbon nanoring synthesized by Yagi et al. [35] and is believed to possess extra-ordinary properties such as long fluorescence lifetime [55] and excimer emission [56], owing to the structural and physical properties of pyrene and its derivatives.

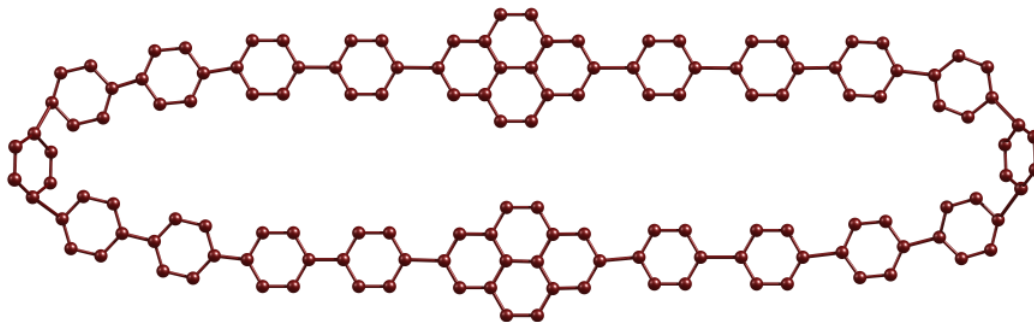


Figure 2: Cycloparaphenylene-2,7-pyrenylene structure CPPyr[9]

Hexa-peri-hexabenzocoronene (HBC) [57, 58] is a discotic polycyclic aromatic hydrocarbon which serves as a well defined  $D_{6h}$ -symmetrical substructure of graphene [1]. It is found to be a highly stable and insoluble molecular compound with strong intermolecular forces that strengthens its self-assembling

behavior [59] and its ability to store high levels of lithium and sodium signifies its rich optoelectronic applications [58, 60, 61]. Cyclo[12]-paraphenylene[2]-2,11-hexabenzocoronenylene (CPPhbc) is another hexabenzocoronene-containing CPP carbon nanoring as shown in Figure 3, which is recently synthesized via Pd- and Ni- mediated cross-coupling reactions [34] and characterized by high resolution mass spectrometry (HR-MS) and nuclear magnetic resonance (NMR) spectroscopy techniques. These HBC bearing carbon nanorings are expected to be acceptable precursors in the revolution of various carbon nanotube structures and this study facilitates it with the structural characterization of the above discussed novel CPP-based structures.

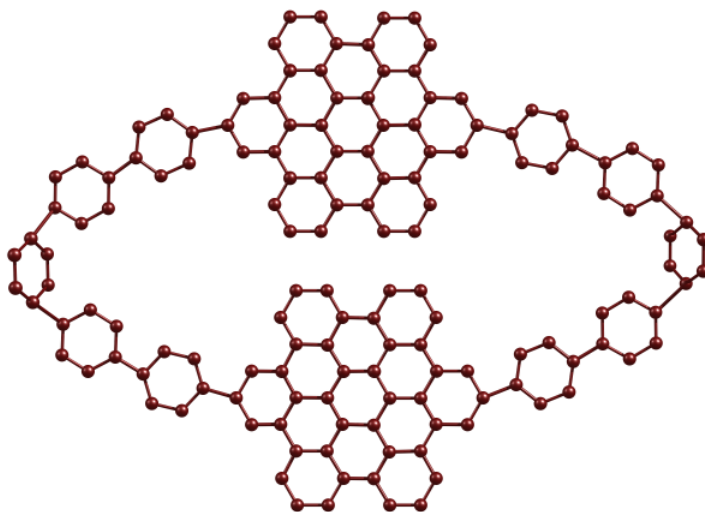


Figure 3: Cyclo[12]-paraphenylene[2]-2,11-hexabenzocoronenylene structure CPPhbc[5]

Chemical graph theory deals with the theoretical study of molecular compounds by envisaging the molecular structure comprising of atoms and bonds as a graph with vertices and edges respectively. Numerous graph-theoretical techniques are employed to quantify the molecular structure via different structural parameters. As most of the attributes of the molecule depends on the underlying topology and connectivity of the chemical structure, the structural parameters tend to reflect certain physico-chemical properties including superaromaticity, aromaticity, topological resonance energies, ring-current diamagnetism, and drug activity of the concerned molecular compound [62–67]. They encode the given structure with a numerical value based on its molecular topology describing various attributes such as centrality, cyclicity, extremality etc., and are usually called as topological indices. This ability of the descriptors in portraying the atomic structure with a unique numerical entity play a remarkable role in the advancement of quantitative structure property and activity relationships [68–71]. In addition to biological networks, nowadays they are also employed in analyzing various complex networks including communication and social networks. Consequently, an extremely large amount of topological descriptors are discovered and studied till date for the study of the structure-dependent behaviour and characteristics

of many novel molecular structures [72–79].

The mathematical computation of topological indices based on the distance-degree is complicated for ring-shaped structures. As evident from the literature, for instance, the Wiener index of cycloparaphenylene computed by algorithms [80] and a large number of molecular descriptors have recently been computed for a series of cycloparaphenylenes [81] by the cut method. But it is unfortunate that the results pertaining to the Wiener index do not match in both papers [80,81] and we prove that the results of the paper [81] were erroneous due to constructional defects. The exact values of the topological indices of cycloparaphenylenes and their related structures are computed using rigorous mathematical techniques in this study. We have derived the thermodynamic and kinetic stabilities of the three structures computed from their graph spectra, resonance energies, HOMO-LUMO gaps and Kekulé counts. Furthermore, we have computed the NMR and ESR spectra of three of the compounds in the series using graph theory and combinatorial generating function methods.

## 2 Mathematical Preliminaries

In this section, we discuss definitions, concepts, and known results from the area of chemical graph theory needed in this paper. Let  $V(G)$  and  $E(G)$  denote the vertex set and the edge set, respectively, of a simple connected graph  $G$ . The number of edges incident to a vertex  $u$  is called the degree  $d_G(u)$  of the vertex  $u$ , and the number of edges adjacent to the edge  $f$  is termed as the degree of the edge  $d_G(f)$ . The number of edges on a shortest path connecting the vertices  $a$  and  $b$  is defined as the distance  $d_G(a, b)$  between them. In a similar way, the distance  $d_G(u, f)$  between a vertex  $u$  and an edge  $f = ab$  is defined as  $\min\{d_G(u, a), d_G(u, b)\}$  and the distance  $D_G(f, g)$  between two edges  $f = ab$  and  $g = cd$  is given as  $\min\{d_G(f, c), d_G(f, d)\}$ . Note that if  $f$  and  $g$  are incident edges, then  $d_G(f, g) = 0$ , although the edges  $f$  and  $g$  are different. Hence the distance function and the set  $E(G)$  do not form a metric space, but the definition is nevertheless suitable for our purposes and by abuse of language the function can still be called a distance. For any edge  $f = ab$  in  $E(G)$ , we define its weighted sum and weighted product as  $w_e^+(f) = d_G(a) + d_G(b)$  and  $w_e^*(f) = d_G(a)d_G(b)$  respectively.

We now define the neighborhood  $N_G(u)$  of a vertex  $u$  and the closeness sets  $N_a(f|G)$ ,  $M_a(f|G)$  of an edge  $f = ab$  as follows:

$$\begin{aligned} N_G(u) &= \{x \in V(G) : d_G(x, u) = 1\}, \\ N_a(f|G) &= \{y \in V(G) : d_G(a, y) < d_G(b, y)\}, \\ M_a(f|G) &= \{e \in E(G) : d_G(a, e) < d_G(b, e)\}. \end{aligned}$$

The parameters  $n_a(f|G)$  and  $m_a(f|G)$  represent the cardinalities of the sets  $N_a(f|G)$  and  $M_a(f|G)$  respectively and  $t_a(f|G) = n_a(f|G) + m_a(f|G)$ . In a similar way, we can define the parameters  $n_b(f|G)$ ,  $m_b(f|G)$  and  $t_b(f|G)$  for an edge  $f = ab$ . A subgraph  $K$  of a graph  $G$  is said to be convex if all the shortest paths between any two vertices  $a, b \in K$  lie completely in  $K$ , and isometric if for any two vertices  $a, b \in K$ ,  $d_G(a, b) = d_K(a, b)$ . A  $n$ -dimensional hypercube  $Q_n$  is obtained by taking the Cartesian product of  $n$  copies of the complete graph  $K_2$ . Isometric subgraphs of  $Q_n$  are called partial cubes. The quotient graph  $G/F$ , where  $F \subseteq E(G)$ , is defined as a graph in which the vertices are the connected components of the graph  $G - F$ , and two components  $A$  and  $B$  are linked by an edge if there exists an edge  $ab \in F$  such that  $a \in A$  and  $b \in B$ .

A graph  $G$  in which a pair of strength-weighted functions  $(SW_V, SW_E)$  is assigned to the vertex set  $V(G)$  and edge set  $E(G)$  is a strength-weighted graph [76]  $G_{sw} = (G, SW_V, SW_E)$ , wherein the strength-weighted functions  $(SW_V, SW_E)$  are defined as follows:

- (i)  $SW_V = (w_v, s_v)$ , where  $w_v, s_v : V(G) \rightarrow \mathbb{R}_0^+$  are vertex-weight and strength functions,
- (ii)  $SW_E = (w_e, s_e)$ , where  $w_e, s_e : E(G) \rightarrow \mathbb{R}_0^+$  are edge-weight and strength functions.

