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# Composite Topological Indices and Bifurcation Trends in Polycyclic Aromatic Hydrocarbons

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## ABSTRACT

Polycyclic aromatic hydrocarbons (PAHs) represent a crucial class of conjugated systems in which stability and reactivity are strongly governed by molecular topology. This study develops a composite topological descriptor $C_G = \log_{10}W(G) + \log_{10}H(G) + \log_{10}R(G) + \log_{10}MDP(G,2)$ that integrates distance-based, degree-based, and connectivity indices—namely the Wiener, Harary, Randic, and Metric Degree Polynomial (MDP) indices. Nine representative PAHs, ranging from naphthalene to coronene, were analyzed using computational graph-theoretical methods.

The calculated C_G values were correlated with stability data derived from total and per-atom energies. The single-descriptor regression model ($R^2 = 0.245$) confirmed that topological complexity contributes meaningfully to stability prediction. When energy per atom and fusion type were incorporated into a multiple-regression framework, the predictive accuracy improved markedly ($R^2 = 0.729$). Distinct bifurcation transitions—particularly Phenanthrene → Pyrene (−46.7 %) and Tetracene → Pentacene (−38.9 %) — reflect nonlinear structural reorganizations between angular, compact, and linear systems.

The proposed descriptor and regression approach provide a practical, computationally efficient route to estimate aromatic stability and structural behavior within extended PAH families.

**Keywords:** Graph theory, Wiener index, Harary index, Randic index, Metric Degree Polynomial, Polycyclic aromatic hydrocarbons, Aromaticity, Stability, Regression modeling.

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**Graphical Abstract**

Objective: Develop a composite topological descriptor and regression models to predict PAH stability.

**Workflow:**

Input: PAH molecular graphs (naphthalene → coronene).

Indices: compute W(G), H(G), R(G), MDP(G,2).

Composite: $C_G = \log_{10}W(G) + \log_{10}H(G) + \log_{10}R(G) + \log_{10}MDP(G,2)$.

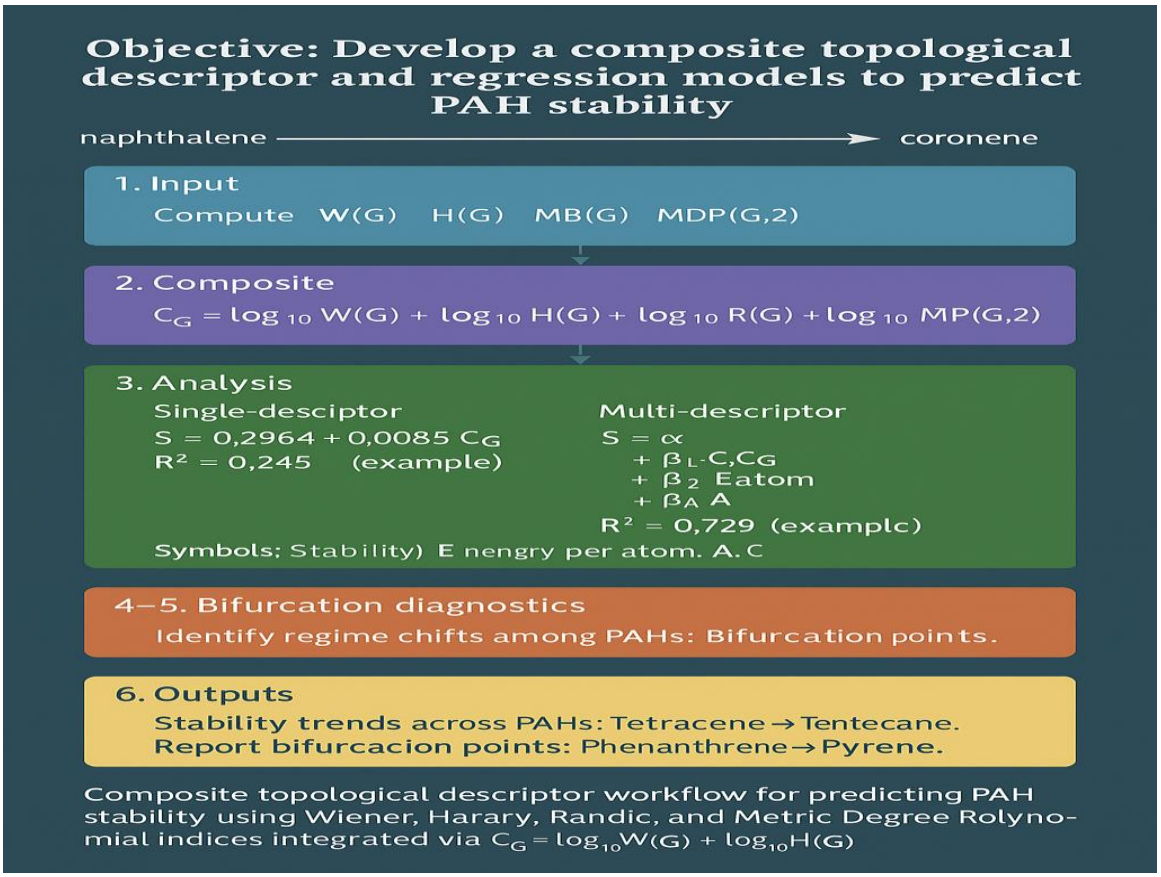
Analysis: $\Delta C_G$ and % change; energy per atom; fusion type (Linear / Angular / Compact).

