Graph-theoretic indicators of fullerene stability

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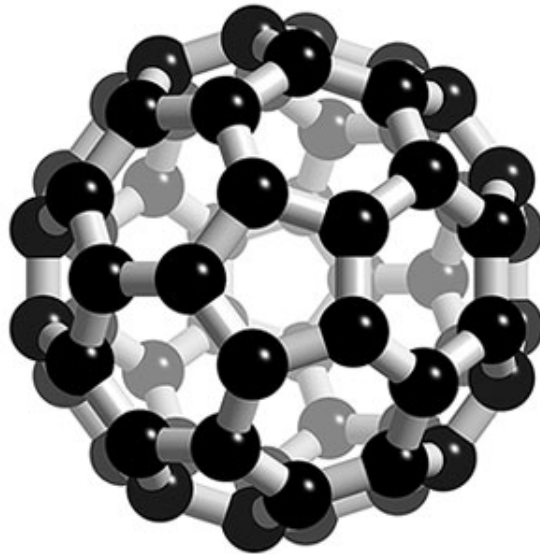
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Fullerenes

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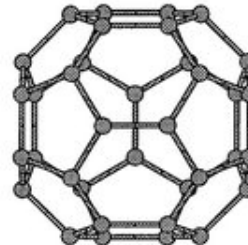
Fullerene graphs

A fullerene graph is a planar, 3-regular and 3-connected graph, twelve of whose faces are pentagons and any remaining faces are hexagons.

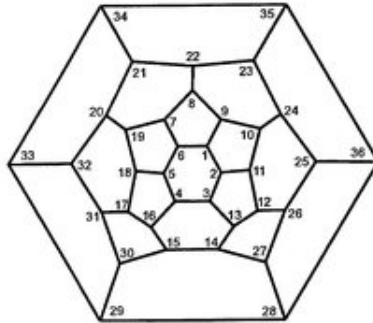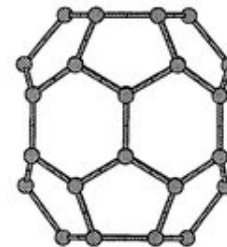# Fullerene graphs

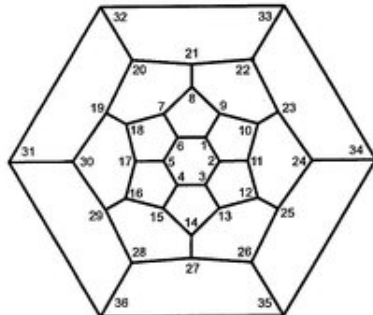A fullerene graph is a planar, 3-regular and 3-connected graph, twelve of whose faces are pentagons and any remaining faces are hexagons.

36:14 (1 D_{2d} 0.0)

36:15 (2 C_{6v} 11.6)

Number of fullerenes

n	Isomers	IPR isomers
20	1	-
30	3	-
40	40	-
50	271	-
60	1812	1
70	8149	1
80	31924	7
90	99918	46
100	285914	450
110	713319	2355
120	1674171	10774
130	3580637	39393
140	7341204	121354
150	14059173	335569
160	26142839	836497
170	46088148	1902265