For a strength-weighted graph  $G_{sw}$ , all the notations and terminologies of the structural parameters remains the same as that of a simple graph  $G$  except the degree and the closeness set parameters of a vertex  $u$  and an edge  $h = uv$  which are defined as follows:

$$d_{G_{sw}}(u) = \sum_{x \in N_{G_{sw}}(u)} s_e(ux),$$

$$n_u(h|G_{sw}) = \sum_{x \in N_u(h|G_{sw})} w_v(x),$$

$$m_u(h|G_{sw}) = \sum_{x \in N_u(h|G_{sw})} s_v(x) + \sum_{f \in M_u(h|G_{sw})} s_e(f).$$

The Wiener index is the first and one of the most studied molecular descriptors used to characterize chemical compounds. Based on its significance in analyzing the potential physicochemical properties of the structure, a wide variety of topological indices based on various parameters of the molecular graph have been proposed in mathematical chemistry and are investigated for different families of molecular structures till date. The topological indices ( $TI$ ) based on distance-degree such as Wiener ( $W$ ), edge-Wiener ( $W_e$ ), vertex-edge Wiener ( $W_{ev}$ ), vertex-Szeged ( $Sz_v$ ), edge-Szeged ( $Sz_e$ ), edge-vertex Szeged ( $Sz_{ev}$ ), total-Szeged ( $Sz_t$ ), Padmakar-Ivan ( $PI$ ), Schultz ( $S$ ), Gutman ( $Gut$ ), Mostar ( $Mo$ ), edge-Mostar ( $Mo_e$ ), total-Mostar ( $Mo_t$ ), weighted plus mostar variants ( $w^+Mo$ ,  $w^+Mo_e$ ,  $w^+Mo_t$ ), and weighted product Mostar variants ( $w^*Mo$ ,  $w^*Mo_e$ ,  $w^*Mo_t$ ) are originally defined for a molecular graph and we

now rewrite for a strength-weighted graph  $G_{sw}$  in the following to ease the computation process.

(i) Distance-based topological indices:

- $W(G_{sw}) = \sum_{\{x,y\} \subseteq V(G_{sw})} w_v(x)w_v(y)d_{G_{sw}}(x,y)$
- $W_e(G_{sw}) = \sum_{\{x,y\} \subseteq V(G_{sw})} s_v(x) s_v(y) d_{G_{sw}}(x,y) + \sum_{\{g,h\} \subseteq E(G_{sw})} s_e(g) s_e(h) D_{G_{sw}}(g,h)$   
 $+ \sum_{x \in V(G_{sw})} \sum_{h \in E(G_{sw})} s_v(x) s_e(h) d_{G_{sw}}(x,h)$
- $W_{ev}(G_{sw}) = \frac{1}{2} \left( \sum_{\{x,y\} \subseteq V(G_{sw})} \{w_v(x) s_v(y) + w_v(y) s_v(x)\} d_{G_{sw}}(x,y) \right.$   
 $\left. + \sum_{x \in V(G_{sw})} \sum_{h \in E(G_{sw})} w_v(x) s_e(h) d_{G_{sw}}(x,h) \right)$

(ii) Degree and distance-based topological indices:

- $S(G_{sw}) = \sum_{\{x,y\} \subseteq V(G_{sw})} \left[ w_v(y)[d_{G_{sw}}(x) + 2s_v(x)] + w_v(x)[d_{G_{sw}}(y) + 2s_v(y)] \right] d_{G_{sw}}(x,y)$
- $Gut(G_{sw}) = \sum_{\{x,y\} \subseteq V(G_{sw})} [d_{G_{sw}}(x) + 2s_v(x)][d_{G_{sw}}(y) + 2s_v(y)]d_{G_{sw}}(x,y)$

(iii) Bond-based topological indices:

(a) Variants of Szeged indices:

- $Sz_v(G_{sw}) = \sum_{h \in E(G_{sw})} s_e(h)n_u(h|G_{sw})n_v(h|G_{sw})$
- $Sz_e(G_{sw}) = \sum_{h \in E(G_{sw})} s_e(h)m_u(h|G_{sw})m_v(h|G_{sw})$
- $Sz_{ev}(G_{sw}) = \frac{1}{2} \sum_{h \in E(G_{sw})} s_e(h) \left[ n_u(h|G_{sw})m_v(h|G_{sw}) + n_v(h|G_{sw})m_u(h|G_{sw}) \right]$
- $PI(G_{sw}) = \sum_{h \in E(G_{sw})} s_e(h) \left[ m_u(h|G_{sw}) + m_v(h|G_{sw}) \right]$

(b) Variants of Mostar indices:

- $Mo(G_{sw}) = \sum_{h \in E(G_{sw})} s_e(h)|n_u(h|G_{sw}) - n_v(h|G_{sw})|$
- $w^+ Mo(G_{sw}) = \sum_{h \in E(G_{sw})} w_e^+(h)|n_u(h|G_{sw}) - n_v(h|G_{sw})|$
- $w^* Mo(G_{sw}) = \sum_{h \in E(G_{sw})} w_e^*(h)|n_u(h|G_{sw}) - n_v(h|G_{sw})|$

(c) Variants of edge-Mostar indices:

- $Mo_e(G_{sw}) = \sum_{h \in E(G_{sw})} s_e(h)|m_u(h|G_{sw}) - m_v(h|G_{sw})|$

- $w^+ Mo_e(G_{sw}) = \sum_{h \in E(G_{sw})} w_e^+(h) |m_u(h|G_{sw}) - m_v(h|G_{sw})|$
- $w^* Mo_e(G_{sw}) = \sum_{h \in E(G_{sw})} w_e^*(h) |m_u(h|G_{sw}) - m_v(h|G_{sw})|$

(d) Variants of total-Mostar indices:

- $Mo_t(G_{sw}) = \sum_{h \in E(G_{sw})} s_e(h) |t_u(h|G_{sw}) - t_v(h|G_{sw})|$
- $w^+ Mo_t(G_{sw}) = \sum_{h \in E(G_{sw})} w_e^+(h) |t_u(h|G_{sw}) - t_v(h|G_{sw})|$
- $w^* Mo_t(G_{sw}) = \sum_{h \in E(G_{sw})} w_e^*(h) |t_u(h|G_{sw}) - t_v(h|G_{sw})|$

It should be noted that  $TI(G_{sw}) = TI(G)$  if  $w_v = 1$ ,  $s_v = 0$ ,  $w_e = 1$  and  $s_e = 1$ . Computational techniques for determining topological indices serve as powerful tools in the evaluation of molecular descriptors by dissecting the original graph into smaller fragments to study the properties of the whole graph structure [74–76, 82]. The cut method is an important computational procedure developed to evaluate the topological indices. It was designed for the first time in [83] for the case of the Wiener index. The method was then extensively developed for other indices and was also generalized in different directions. It is still being revised to suit the different graph families, cf. [72, 74, 76, 82]. The Djoković-Winkler relation  $\Theta$  is defined on the edge set of a graph  $G$  as follows: edges  $f = ab$  and  $g = cd$  are in relation  $\Theta$  if  $d_G(b, d) + d_G(a, c) \neq d_G(a, d) + d_G(b, c)$ . The relation continues to play a prominent role in the development of the cut method. Obviously,  $\Theta$  is reflexive and symmetric, but not transitive in general whereas the transitive closure  $\Theta^*$  forms an equivalence relation thereby enabling the  $\Theta^*$ -partition of the edge set  $E(G)$  as  $E_1, \dots, E_p$ . These classes split each of the graphs  $G - E_i$  into two or more smaller convex components to analyze the given descriptor of the chemical graph. The computational technique of various topological indices  $TI$  is described in the following theorem.

**Theorem 1.** [74–76] *Let  $G$  be a molecular graph that admits a  $\Theta^*$ -partition  $\mathcal{E}(G) = \{E_1, E_2, \dots, E_p\}$ . If  $TI \in \{W, W_e, W_{ev}, Sz_v, Sz_e, Sz_{ev}, PI, S, Gut, Mo, Mo_e, Mo_t, w^+ Mo, w^+ Mo_e, w^+ Mo_t, w^* Mo, w^* Mo_e, w^* Mo_t\}$ , then*

$$TI(G) = \sum_{i=1}^p TI(G/E_i, (w_v^i, s_v^i), (w_e^i, s_e^i)),$$

where

$$(i) \ w_v^i : V(G/E_i) \rightarrow \mathbb{R}_0^+, w_v^i(X) = \sum_{x \in V(X)} w_v(x), \forall X \in V(G/E_i),$$

$$(ii) \ s_v^i : V(G/E_i) \rightarrow \mathbb{R}_0^+, s_v^i(X) = \sum_{xy \in E(X)} s_e(xy) + \sum_{x \in V(X)} s_v(x), \forall X \in V(G/E_i),$$



$$(iii) \ w_e^i : E(G/E_i) \rightarrow \mathbb{R}_0^+, \ w_e^i(XY) = \sum_{\substack{xy \in E_i \\ x \in V(X), y \in V(Y)}} w_e(xy), \forall XY \in E(G/E_i),$$

and whenever

$$\bullet \text{ if } TI \in \{w^+Mo, w^+Mo_e, w^+Mo_t\}, \ w_e^i(XY) = w_e^{+i}(XY) = \sum_{\substack{xy \in E_i \\ x \in V(X), y \in V(Y)}} (d_G(x) + d_G(y)),$$

$$\forall XY \in E(G/E_i),$$

$$\bullet \text{ if } TI \in \{w^*Mo, w^*Mo_e, w^*Mo_t\}, \ w_e^i(XY) = w_e^{*i}(XY) = \sum_{\substack{xy \in E_i \\ x \in V(X), y \in V(Y)}} d_G(x)d_G(y),$$

$$\forall XY \in E(G/E_i).$$

• if  $TI$  is other than the above indices,  $w_e^i$  is not needed.

$$(iv) \ s_e^i : E(G/E_i) \rightarrow \mathbb{R}_0^+, \ s_e^i(XY) = \sum_{\substack{xy \in E_i \\ x \in V(X), y \in V(Y)}} s_e(xy), \forall XY \in E(G/E_i).$$

In addition to distance based topological indices, the vertex degree based indices are generally defined as  $TI(G) = \sum_{(\alpha, \beta) \in E(G)} TI(d_G(\alpha), d_G(\beta))$ . If we denote  $d_{rs}(G) = |\{\alpha\beta \in E(G) : d_G(\alpha) = r \text{ and } d_G(\beta) = s\}|$ , then  $TI(G) = \sum_{(r,s) \in P} d_{rs}(G) TI(r, s)$  where  $P$  represents the degree edge partition of  $G$ . Here we list some popular index functions such as first Zagreb index  $M_1(r, s) = r + s$ , Sombor index  $SO(r, s) = \sqrt{r^2 + s^2}$ , second Zagreb index  $M_2(r, s) = rs$ , sum-connectivity index  $SC(r, s) = \frac{1}{\sqrt{r+s}}$ , inverse sum indeg index  $ISI(r, s) = \frac{rs}{r+s}$ , atom-bond connectivity index  $ABC(r, s) = \sqrt{\frac{r+s-2}{rs}}$ , symmetric degree division index  $SDD(r, s) = \frac{r}{s} + \frac{s}{r}$ , harmonic index  $H(r, s) = \frac{2}{r+s}$ , forgotten index  $F(r, s) = r^2 + s^2$ , augmented Zagreb index  $AZ(r, s) = \left(\frac{rs}{r+s-2}\right)^3$ , and geometric-arithmetic index  $GA(r, s) = \frac{2\sqrt{rs}}{r+s}$ .