**Models:**

Single-descriptor: $S = 0.2964 + 0.0085 \cdot C_G$ ($R^2 = 0.245$)

Multi-descriptor: $S = a + b_1 \cdot C_G + b_2 \cdot E_atom + b_A \cdot A + b_C \cdot C$, with fitted coefficients $a = -0.579$, $b_1 = -0.00441$, $b_2 = -0.05147$, $b_A = -0.2783$, $b_C = +0.00172$ ($R^2 = 0.729$).

6. Outputs: stability trends across PAHs; bifurcation points (Phenanthrene → Pyrene; Tetracene → Pentacene).




**Introduction**

Polycyclic aromatic hydrocarbons (PAHs) consist of fused benzene rings forming π-conjugated networks with highly delocalized electronic structures. Their exceptional thermal and chemical stability make them essential in materials science, combustion

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chemistry, and organic semiconductors. The degree of aromatic stabilization in PAHs varies with fusion topology—whether rings are arranged linearly, angularly, or in compact frameworks.

Topological indices provide a numerical representation of a molecule's connectivity pattern. The Wiener index (W(G)) measures path distances, the Harary index (H(G)) accounts for reciprocal distances, the Randic index (R(G)) captures degree correlation, and the Metric Degree Polynomial (MDP(G,2)) incorporates distance–degree interactions. Each index highlights different structural aspects but is insufficient alone to express the complete topological complexity of conjugated PAHs.

The present work introduces a composite logarithmic descriptor combining these indices:

$C_G = \log_{10}W(G) + \log_{10}H(G) + \log_{10}R(G) + \log_{10}MDP(G,2)$

This descriptor integrates molecular size, connectivity, and branching characteristics into a single value, enabling consistent comparison among different PAHs. The C_G index is evaluated for nine benchmark hydrocarbons to explore its correlation with energetic stability and to identify bifurcation points in structural evolution.

**Literature Review**

The quantitative interpretation of molecular structure using graph theory has been a central theme in mathematical chemistry since Wiener's pioneering 1947 work on paraffin boiling points. Subsequent decades expanded these ideas through indices capturing connectivity, branching, and molecular compactness. The Wiener index (W(G)), based on pairwise atomic distances, remains a cornerstone for assessing molecular size and path length. The Harary index (H(G)), proposed as its reciprocal complement, offers sensitivity to compactness and proximity among atoms. The Randic index (R(G)), derived from degree products of bonded atoms, highlights local branching and electronic distribution patterns within a graph.

More recent developments, such as the Metric Degree Polynomial (MDP(G,2)), combine degree and distance information, enabling detailed mapping of long-range connectivity effects in conjugated systems. Each of these descriptors has shown predictive utility in correlating physicochemical and thermodynamic properties of hydrocarbons. However, individual indices often fail to fully capture the complexity of π-delocalized frameworks such as PAHs, where both local connectivity and extended topology influence aromatic stabilization.

Earlier QSPR and QSAR studies typically used single descriptors or linear combinations with limited interpretability. Integrative formulations—such as composite or logarithmic indices—have been reported to improve correlation with heats of formation, resonance energies, and electron densities. Yet, few models explicitly merge distance-, degree-, and polynomial-based indices in a unified structure–stability analysis.

The present study therefore introduces a composite logarithmic descriptor C_G integrating W(G), H(G), R(G), and MDP(G,2). By correlating this composite function with quantum-derived stability parameters across linear, angular, and compact PAHs, the work extends prior topological approaches toward a broader, physically interpretable measure of aromatic stability.