Number of fullerenes
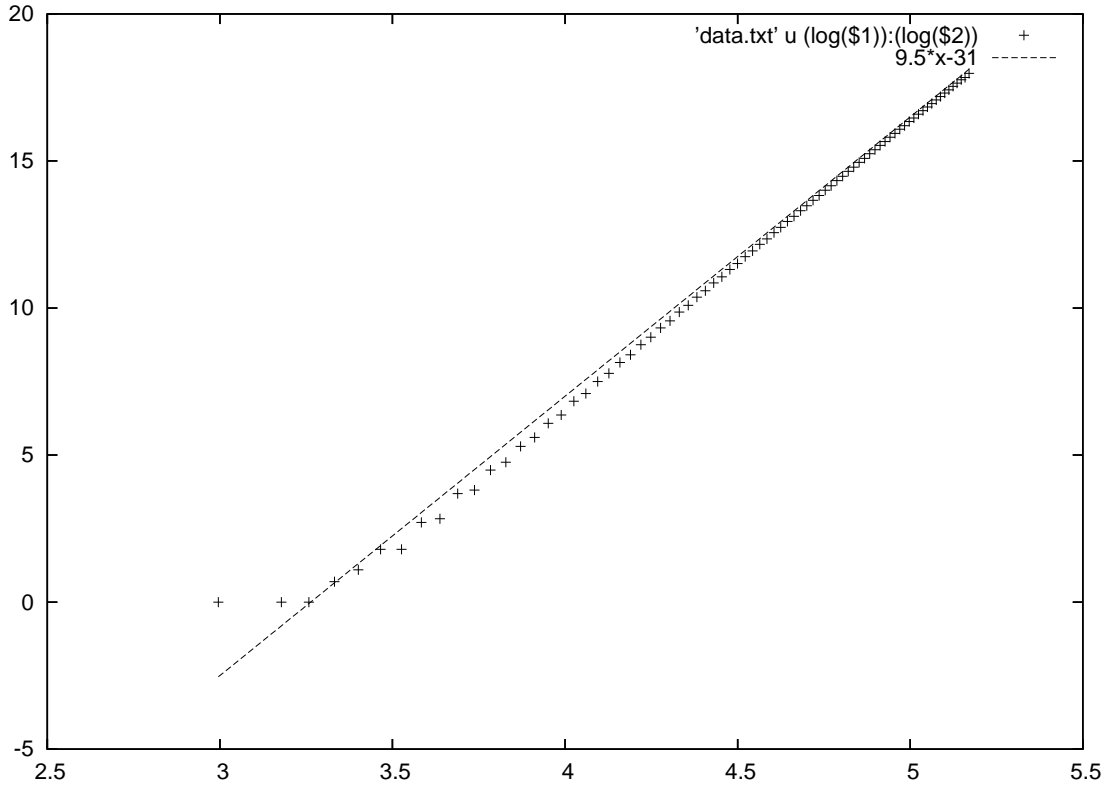
Benzenoids and benzenoid graphs
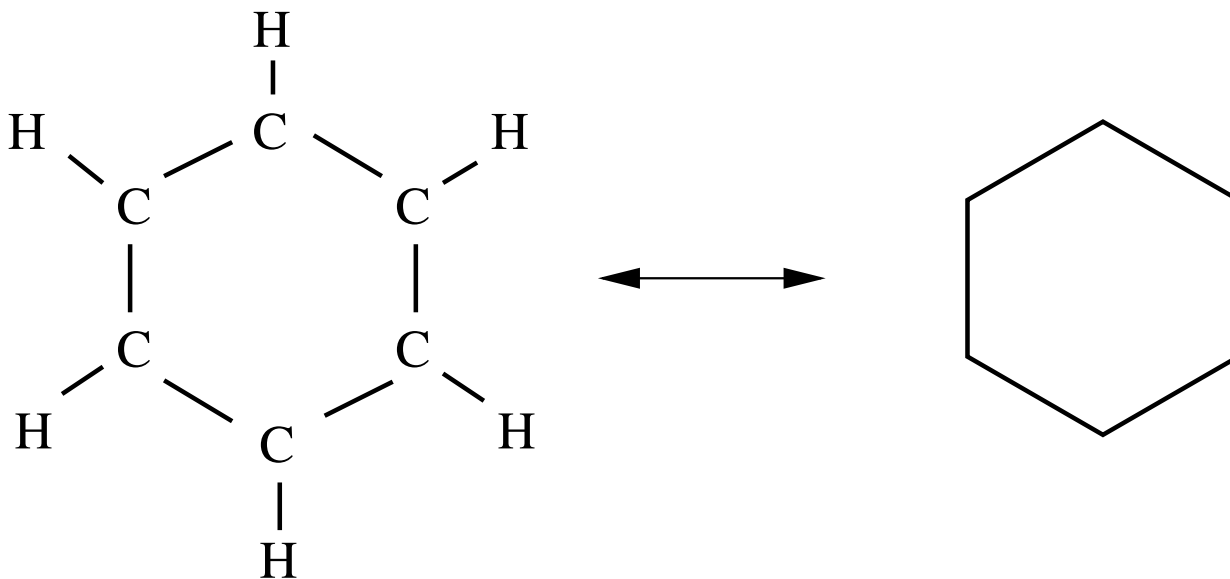
Resonance in benzenoids