### 3 Results and Discussion

The technical inadequacies in that Ref. [81] for the construction of  $\Theta$ -classes of cycloparaphenylenes and their related carbon nanorings are highlighted in this section. We also use the transitive closure of the  $\Theta$  relation to correct the class formation approach and confirming that these structures are not members of the partial cube family. We use strength-weighted graphs to derive the correct analytic expressions of distance-bond topological indices based on that  $\Theta^*$ -partition and degree edge partition to find the degree-based indices.

The cycloparaphenylenes CPP[ $n$ ] with even number of benzenes were considered [81] as members of the partial cube family and taken diametrically opposite acute/obtuse slanting bonds of two benzenes at an equal interval to form  $\Theta$ -classes. Before arguing that this is not the case, we prove the following

general result that will simplify our arguing. Recall that an edge  $e$  of a connected graph  $G$  is a bridge if  $G - e$  is not connected.

**Proposition 2.** *Let  $G$  be a connected graph and  $e$  a bridge of  $G$ . If edges  $f$  and  $f'$  lie in different components of  $G - e$ , then  $f$  and  $f'$  are not in relation  $\Theta$ .*

To prove Proposition 2, let  $e = xx'$  be a bridge of  $G$  and suppose that  $f = uv$  and  $f' = u'v'$  are edges of  $G$  such that they lie in different components of  $G - e$ . We may assume without loss of generality that  $uv$  lies in the same component as  $x$  and that  $u'v'$  lies in the component together with  $x'$ . There are three cases to consider. If  $d_G(u, x) < d_G(v, x)$  (or the other way around) and  $d_G(u', x') < d_G(v', x')$  (or the other way around), then the edges  $f$  and  $f'$  lie on a common shortest path between  $v$  and  $v'$  that is passing through the edge  $e$ . Since in general no two edges of a shortest path can be in relation  $\Theta$ , we conclude that  $f$  and  $f'$  are not in relation  $\Theta$ . In the second case suppose that  $d_G(u, x) = d_G(v, x) = k$  and  $d_G(u', x') = d_G(v', x') = \ell$ . Then  $d_G(u, u') + d_G(v, v') = 2k + 2\ell + 1 = d_G(u, v') + d_G(v, u')$ , hence  $f$  and  $f'$  are again not in relation  $\Theta$ . In the final case suppose that  $d_G(u, x) = d_G(v, x) = k$  and that, without loss of generality,  $\ell = d_G(u', x') < d_G(v', x')$ . Then, clearly,  $d_G(v', x') = \ell + 1$ . But now  $d_G(u, u') + d_G(v, v') = 2k + 2\ell + 3 = d_G(u, v') + d_G(v, u')$ , and we have the same conclusion. This proves the proposition.

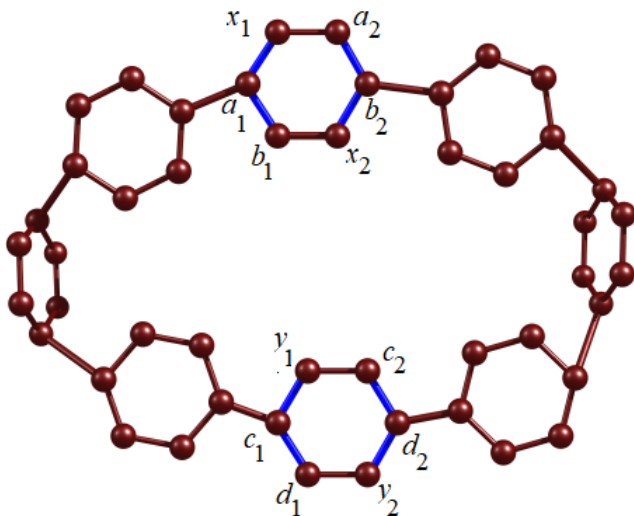


Figure 4: Construction procedure for  $\Theta^*$ -class in CPP[8]

As shown in Figure 4, the set  $A = \{a_1b_1, a_2b_2, c_1d_1, c_2d_2\}$  was taken [81] as one such  $\Theta$ -class. Since  $a_1b_1$  and  $a_2b_2$  as well as  $c_1d_1$  and  $c_2d_2$  are diametrically opposite bonds of benzenes, they are clearly in  $\Theta$ -relation. Consider now the graph obtained from CPP[8] by removing the edges  $x_1a_2$ ,  $b_1x_2$ ,  $y_1c_2$ , and  $d_1y_2$ . It contains two components, and observe that both of them are convex. Consider the left (in view of Figure 4) component. Proposition 2 in particular implies that  $a_1b_1$  is not in relation  $\Theta$  with any other

edge of the component. So  $a_1b_1$  cannot be in relation  $\Theta$  with  $c_1d_1$ . This argument works in general, while for the particular case of the edges  $a_1b_1$  and  $c_1d_1$  this can be of course checked directly. Indeed, we can see that  $d_{\text{CPP}[8]}(a_1, c_1) = 13$ ,  $d_{\text{CPP}[8]}(b_1, d_1) = 15$ ,  $d_{\text{CPP}[8]}(a_1, d_1) = 14$ ,  $d_{\text{CPP}[8]}(b_1, c_1) = 14$  and resulting that  $d_{\text{CPP}[8]}(a_1, c_1) + d_{\text{CPP}[8]}(b_1, d_1) = d_{\text{CPP}[8]}(a_1, d_1) + d_{\text{CPP}[8]}(b_1, c_1)$ . We have thus seen that  $a_1b_1$  is not  $\Theta$  related to  $c_1d_1$ . On the other hand,  $a_1b_1$  is  $\Theta$  related to  $c_2d_2$  because these two edges are opposite edges of a long isometric cycle going all around CPP[8].  $\Theta$  is thus not transitive on CPP[8]. The same arguments work on an arbitrary CPP[ $n$ ] with the help of Proposition 2 and considering long isometric cycles going around CPP[ $n$ ]. Therefore, CPP[ $n$ ],  $n$  even, is not a member of the class of partial cubes. Again from the same Figure 4, we see that  $c_1d_1$  is  $\Theta$  related to  $x_2b_2$  because of  $d_{\text{CPP}[8]}(c_1, x_2) = 15$ ,  $d_{\text{CPP}[8]}(d_1, b_2) = 15$ ,  $d_{\text{CPP}[8]}(c_1, b_2) = 16$  and  $d_{\text{CPP}[8]}(d_1, x_2) = 16$ . We now extend the set  $A$  by including the bonds  $a_1x_1$ ,  $b_2x_2$ ,  $c_1y_1$  and  $d_2y_2$  to form a  $\Theta^*$ -class. As we showed that the acute slanting bond  $x_2b_2$  and obtuse slanting bond  $c_1d_1$  are  $\Theta$  related when  $n$  is even, we could easily see that the acute/obtuse slanting bonds of benzenes at an interval of  $\lceil \frac{(n-2)}{2} \rceil$  are  $\Theta$  related when  $n$  is odd and covering all the slanting bonds to build a single  $\Theta^*$ -class.

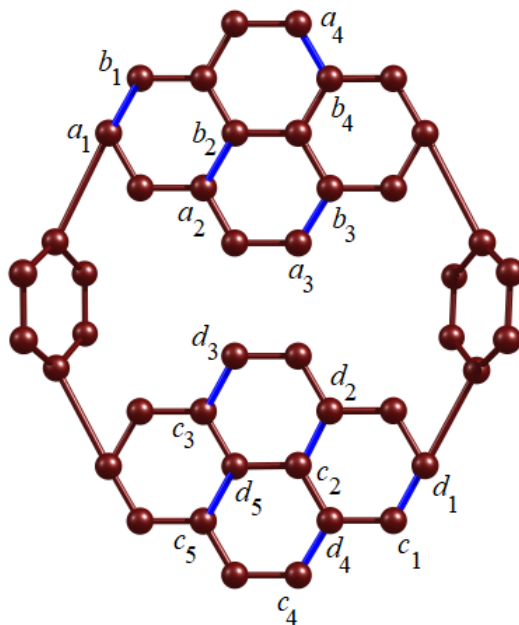


Figure 5: Construction procedure for  $\Theta^*$ -class in CPPyr[1]

The cycloparaphenylene-2,7-pyrenylene CPPyr[ $n$ ] has also been dealt with the same sort of technical flaws [81] as mentioned in CPP[ $n$ ] in the benzene nanorings. In addition to that, there are issues with the formation of  $\Theta$ -classes covering the slanting bonds of pyrenes. For example, the set  $B = \{a_1b_1, a_2b_2, a_3b_3, c_1d_1, c_2d_2, c_3d_3\}$  was considered [81] as one of the  $\Theta$ -class CPPyr[1] as shown in

Figure 5. By the nature of the diametrically opposite edges, the three bonds  $a_1b_1, a_2b_2$  and  $a_3b_3$  together  $\Theta$  related and similarly the other bonds  $c_1d_1, c_2d_2$  and  $c_3d_3$  are  $\Theta$  related. But  $d_{\text{CPPyr}[1]}(a_1, c_2) = 9$ ,  $d_{\text{CPPyr}[1]}(b_1, d_2) = 11$ ,  $d_{\text{CPPyr}[1]}(a_1, d_2) = 10$ ,  $d_{\text{CPPyr}[1]}(b_1, c_2) = 10$  and resulting that  $a_1b_1$  is not  $\Theta$  related to  $c_2d_2$  whereas  $a_1b_1$  is  $\Theta$  related to  $c_1d_1$ . Therefore,  $\text{CPPyr}[n]$  is not a member of partial cubes. Furthermore, we can notice from the Figure 5 that  $a_2b_2 \Theta c_4d_4$  and  $a_4b_4 \Theta c_5d_5$  which in turn implies that all the slanting bonds of both pyrenes form a single  $\Theta^*$ -class.