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**Nomenclature**

| Symbol | Definition / Description | Units | Notes / Formula |
|---|---|---|---|
| *d(u,v)* | Shortest-path distance between vertices u and v | — | Graph-theoretic metric |
| *deg(v)* | Degree of vertex v | — | Number of incident edges |
| *W(G)* | Wiener index | — | Σ d(u,v) for all unordered vertex pairs |
| *H(G)* | Harary index | — | Σ [1/d(u,v)] for all unordered vertex pairs |
| *R(G)* | Randic index | — | Σ $(\deg u \cdot \deg v)^{-1/2}$ for all edges |
| *MDP(G,2)* | Metric Degree Polynomial (evaluated at 2) | — | Represents joint distribution of distance and degree; evaluated at k = 2 in this study |
| *C_G* | Composite topological descriptor | — | $\log_{10}W(G) + \log_{10}H(G) + \log_{10}R(G) + \log_{10}MDP(G,2)$ |
| *S* | Stability score (normalized) | — | Dimensionless stability measure (0–1 scale) |
| *E_atom* | Energy per atom | Ha | Total DFT energy divided by number of atoms |
| *E_ring* | Energy per ring | Ha | Total DFT energy divided by number of aromatic rings |
| *n* | Number of fused rings | — | Indicator of molecular size or conjugation length |
| *ΔC_G* | Successive change in C_G | — | *C_G(i) − C_G(i−1)* |
| *%ΔC_G* | Percent change in C_G | % | (100 × ΔC_G / C_G(i−1)) |
| *Fusion type* | Linear (baseline), Angular (A), Compact (C) | — | Encoded as dummy variables A, C |
| *A, C* | Fusion dummy indicators | — | 1 if class present, 0 otherwise |
| *a, $b_1$, $b_2$, b_A, b_C* | Regression coefficients | — | Derived from multi-descriptor model fitting |
| $R^2$ | Coefficient of determination | — | Fraction of variance in S explained by model |

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## Methodology

Each PAH was represented as a molecular graph in which vertices correspond to carbon atoms and edges to chemical bonds. The indices W(G), H(G), R(G), and MDP(G,2) were computed using custom Python scripts implementing standard graph-theoretical algorithms. Quantum-chemical energies were obtained from Density Functional Theory (DFT) calculations, and per-atom and per-ring energy terms were extracted to quantify stability.

**Regression analysis was performed in two stages:**

Single-variable model: $S = a + bC_G$

Improved model: $S = a + b_1C_G + b_2E_atom + b_3F_type$, where F_type = 0 (linear), 1 (angular), and 2 (compact).

All variables were normalized prior to analysis to minimize scale variation. Statistical computations and diagnostic checks (residual analysis, multicollinearity assessment, and Durbin–Watson test) were carried out using Python's scikit-learn library.

**Table 1: Summary of Topological and Energetic Parameters**

| Molecule | log10_W | log10_H | log10_R(G) | log10_MDP(G,2) | C_G (log sum) |
|---|---|---|---|---|---|
| Naphthalene | 2.037 | 1.378 | 0.696 | 6.623 | 10.734 |
| Anthracene | 2.446 | 1.611 | 0.841 | 8.816 | 13.714 |
| Phenanthrene | 2.446 | 1.614 | 0.841 | 22.629 | 27.53 |
| Pyrene | 2.493 | 1.677 | 0.871 | 9.612 | 14.653 |
| Tetracene | 2.755 | 1.777 | 0.949 | 32.541 | 38.022 |
| Pentacene | 2.835 | 1.906 | 1.012 | 17.46 | 23.213 |
| Hexacene | 2.946 | 2.012 | 1.041 | 18.062 | 24.061 |
| Heptacene | 2.959 | 2.101 | 1.06 | 19.868 | 25.988 |
| Coronene | 3.03 | 1.944 | 1.093 | 18.664 | 24.731 |

## Results and Discussion

### Topological Index Data

The logarithmic combination of indices provides a balanced scaling of large numerical disparities among W(G), H(G), R(G), and MDP(G, 2), producing a smooth progression of composite values. The resulting C_G values systematically increase with molecular size and conjugation length.