With the same line of above arguments, we can show that the construction of  $\Theta$ -classes of cyclo[12]-paraphenylene[2]-2,11-hexabenzocoronenylyne  $\text{CPPhbc}[n]$  in Ref. [81] is wrong and can be corrected as we did for  $\text{CPPyr}[n]$  along with a crucial point that slanting bond and horizontal bond of hexabenzocoronenylynes are  $\Theta$  related as shown in Figure 6 that  $d_{\text{CPPhbc}[5]}(a, c) = 32$ ,  $d_{\text{CPPhbc}[5]}(b, d) = 32$ ,  $d_{\text{CPPhbc}[5]}(a, d) = 33$ ,  $d_{\text{CPPhbc}[5]}(b, c) = 33$  and resulting that  $d_{\text{CPPhbc}[5]}(a, c) + d_{\text{CPPhbc}[5]}(b, d) \neq d_{\text{CPPhbc}[5]}(a, d) + d_{\text{CPPhbc}[5]}(b, c)$ .

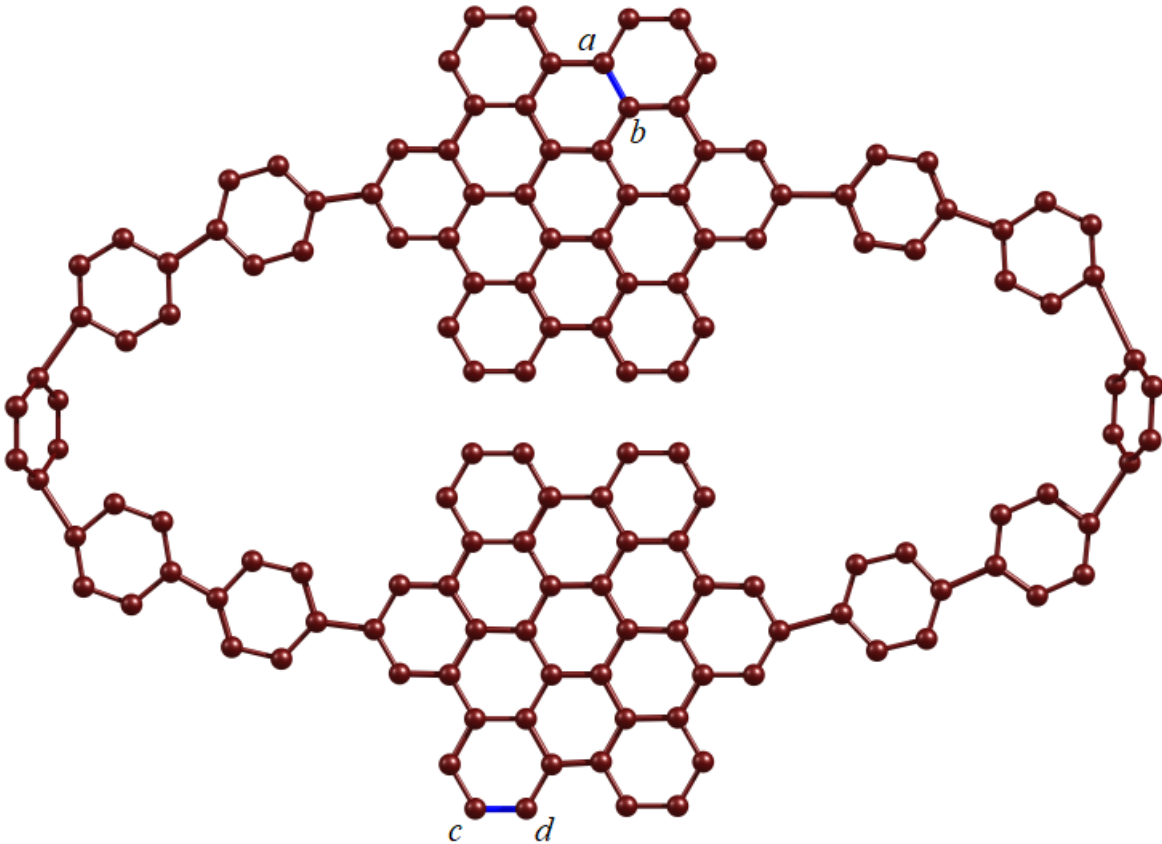


Figure 6: An example of  $\Theta$  related slanting and horizontal bonds in  $\text{CPPhbc}[5]$

**Topological descriptors of cycloparaphenylenes  $\text{CPP}[n]$ :** The distance-degree based and bond additive topological indices such as  $W, W_e, W_{ev}, Sz_v, Sz_e, Sz_{ev}, PI, S, Gut, Mo, Mo_e, Mo_t, w^+Mo, w^+Mo_e, w^+Mo_t, w^*Mo, w^*Mo_e$  and  $w^*Mo_t$  for cycloparaphenylenes are displayed in Table 1.

Table 1: Topological indices of cycloparaphenylene CPP[ $n$ ]

TI	CPP[ $n$ ]	
	$n$ even	$n$ odd
$W$	$18n^3 + 8n$	$18n^3 + 7n$
$W_e$	$n(49n^2 - 49n + 29)/2$	$7n(7n^2 - 7n + 4)/2$
$W_{ev}$	$n(42n^2 - 21n + 16)/2$	$3n(14n^2 - 7n + 5)/2$
$Sz_v$	$63n^3 - 16n$	$n(63n^2 - 4)$
$Sz_e$	$n(343n^2 - 364n + 36)/4$	$n(343n^2 - 350n + 55)/4$
$Sz_{ev}$	$n(147n^2 - 78n - 32)/2$	$3n(49n^2 - 25n - 4)/2$
$PI$	$n(49n - 26)$	$n(49n - 25)$
$S$	$4n(21n^2 + 8)$	$6n(14n^2 + 5)$
$Gut$	$2n(49n^2 + 16)$	$n(98n^2 + 31)$
$Mo$	$16n$	$8n$
$Mo_e$	$16n$	$12n$
$Mo_t$	$32n$	$20n$
$w^+ Mo$	$80n$	$40n$
$w^+ Mo_e$	$80n$	$60n$
$w^+ Mo_t$	$160n$	$100n$
$w^* Mo$	$96n$	$48n$
$w^* Mo_e$	$96n$	$72n$
$w^* Mo_t$	$192n$	$120n$
$M_1$	$34n$	
$M_2$	$41n$	
$SO$	$n(7\sqrt{2} + 4\sqrt{13})$	
$ABC$	$((2 + 9\sqrt{2})n)/3$	
$GA$	$((15 + 8\sqrt{6})n)/5$	
$AZ$	$(3801n)/64$	
$SC$	$((30 + 24\sqrt{5} + 5\sqrt{6})n)/30$	
$ISI$	$83n/10$	
$F$	$86n$	
$H$	$44n/15$	
$SDD$	$44n/3$	

**Techniques:** In the next two cases, we enumerate the  $\Theta^*$ -classes of CPP[ $n$ ] depending on  $n$ , and topological indices are computed with respect to strength-weighted quantities arising from  $\Theta^*$ -classes.

**Case 1 (n even):** For  $1 \leq i \leq n/2$ , let  $D_i$  be a  $\Theta$ -class consisting of horizontal bonds of two diametrically

opposite benzenes of  $\text{CPP}[n]$ . The quotient graph  $\text{CPP}[n]/D_i$  is a complete bipartite graph  $K_{1,1}$  with partite sets  $\{X_i^d\}$  and  $\{Y_i^d\}$ , resulting the weighted measures  $w_v^i(X_i^d) = w_v^i(Y_i^d) = 3n$ ,  $s_v^i(X_i^d) = s_v^i(Y_i^d) = (7n - 4)/2$ ,  $w_e^{+i}(X_i^d Y_i^d) = w_e^{*i}(X_i^d Y_i^d) = 16$  and  $s_e^i(X_i^d Y_i^d) = 4$ .

For  $1 \leq i \leq n/2$ , let  $B_i = \{b_{i1}, b_{i2} : b_{i1} \text{ and } b_{i2} \text{ are two diametrically opposite bridging bonds of } \text{CPP}[n]\}$ . Then  $\text{CPP}[n]/B_i \simeq K_{1,1}$  with partite sets  $\{X_i^b\}$  and  $\{Y_i^b\}$ , implying  $w_v^i(X_i^b) = w_v^i(Y_i^b) = 3n$ ,  $s_v^i(X_i^b) = s_v^i(Y_i^b) = (7n - 2)/2$ ,  $w_e^{+i}(X_i^b Y_i^b) = 12$ ,  $w_e^{*i}(X_i^b Y_i^b) = 18$  and  $s_e^i(X_i^b Y_i^b) = 2$ . For  $1 \leq i \leq n/2$ , let  $S_i$  be a  $\Theta^*$ -class consisting of slanting bonds of two diametrically opposite benzenes of  $\text{CPP}[n]$ . The corresponding graph  $\text{CPP}[n]/S_i \simeq K_{2,4}$  as depicted in Figure 7 has vertex partition sets  $\{X_{i1}^s, X_{i2}^s\}$  and  $\{Y_{ij}^s : 1 \leq j \leq 4\}$  with weighted measures  $w_v^i(X_{ij}^s) = 3n - 4$ ,  $w_v^i(Y_{ij}^s) = 2$ ,  $s_v^i(X_{ij}^s) = (7n - 12)/2$ ,  $s_v^i(Y_{ij}^s) = 1$ ,  $w_e^{+i}(X_{ik}^s Y_{il}^s) = 5$ ,  $w_e^{*i}(X_{ik}^s Y_{il}^s) = 6$  and  $s_e^i(X_{ik}^s Y_{il}^s) = 1$  where  $j, k$  and  $l$  are taken with suitable values.

Then,

$$TI(\text{CPP}[n]) = \sum_{i=1}^{n/2} TI(\text{CPP}[n]/D_i) + \sum_{i=1}^{n/2} TI(\text{CPP}[n]/B_i) + \sum_{i=1}^{n/2} TI(\text{CPP}[n]/S_i).$$

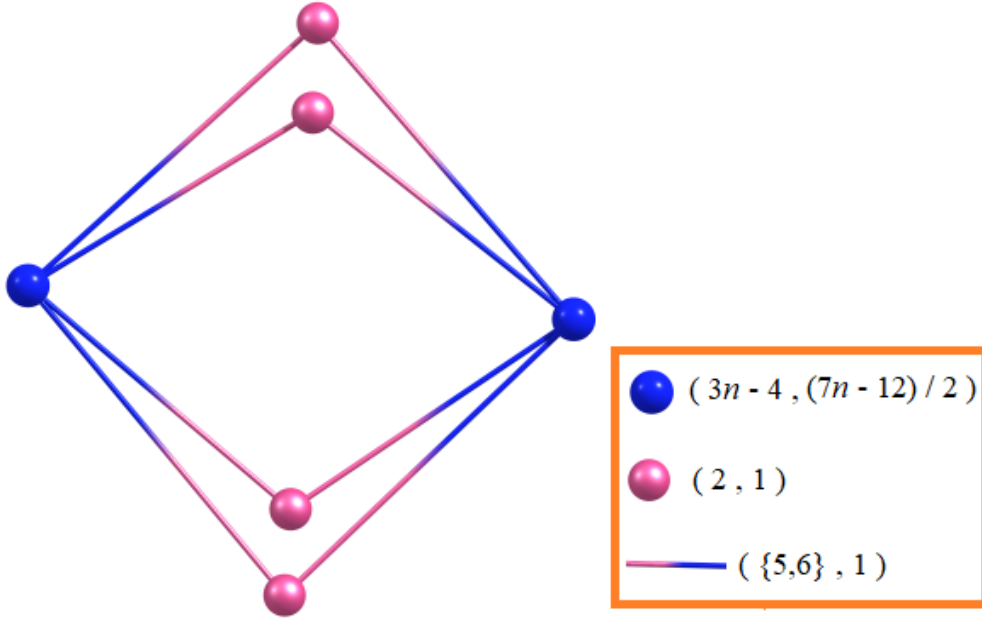


Figure 7: Quotient graph corresponding to slanting bonds of diametrically opposite benzenes in  $\text{CPP}[n]$

**Case 2 (n odd):** For  $1 \leq i \leq n$ , let  $BH_i$  be a set made up of three bonds  $b_i, h_{i1}$  and  $h_{i2}$  such that the bridging bond  $b_i$  is diametrically opposite to two horizontal bonds  $h_{i1}$  and  $h_{i2}$  of benzene. The graph  $\text{CPP}[n]/BH_i \simeq K_{1,1}$  has vertex partition sets  $\{X_i^{bh}\}$  and  $\{Y_i^{bh}\}$  with  $w_v^i(X_i^{bh}) = w_v^i(Y_i^{bh}) = 3n$ ,

$$s_v^i(X_i^{bh}) = s_v^i(Y_i^{bh}) = (7n - 3)/2, w_e^{+i}(X_i^{bh}Y_i^{bh}) = 14, w_e^{*i}(X_i^{bh}Y_i^{bh}) = 17 \text{ and } s_e^i(X_i^{bh}Y_i^{bh}) = 3.$$

Let  $S$  be a collection of all slanting bonds of  $CPP[n]$ . The quotient graph  $CPP[n]/S$  forms a circular arrangement of  $n$  squares by binding vertices as given Figure 8 such that for every vertex  $X$  and edge  $XY$  result with measures  $w_v(X) = 2, s_v(X) = 1, w_e^+(XY) = 5, w_e^*(XY) = 6$  and  $s_e(XY) = 1$ . Hence,

$$TI(CPP[n]) = \sum_{i=1}^n TI(CPP[n]/BH_i) + TI(CPP[n]/S).$$

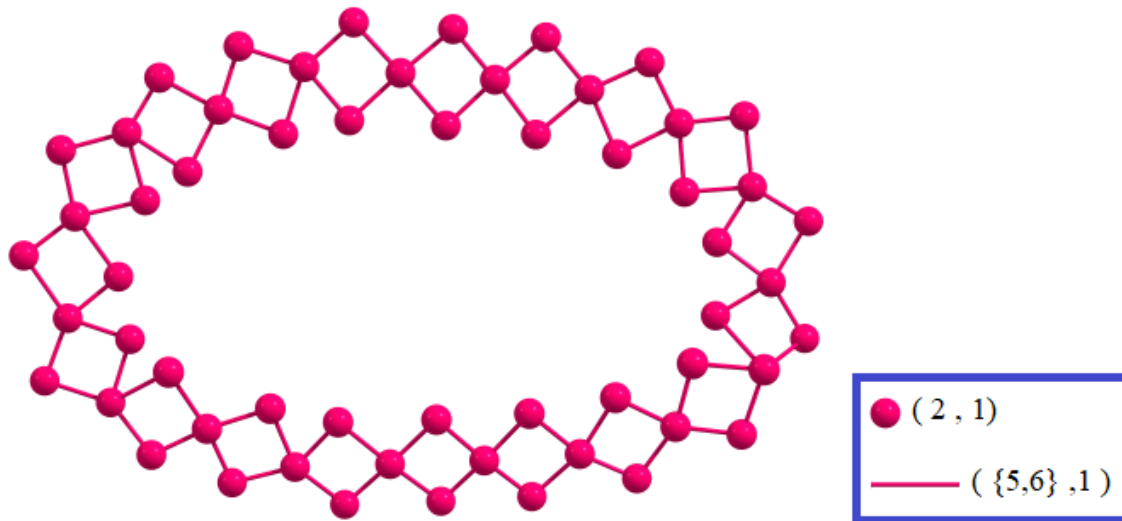


Figure 8: Quotient graph corresponding to slanting bonds in  $CPP[n]$

Furthermore, the analytical expressions presented in Table 1 reflect that the atom-pair additive indices such as Wiener, Schultz and Gutman as well as bond additive Szeged indices have degree-3 polynomials which are matched for infinite graphs with open chains and closed rings in the case of Wiener [84, 85]. But the Mostar-type indices result in linear polynomials and indicate that cycloparaphenylenes have low peripheral imperfection.

To compute degree based indices, we classify the edge partition of  $CPP[n]$  as  $d_{22}(CPP[n]) = 2n, d_{23}(CPP[n]) = 4n, d_{33}(CPP[n]) = n$ , and the following equation is used for computation.

$$TI(CPP[n]) = d_{22}(CPP[n]) TI(2, 2) + d_{23}(CPP[n]) TI(2, 3) + d_{33}(CPP[n]) TI(3, 3).$$

**Topological descriptors of cycloparaphenylene-2,7-pyrenylenes and cyclo[12]-paraphenylene [2]-2,11-hexabenzocoronenylenes:** The various topological indices of  $CPPyr[n]$  and  $CPPhbc[n]$  are shown in Table 2.

**Techniques:** We first point out the common  $\Theta$ -classes of  $CPPyr[n]$  and  $CPPhbc[n]$ , and then split into

two separate parts to discuss the other  $\Theta^*$ -classes. We use the description of  $D_i$ ,  $B_i$  and  $S_i$  as in the case of CPPyr[ $n$ ],  $n$  even, with different ranges of  $i$  for constructing the  $\Theta$ -classes in the benzenes and bridging bonds of the nanorings.

**CPPyr[ $n$ ]:** The weighted measures of the quotient graph due to the  $\Theta$ -classes  $D_i(1 \leq i \leq n)$ ,  $B_i(1 \leq i \leq n+1)$  and  $S_i(1 \leq i \leq n)$  are given in the following.

- $1 \leq i \leq n$ ,  $w_v^i(X_i^d) = w_v^i(Y_i^d) = 6n + 16$ ,  $s_v^i(X_i^d) = s_v^i(Y_i^d) = 7n + 18$ ,  $w_e^{+i}(X_i^d Y_i^d) = w_e^{*i}(X_i^d Y_i^d) = 16$  and  $s_e^i(X_i^d Y_i^d) = 4$ ,
- $1 \leq i \leq n+1$ ,  $w_v^i(X_i^b) = w_v^i(Y_i^b) = 6n + 16$ ,  $s_v^i(X_i^b) = s_v^i(Y_i^b) = 7n + 19$ ,  $w_e^{+i}(X_i^b Y_i^b) = 12$ ,  $w_e^{*i}(X_i^b Y_i^b) = 18$  and  $s_e^i(X_i^b Y_i^b) = 2$ ,
- $1 \leq i \leq n$ ,  $w_v^i(X_{ij}^s) = 6n + 12$ ,  $w_v^i(Y_{ij}^s) = 2$ ,  $s_v^i(X_{ij}^s) = 7n + 14$ ,  $s_v^i(Y_{ij}^s) = 1$ ,  $w_e^{+i}(X_{ik}^s Y_{il}^s) = 5$ ,  $w_e^{*i}(X_{ik}^s Y_{il}^s) = 6$  and  $s_e^i(X_{ik}^s Y_{il}^s) = 1$  where  $j, k$  and  $l$  are taken with suitable values.

We now enumerate the  $\Theta$ -classes to cover the horizontal bonds of two pyrenes. Let  $MH$  be a set consisting of all middle horizontal bonds of both pyrenes. Then CPPyr[ $n$ ]/ $MH \simeq K_{1,1}$  has partite sets  $\{X_i^{mh}\}$  and  $\{Y_i^{mh}\}$  with  $w_v^i(X_i^{mh}) = w_v^i(Y_i^{mh}) = 6n + 16$ ,  $s_v^i(X_i^{mh}) = s_v^i(Y_i^{mh}) = 7n + 17$ ,  $w_e^{+i}(X_i^{mh} Y_i^{mh}) = 28$ ,  $w_e^{*i}(X_i^{mh} Y_i^{mh}) = 34$  and  $s_e^i(X_i^{mh} Y_i^{mh}) = 6$ . Let  $LH$  be a set consisting of all left horizontal bonds of top pyrene and right horizontal bonds of bottom pyrene. Again, CPPyr[ $n$ ]/ $LH \simeq K_{1,1}$  has partite sets  $\{X_i^{lh}\}$  and  $\{Y_i^{lh}\}$  with  $w_v^i(X_i^{lh}) = w_v^i(Y_i^{lh}) = 6n + 16$ ,  $s_v^i(X_i^{lh}) = s_v^i(Y_i^{lh}) = 7n + 18$ ,  $w_e^{+i}(X_i^{lh} Y_i^{lh}) = 20$ ,  $w_e^{*i}(X_i^{lh} Y_i^{lh}) = 24$  and  $s_e^i(X_i^{lh} Y_i^{lh}) = 4$ . In an analogous way, the class  $RH$  constructed by taking right horizontal bonds of top pyrene and left horizontal bonds of bottom pyrene.