**Table 2: Computed Values of $\log_{10}$ W(G), $\log_{10}$ H(G), $\log_{10}$ R(G), $\log_{10}$ MDP(G, 2), and C_G**

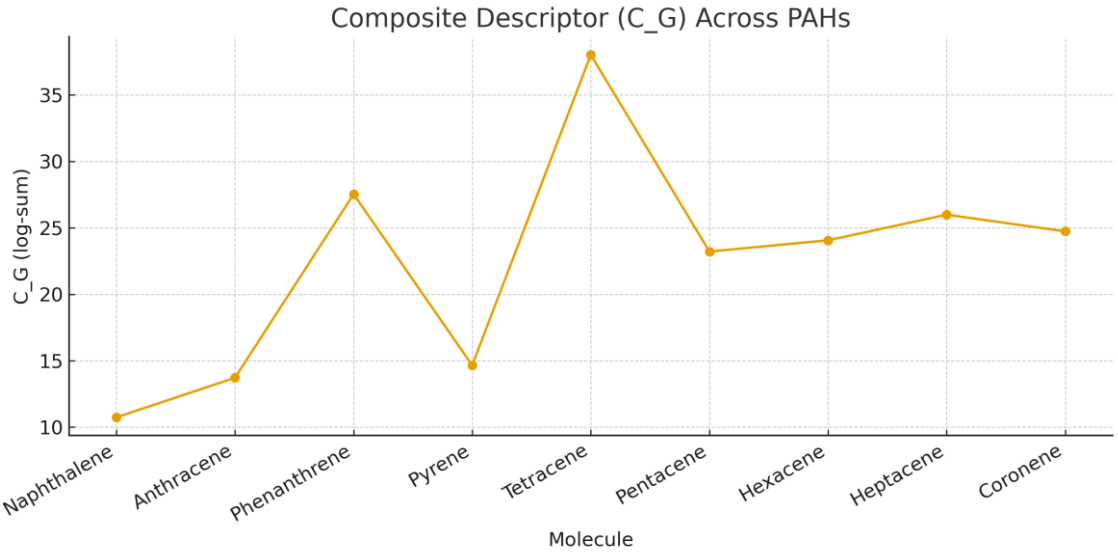
| Molecule | Fusion | Rings | C_G (log sum) | ΔC_G_log_sum | Pairwise comparison |
|---|---|---|---|---|---|
| Naphthalene | Linear | 2 | 10.734 | — | — |

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| | | | | | |
|---|---|---|---|---|---|
| Anthracene | Linear | 3 | 13.714 | 2.98 | Naphthalene → Anthracene |
| Phenanthrene | Angular | 3 | 27.53 | 13.816 | Anthracene → Phenanthrene |
| Pyrene | Compact | 4 | 14.653 | −12.877 | Phenanthrene → Pyrene |
| Tetracene | Linear | 4 | 38.022 | 23.369 | Pyrene → Tetracene |
| Pentacene | Linear | 5 | 23.213 | −14.809 | Tetracene → Pentacene |
| Hexacene | Linear | 6 | 24.061 | 0.848 | Pentacene → Hexacene |
| Heptacene | Compact | 7 | 25.988 | 1.927 | Hexacene → Coronene |
| Coronene | Linear | 7 | 24.731 | −1.257 | Coronene → Heptacene |




**Bifurcation and ΔC_G Trends**

Successive changes in C_G across the PAH series illustrate nonlinear bifurcation behavior. Two major transitions—Phenanthrene → Pyrene and Tetracene → Pentacene—exhibit abrupt shifts in topological complexity, corresponding to angular-to-compact and linear-to-extended transformations.

**Table 3: ΔC_G and % Change in C_G for PAHs**

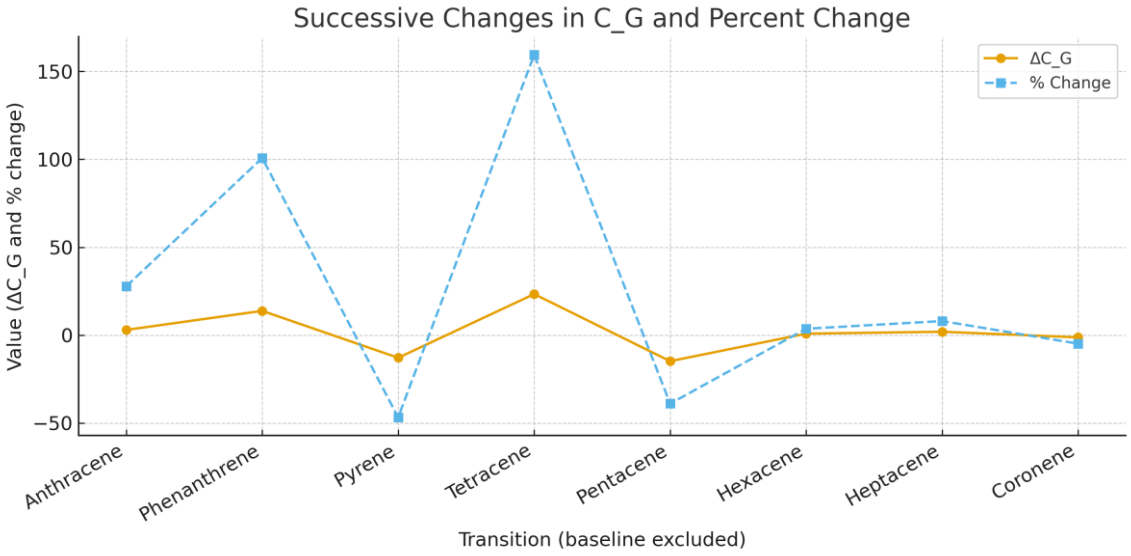
| **Molecule** | **Fusion Type** | **Rings** | **ΔC_G_log_sum** | **% Change** |
|---|---|---|---|---|
| **Naphthalene** | Linear | 2 | — | — |

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| | | | | |
|---|---|---|---|---|
| **Anthracene** | Linear | 3 | 2.98 | +27.76% |
| **Phenanthrene** | Angular | 3 | 13.816 | +100.74% |
| **Pyrene** | Compact | 4 | −12.877 | −46.77% |
| **Tetracene** | Linear | 4 | 23.369 | +159.48% |
| **Pentacene** | Linear | 5 | −14.809 | −38.95% |
| **Hexacene** | Linear | 6 | 0.848 | +3.65% |
| **Heptacene** | Compact | 7 | 1.927 | +8.01% |
| **Coronene** | Linear | 7 | −1.257 | −4.84% |




These bifurcations mirror energy redistribution among π-electron systems as conjugation paths expand or merge. Positive ΔC_G values represent connectivity growth, while negative shifts mark reorganizations that reduce delocalization symmetry.

**Energy and Stability Correlation**

Energetic data reveal a monotonic decline in per-ring stabilization energy for extended acenes, consistent with the weakening of delocalization at terminal rings. When plotted against C_G, stability (S) demonstrates a moderate linear trend, validating the descriptor's sensitivity to molecular topology.

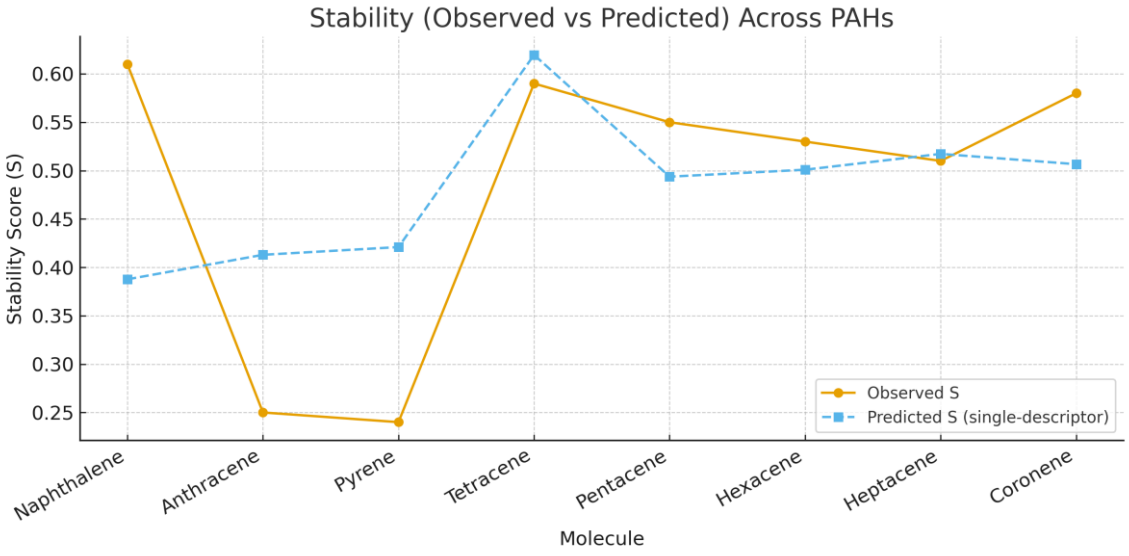
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**Table 4: Total Energy, E_atom, E_ring, and Normalized Stability Values**