Let  $S$  be a  $\Theta^*$ -class covering all slanting bonds of both pyrenes. The resulting quotient graph CPPyr[ $n$ ]/ $S$  formed by binding the diagonal corner vertices of two copies of  $4 \times 4$  grid as shown in Figure 9 in which binding vertices have strength-weighted values  $(6n + 2, 7n + 1)$  and other vertices with  $(2, 1)$ . Finally, the required topological indices are derived from the following equation.

$$\begin{aligned}
TI(\text{CPPyr}[n]) &= \sum_{i=1}^n TI(\text{CPPyr}[n]/D_i) + \sum_{i=1}^{n+1} TI(\text{CPPyr}[n]/B_i) + \sum_{i=1}^n TI(\text{CPPyr}[n]/S_i) \\
&\quad + TI(\text{CPPyr}[n]/MH) + 2 TI(\text{CPPyr}[n]/LH) + TI(\text{CPPyr}[n]/S).
\end{aligned}$$

The edge partition of CPPyr[ $n$ ] is classified as  $d_{22}(\text{CPPyr}[n]) = 4(n + 1)$ ,  $d_{23}(\text{CPPyr}[n]) = 4(2n + 6)$ ,  $d_{33}(\text{CPPyr}[n]) = 2(n + 6)$ , and the degree based topological expressions are deduced using the following equation.

$$TI(\text{CPPyr}[n]) = d_{22}(\text{CPPyr}[n]) TI(2, 2) + d_{23}(\text{CPPyr}[n]) TI(2, 3) + d_{33}(\text{CPPyr}[n]) TI(3, 3).$$



Table 2: Topological indices of cycloparaphenylene-2,7-pyrenylene CPPyr[ $n$ ] and cyclo[12]-paraphenylene[2]-2,11-hexabenzocoronenylenes CPPhbc[ $n$ ]

TI	CPPyr[ $n$ ]	CPPhbc[ $n$ ]
$W$	$144n^3 + 1056n^2 + 2576n + 2208$	$144n^3 + 2448n^2 + 13408n + 25392$
$W_e$	$196n^3 + 1414n^2 + 3309n + 2666$	$196n^3 + 3570n^2 + 20165n + 36741$
$W_{ev}$	$168n^3 + 1222n^2 + 2920n + 2424$	$168n^3 + 2958n^2 + 16432n + 30570$
$Sz_v$	$504n^3 + 4128n^2 + 11232n + 9824$	$504n^3 + 10440n^2 + 72616n + 160816$
$Sz_e$	$686n^3 + 5516n^2 + 14210n + 11240$	$686n^3 + 15022n^2 + 106036n + 224952$
$Sz_{ev}$	$588n^3 + 4772n^2 + 12640n + 10504$	$588n^3 + 12528n^2 + 87700n + 190300$
$PI$	$196n^2 + 1068n + 1376$	$196n^2 + 3028n + 11168$
$S$	$672n^3 + 5056n^2 + 12608n + 10976$	$672n^3 + 12000n^2 + 68224n + 131520$
$Gut$	$784n^3 + 6048n^2 + 15424n + 13640$	$784n^3 + 14672n^2 + 86768n + 170232$
$Mo$	$32n + 160$	$224n + 2592$
$Mo_e$	$32n + 200$	$256n + 3432$
$Mo_t$	$64n + 360$	$480n + 6024$
$w^+Mo$	$160n + 800$	$1120n + 13392$
$w^+Mo_e$	$160n + 1008$	$1280n + 17704$
$w^+Mo_t$	$320n + 1808$	$2400n + 31096$
$w^*Mo$	$192n + 960$	$1344n + 17216$
$w^*Mo_e$	$192n + 1224$	$1536n + 22728$
$w^*Mo_t$	$384n + 2184$	$2880n + 39944$
$M_1$	$68n + 208$	$68n + 596$
$M_2$	$82n + 268$	$82n + 814$
$SO$	$2(4\sqrt{13}n + 7\sqrt{2}n + 12\sqrt{13} + 22\sqrt{2})$	$2(4\sqrt{13}n + 7\sqrt{2}n + 16\sqrt{13} + 109\sqrt{2})$
$ABC$	$2(9\sqrt{2}n + 2n + 21\sqrt{2} + 12)/3$	$2(9\sqrt{2}n + 2n + 36\sqrt{2} + 62)/3$
$GA$	$6n + (\sqrt{6}(16n + 48))/5 + 16$	$6n + (\sqrt{6}(16n + 64))/5 + 78$
$AZ$	$(3801n + 11542)/32$	$(3801n + 34887)/32$
$SC$	$2n + (\sqrt{6}(2n + 12))/6 + (\sqrt{5}(8n + 24))/5 + 2$	$2n + (\sqrt{5}(8n + 32))/5 + (\sqrt{6}(2n + 62))/6 + 8$
$ISI$	$(83n + 254)/5$	$(83n + 737)/5$
$F$	$172n + 560$	$172n + 1660$
$H$	$2(44n + 117)/15$	$2(44n + 311)/15$
$SDD$	$4(22n + 63)/3$	$4(22n + 169)/3$

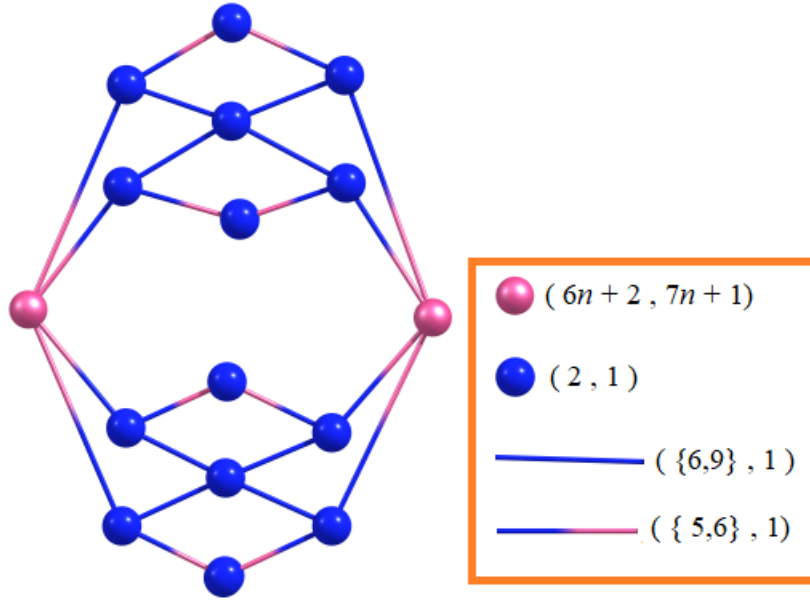


Figure 9: Quotient graph  $\text{CPPyr}[n]/S$

**CPPhbc[n]:** We first compute the weighted measures of the quotient graph arising from the  $\Theta$ -classes  $D_i(1 \leq i \leq n)$ ,  $B_i(1 \leq i \leq n+1)$  and  $S_i(1 \leq i \leq n)$  as in the case of  $\text{CPPyr}[n]$ .

- $1 \leq i \leq n$ ,  $w_v^i(X_i^d) = w_v^i(Y_i^d) = 6n + 42$ ,  $s_v^i(X_i^d) = s_v^i(Y_i^d) = 7n + 53$ ,  $w_e^{+i}(X_i^d Y_i^d) = w_e^{*i}(X_i^d Y_i^d) = 16$  and  $s_e^i(X_i^d Y_i^d) = 4$ ,
- $1 \leq i \leq n+1$ ,  $w_v^i(X_i^b) = w_v^i(Y_i^b) = 6n + 42$ ,  $s_v^i(X_i^b) = s_v^i(Y_i^b) = 7n + 54$ ,  $w_e^{+i}(X_i^b Y_i^b) = 12$ ,  $w_e^{*i}(X_i^b Y_i^b) = 18$  and  $s_e^i(X_i^b Y_i^b) = 2$ ,
- $1 \leq i \leq n$ ,  $w_v^i(X_{ij}^s) = 6n + 38$ ,  $w_v^i(Y_{ij}^s) = 2$ ,  $s_v^i(X_{ij}^s) = 7n + 49$ ,  $s_v^i(Y_{ij}^s) = 1$ ,  $w_e^{+i}(X_{ik}^s Y_{il}^s) = 5$ ,  $w_e^{*i}(X_{ik}^s Y_{il}^s) = 6$  and  $s_e^i(X_{ik}^s Y_{il}^s) = 1$  where  $j, k$  and  $l$  are taken with suitable values.

As we have done for horizontal bonds of pyrenes in  $\text{CPPyr}[n]$ , we now consider the  $\Theta$ -classes  $MH$ ,  $LH$  and  $RH$  to cover the horizontal bonds of hexabenzocoronenylenes in  $\text{CPPhbc}[n]$ , except the vertical second left and right layers bonds because these bonds are  $\Theta$  related with slanting bonds as we have pointed out in Figure 6. Hence, we have  $w_v^i(X_i^{mh}) = w_v^i(Y_i^{mh}) = 6n + 42$ ,  $s_v^i(X_i^{mh}) = s_v^i(Y_i^{mh}) = 7n + 51$ ,  $w_e^{+i}(X_i^{mh} Y_i^{mh}) = 48$ ,  $w_e^{*i}(X_i^{mh} Y_i^{mh}) = 72$ ,  $s_e^i(X_i^{mh} Y_i^{mh}) = 8$ , and  $w_v^i(X_i^{lh}) = w_v^i(Y_i^{lh}) = 6n + 42$ ,  $s_v^i(X_i^{lh}) = s_v^i(Y_i^{lh}) = 7n + 53$ ,  $w_e^{+i}(X_i^{lh} Y_i^{lh}) = 20$ ,  $w_e^{*i}(X_i^{lh} Y_i^{lh}) = 24$  and  $s_e^i(X_i^{lh} Y_i^{lh}) = 4$ .

The  $\Theta$ -classes  $TC_i$  ( $1 \leq i \leq 4$ ) are constructed by taking two slanting bonds of North-West (obtuse), North-East (acute), South-East (obtuse), South-West (acute) corner benzenes of top hexabenzocoronenylylene. These  $\Theta$ -classes leave the quotient graph  $K_{1,1}$  with vertex partition  $\{X_i^{tc}\}$  and  $\{Y_i^{tc}\}$  such that  $w_v^i(X_i^{tc}) = 3$ ,  $w_v^i(Y_i^{tc}) = 12n + 81$ ,  $s_v^i(X_i^{tc}) = 2$ ,  $s_v^i(Y_i^{tc}) = 14n + 106$ ,  $w_e^{+i}(X_i^{tc} Y_i^{tc}) = 10$ ,  $w_e^{*i}(X_i^{tc} Y_i^{tc}) = 12$

and  $s_e^i(X_i^{tc}Y_i^{tc}) = 2$ . In the same way, the  $\Theta$ -classes  $BC_i$  ( $1 \leq i \leq 4$ ) can be constructed for bottom hexabenzocoronene.

At last, we take all the slanting bonds of both hexabenzocoronenylenes, except  $\{TC_i, BC_i : 1 \leq i \leq 4\}$  and horizontal bonds of vertical second left and right layers of hexabenzocoronenylenes to form a  $\Theta^*$ -class, denoted by  $SH$  and the corresponding quotient graph  $CPPhbc[n]/SH$  is shown in Figure 10.

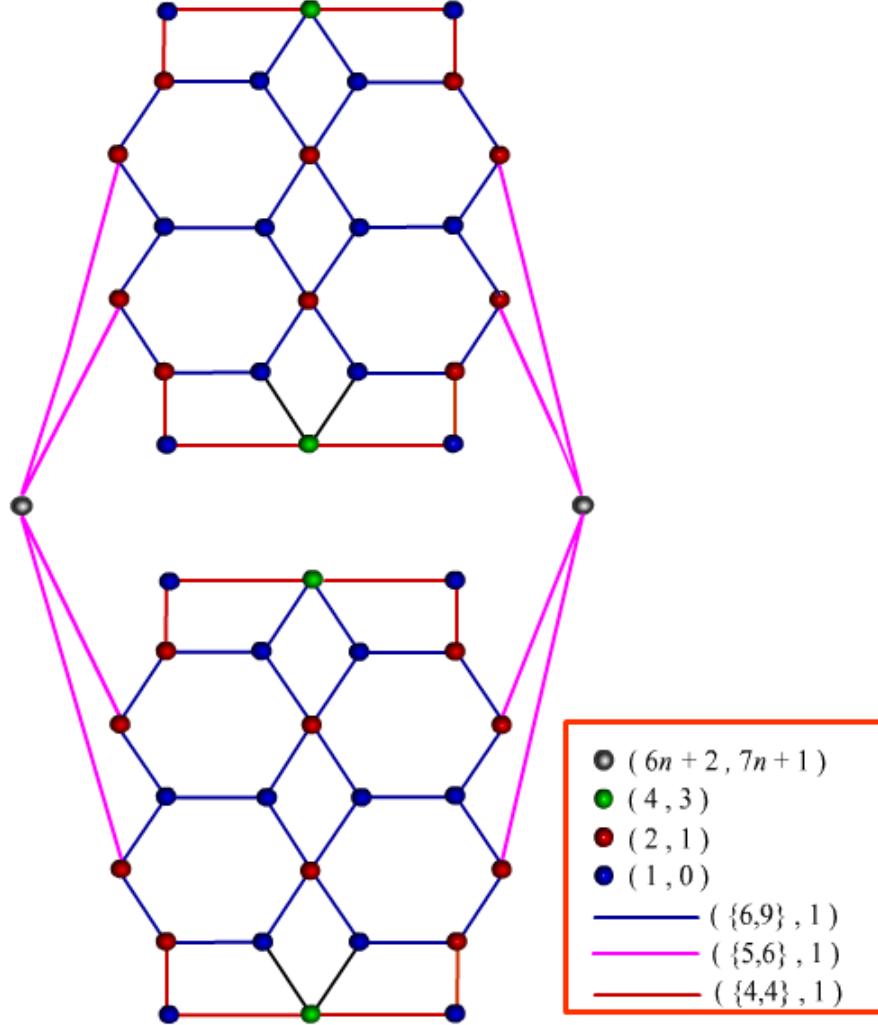


Figure 10: Quotient graph  $CPPhbc[n]/SH$

Then, the computation of the topological indices is done from the following equation.

$$\begin{aligned}
 TI(CPPhbc[n]) &= \sum_{i=1}^n TI(CPPhbc[n]/D_i) + \sum_{i=1}^{n+1} TI(CPPhbc[n]/B_i) + \sum_{i=1}^n TI(CPPhbc[n]/S_i) \\
 &\quad + 2 \sum_{i=1}^4 TI(CPPhbc[n]/TC_i) + TI(CPPhbc[n]/MH) + 2 TI(CPPhbc[n]/LH)
 \end{aligned}$$

$$+ TI(\text{CPPhbc}[n]/SH).$$

For computing the degree based indices, the edge partition of  $\text{CPPhbc}[n]$  is classified as  $d_{22}(\text{CPPhbc}[n]) = 4(n + 4)$ ,  $d_{23}(\text{CPPhbc}[n]) = 4(2n + 8)$ ,  $d_{33}(\text{CPPhbc}[n]) = 2(n + 31)$ , and we use the following equation for deriving the expressions.

$$TI(\text{CPPhbc}[n]) = d_{22}(\text{CPPhbc}[n]) TI(2, 2) + d_{23}(\text{CPPhbc}[n]) TI(2, 3) + d_{33}(\text{CPPhbc}[n]) TI(3, 3).$$

When  $n$  is large, the leading elements of the Wiener, Szeged, PI, Schultz, and Gutman indices of  $\text{CPPyr}[n]$  and  $\text{CPPhbc}[n]$  are identical, implying asymptotic degeneracy regardless of the presence of pyrenylene in  $\text{CPPyr}[n]$  and hexabenzocoronene in  $\text{CPPhbc}[n]$ . It is important to note from Table 2 that Mostar-type indices lead to the topological discrimination between  $\text{CPPyr}[n]$  and  $\text{CPPhbc}[n]$  for infinite nanorings. As we know, asymptotic behaviors between polynomials of the same degree are obtained by the corresponding leading coefficient, we have

$$\lim_{n \rightarrow \infty} \frac{Mo(\text{CPPyr}[n])}{Mo(\text{CPPhbc}[n])} = \frac{w^+ Mo(\text{CPPyr}[n])}{w^+ Mo(\text{CPPhbc}[n])} = \frac{w^* Mo(\text{CPPyr}[n])}{w^* Mo(\text{CPPhbc}[n])} = \frac{1}{7},$$

$$\lim_{n \rightarrow \infty} \frac{Mo_e(\text{CPPyr}[n])}{Mo_e(\text{CPPhbc}[n])} = \frac{w^+ Mo_e(\text{CPPyr}[n])}{w^+ Mo_e(\text{CPPhbc}[n])} = \frac{w^* Mo_e(\text{CPPyr}[n])}{w^* Mo_e(\text{CPPhbc}[n])} = \frac{1}{8},$$

and

$$\lim_{n \rightarrow \infty} \frac{Mo_t(\text{CPPyr}[n])}{Mo_t(\text{CPPhbc}[n])} = \frac{w^+ Mo_t(\text{CPPyr}[n])}{w^+ Mo_t(\text{CPPhbc}[n])} = \frac{w^* Mo_t(\text{CPPyr}[n])}{w^* Mo_t(\text{CPPhbc}[n])} = \frac{2}{15}.$$

A recent study by Tsuchido et al. [52] has considered the exciting possibility of inserting  $\text{Au}_2$  (diphosphine) corners into cycloparaphenylene crowns which result in novel twisted crowns. The insertion of such heavy dimers as  $\text{Au}_2$  then offers the possibility of topological studies of such complexes by incorporating relativistic parameters into the topological indices. Indeed, one such previous study from our group [77] considers incorporation of relativistic parameters into topological indices. Consequently, the present techniques pave the way for such generalizations of incorporating relativistic parameters. Such topic could be the stimulating subject matter of future studies. Moreover, in a recent study [71], it has been shown that the topological indices such as the ones obtained in the present study are extremely valuable in predicting drug activities, for example, the antiepileptic activities of a series of anticonvulsant drugs. In these cases structure-activity relations were obtained by correlating the observed  $\ln(\text{ED}_{50})$  for a series of anticonvulsant drugs with topological indices, in particular the  $W$  and  $PI$  indices, with a very high

statistical correlation and confidence [71]. Consequently, the present study makes a clear and compelling case for such future QSAR studies on cycloparaphenylene and their derivatives when more experimental data becomes available on these systems.

## 4 Chemical Applications

The various topological indices that we have computed here for cycloparaphenylene series are expected to have a number of chemical applications, especially in the prediction of the physicochemical properties, toxicity, electronic and spectroscopic properties. For example, it has been recently shown that the viscoelasticity of long-chain branched polypropylene (LCB-PP) compounds strongly depended on the degree of branching of these polymers [86]. As the degree of branching increases, the foam exhibits enhanced resistance to bubble coalescence, thus causing a more regular bubble structure with a larger expansion ratio [86]. The degree of molecular branching is well characterized by a number of distance based topological indices that are computed here, such as the Wiener index, Szeged index, PI index, ABC index, Sombor index and so forth. Hence we anticipate in future when such viscosity data become available on cycloparaphenylene series, the computed topological indices in the present study could provide valuable insights into the structure-activity and structure-property correlations of such physical properties. In a previous study [87], it has been shown that the dermal penetrations of polycyclic aromatic compounds were strongly correlated with the octanol partition coefficients, which in turn, correlate with the topological distance based indices such as the Wiener, Szeged and PI indices. In yet another study, an inverse correlation was found between the observed anticonvulsant activity of drugs administered for epilepsy, several of which contain aromatic rings [71]. This is a consequence of the fact that the efficacy of anticonvulsant drugs strongly depends on their ability to penetrate the blood-brain-barrier (BBB), which in turn depends on a number of topological parameters and hence these properties correlated extremely well with the Wiener and PI indices. Statistical and neural network studies have shown that the hepatotoxicity of several halocarbons depended approximately 45% on topochemical descriptors [88]. It has been shown that the protonation constant and lipophilicity of polycyclic aromatics exhibit strong correlation to Szeged and PI indices [89]. Therefore the topological indices computed here exhibit considerable promise in structure-activity and structure-property relations in predicting a number of physicochemical properties, toxicity parameters and bioactivities of the compounds considered here.