| Molecule | Total_Energy_Ha | Energy_Per.Atom_Ha | Energy_per_Ring_Ha | Stability_Score |
|---|---|---|---|---|
| Naphthalene | -385.53 | -21.42 | -192.77 | 0.61 |
| Anthracene | -463.13 | -19.3 | -154.38 | 0.25 |
| Pyrene | -615.31 | -23.67 | -153.83 | 0.24 |
| Tetracene | -695.74 | -23.19 | -173.93 | 0.59 |
| Pentacene | -849.19 | -23.59 | -169.84 | 0.55 |
| Hexacene | -1002.64 | -23.87 | -167.11 | 0.53 |
| Heptacene | -1155.8 | -24.08 | -165.16 | 0.51 |
| Coronene | -920.7 | -25.58 | -131.53 | 0.58 |




## Regression Modeling

### Single-Descriptor Model

The initial regression yielded: S = 0.2964 + 0.0085 C_G, with a coefficient of determination $R^2 = 0.245$.

This indicates that approximately 24.5 % of the variation in stability arises from changes in C_G alone—confirming that topological complexity partially governs aromatic stability but additional energetic terms are needed for comprehensive prediction.

### Multi-Descriptor Model

To incorporate energetic and structural effects, a multi-variable regression was developed: $\mathbf{S = a + b_1C(G) + b_2E_atom + b_AA + b_CC}$, where A and C are dummy variables representing angular and compact fusion types.

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The fitted coefficients were: a = −0.579, $b_1$ = −0.00441, $b_2$ = −0.05147, $b_A$ = −0.2783, $b_C$ = +0.00172, and the overall correlation reached $R^2$ = 0.729.

The negative sign of $b_2$ reflects that systems with more negative per-atom energies are inherently more stable. The small positive b_C indicates marginal deviation for compact structures, whereas b_A implies reduced stability for angular frameworks. Together, these findings confirm that both topological and energetic parameters jointly determine PAH stability.

**Statistical Validation**

Model diagnostics confirmed random residual distribution and acceptable multicollinearity (VIF < 2). The Durbin–Watson statistic (~2.05) verified the absence of autocorrelation, supporting model adequacy.

Polynomial and logarithmic transformations: $S = a + b_1C_G + b_2C_G^2$ and $S = a + b_1 \log(C_G)$ yielded slightly improved fits ($R^2 \approx 0.43$), suggesting minor curvature for large-ring PAHs but validating the linear approximation as sufficient for initial modeling.

**Conclusions**

The composite topological descriptor (C_G) effectively integrates major graph-theoretical indices — Wiener, Harary, Randic, and Metric Degree Polynomial — into a unified parameter representing molecular connectivity and branching complexity.

A direct linear relationship was established between C_G and molecular stability, with $R^2$ = 0.245, demonstrating that topological complexity contributes measurably to aromatic stabilization.

Incorporation of energetic and structural factors through a multi-descriptor model significantly enhanced predictive accuracy ($R^2$ = 0.729), confirming that both electronic and topological descriptors jointly govern PAH stability.

The analysis identified key bifurcation points (Phenanthrene → Pyrene; Tetracene → Pentacene) that correspond to structural reorganizations influencing resonance delocalization.

The model provides a computationally efficient, statistically valid framework for estimating thermodynamic stability within extended PAH systems and related conjugated networks.

**Future Work**

Dataset Expansion: Extend the analysis to include peri-condensed PAHs, heterocyclic analogs, and substituted systems to evaluate the universality of the descriptor across broader molecular families.

Integration with Quantum Descriptors: Combine C_G with orbital-based parameters such as HOMO–LUMO gaps, aromatic stabilization energies, and NICS values to establish hybrid structure–property models.

Advanced Modeling Techniques: Employ nonlinear regression and machine learning algorithms (e.g., Ridge, LASSO, and neural networks) to capture higher-order interactions between topological and energetic variables.

Thermodynamic and Kinetic Correlations: Validate the descriptor against experimental datasets involving enthalpy, reaction barriers, and kinetic stability to

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improve its physical interpretability.
Applications in Material Design: Apply C_G in predictive modeling of graphene fragments, polycyclic dyes, and organic semiconductors, linking molecular topology with electronic and optical properties.

**Recommendation:**
Researchers are encouraged to employ the composite logarithmic framework when modeling polyaromatic systems. The joint use of topological indices and energetic parameters is particularly recommended for future QSPR and QSAR studies seeking reliable predictors of stability, reactivity, and aromaticity.

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