We demonstrate that the connectivity information contained in the various topological indices could also provide valuable information on spectroscopic properties as well as thermodynamic and kinetic stabilities of the cycloparaphenylene series considered here. Let us consider the three compounds shown in Figures 1–3 to demonstrate the utility of the various topological parameters. For this purpose, we have

made additional computations on the energy spectra of the adjacency matrices of the three structures shown in Figures 1–3. We have also derived the Kekulé counts of the three structures which are the constant terms of the matching polynomials in order to shed further light on the relative thermodynamic stabilities of the three structures through the resonance and delocalization energy parameters. Table 3 shows our computational results for the three structures where we have shown the HOMO-LUMO gaps in addition to the scaled delocalization energies and scaled resonance energies. The HOMO-LUMO gap is directly related to the hardness of these compounds and thus a higher HOMO-LUMO gap implies a greater kinetic stability. As seen from Table 3, the largest HOMO-LUMO gap is exhibited by CPPyr[9] (Figure 2) suggesting that CPPyr[9] is kinetically the most stable among the three compounds while CPPhbc[5] (Figure 3) is kinetically the least stable. However, as seen from Table 3, all three compounds exhibit a large HOMO-LUMO gap. On the other hand, the thermodynamic stability pertains the most stable compound as measured by the delocalization energies and resonance energies which in turn depend on the Kekulé counts of the three structures that are shown in Table 3. On the basis of the scaled delocalization energies shown in Table 3, the CPPhbc[5] structure is thermodynamically the most stable structure which also has the largest Kekulé count of 63,999,375 among the three structures. We have computed the scaled resonance energies of the three structures using Herndon’s method [90] of calculating the resonance energy that uses a formula in direct proportionality to  $\ln(KC)$ . On the basis of the scaled resonance energy too, the CPPhbc[5] structure is predicted to be the most stable.

We have employed the distance degree sequence vector (DDSV) introduced by Bloom et al. [91] to obtain the partitions of nuclear equivalence classes. In essence, the DDSV method provides a vector in a multi-dimensional vector space for each vertex of the graph on the basis of the distance of that vertex to other vertices as defined by a  $p$ -tuple sequence vector [91]. If two vertices carry the same  $p$ -tuple sequence, where  $p$  is the eccentricity of the vertex then the vertices are grouped into the same equivalence class. On the basis of the DDSV method, the vertices are partitioned using the TopoChemie-2020 [92] computational package. The results thus obtained for the nuclear equivalence classes are shown in Table 3 for both carbon nuclei and the protons. It is evident from Table 3, the three structures exhibit a contrasting sets of nuclear equivalence classes, thereby suggesting that the NMR and ESR spectroscopic methods could be employed for their structure elucidations. As can be seen from Table 3, all three structures exhibit different  $^{13}\text{C}$  NMR patterns as well as proton NMR patterns. Furthermore, if a radical can be generated by the deprotonation from a C–H bond then the computed nuclear equivalence classes yield powerful combinatorial generating functions based on the operator methods described in extensive details in previous studies [93, 94]. By the use of combinatorial generating functions, as an illustration,

Table 3: Spectral properties, HOMO-LUMO gaps and NMR spectral patterns of cycloparaphenylene series

CPP Series	Molecular Formulas	HOMO-LUMO	KC	$E_{\pi}$	Delocalization Energy/Bond	Resonance Energy/Bond #	Nuclear Equivalence Classes	$^{13}\text{C}$ NMR	Proton NMR
CPP[24] (Figure 1)	$\text{C}_{144}\text{H}_{96}$	$0.8284\beta$	16,777,215	$201.349114\beta$	$0.398258\beta$	$0.1369\beta$	$\text{C}(96^1 48^1)$ $\text{H}(96^1)$	1:2	1
CPP <sub>yr</sub> [9] (Figure 2)	$\text{C}_{140}\text{H}_{88}$	$0.8609\beta$	9,437,183	$196.782929\beta$	$0.405593\beta$	$0.1359\beta$	$\text{C}(4^{11} 8^{12})$ $\text{H}(8^{11})$	1:1...:1(11) 2:2...:2(12)	1:1...:1(11)
CPPhbc[5] (Figure 3)	$\text{C}_{144}\text{H}_{72}$	$0.7917\beta$	63,999,375	$207.405222\beta$	$0.440314\beta$	$0.1479\beta$	$\text{C}(4^8 8^{14})$ $\text{H}(4^{18})$	1:1...:1(8) 2:2...:2(14)	1:1...:1(18)

# Herndon's RE ( [90] )

we have shown in Figure 11, a typical ESR hyperfine structure arising from the coupling of  $^{13}\text{C}$  nuclei in equivalence classes closest to the unpaired electron for the structures shown in Figures 2 and 3. The experimental hyperfine pattern would, of course, depend on the location of the unpaired electron; in the present case we take it near the center of the molecule. Consequently, the graph theoretical techniques described here have the power to predict energetics, stabilities, reactivity, and spectral properties of these compounds to first order following which more refined quantum chemical techniques can be employed for further quantitative predictions. In this context we would like to point out that hybrid methods such as integration of graph theory and the PPP method [95] can be powerful in obtaining quantum chemical parameters for hybrid quantum methods where the needed parameters can be computed from high level computations using machine learning techniques on a library of smaller molecules carried out using high level *ab initio* quantum computations.

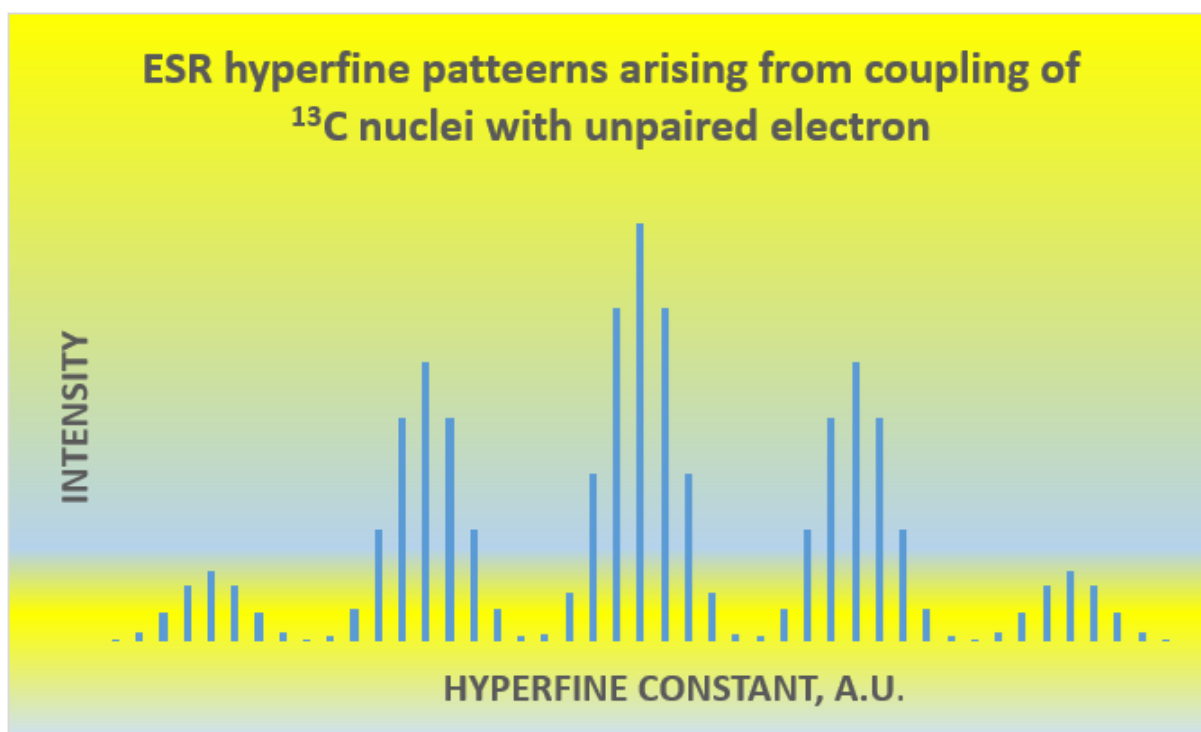


Figure 11: A typical hyperfine pattern arising from the coupling of equivalence classes of  $^{13}\text{C}$  nuclei closest to the unpaired electron for the structures shown in Figures 2 and 3

## 5 Concluding Remarks

We have presented the theoretical analysis of the structural characterization of the nanostructures such as cycloparaphenylene, cycloparaphenylene-2,7-pyrenylene and cyclo[12]-paraphenylene[2]2-2,11-hexabenzocoronylene, inspired by their novelty and fascinating properties. The recently revised edition of the cut method enables the successful computation of analytical expressions of a large number of molecular de-



scriptors of the significant indices including Wiener index, Szeged index, Mostar index and their variants. It is believed that the structural invariants of this study illustrate the promising and intriguing attributes of these newly synthesized compounds and can be utilized as an important tool in the fields of pharmaceutical science, supramolecular research and synthetic chemistry, to grasp and deduce the functionalities of the compounds. Being the nanostructures, the results obtained for the CPP-based structures, can also be employed in accelerating their role in various industries owing to their actual optical, electronic, and biomedical applications. We have demonstrated that combinatorial and graph theoretical techniques can be utilized to generate the NMR and ESR spectral patterns of the cycloparaphenylene series. Our computed energetics and stabilities deduced through delocalization and resonance energies as well as the HOMO-LUMO gaps reveal that the CPPhbc[5] structure is thermodynamically more stable whereas the CPPyr[9] is kinetically more stable. These computations reveal that robust hybrid techniques could be developed in the future by combining machine learning and graph theoretical methods on a combinatorial library of a set of small related molecules to derive quantum chemical parameters that can be effectively employed on a larger system of nanomaterials comprising of polycyclic aromatic rings, thus paving a method to integrate graph theory and quantum chemical methods.

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