Stability of benzenoid compounds
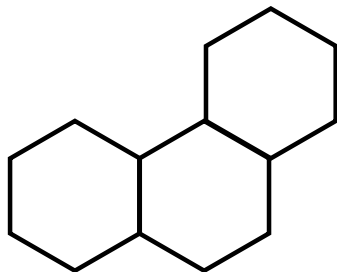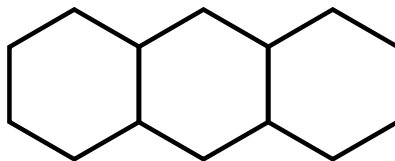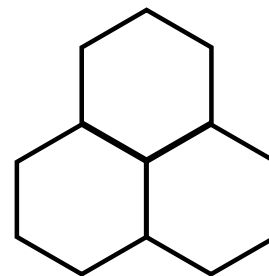
5   4   0
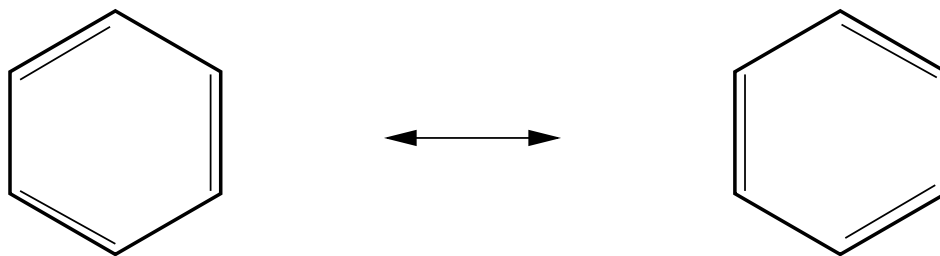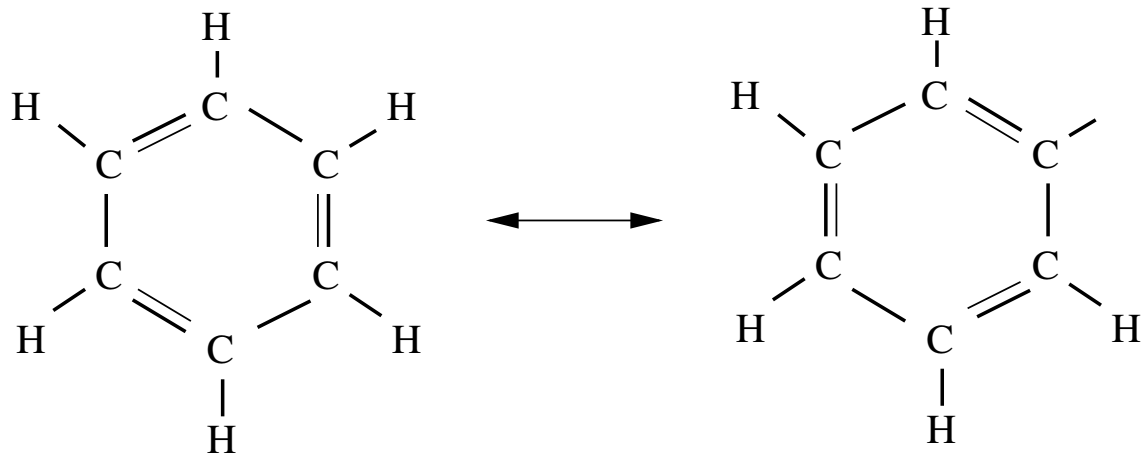
Perfect matchings and stability of benzenoids

A matching M in a graph G is a set of edges from $E(G)$ such that no two edges from M have a vertex in common.

A matching M is perfect if every vertex of G is incident with an edge from M.

$\Phi(G)$ denotes the number of perfect matchings in G.

For benzenoids $\mathcal{B}_1$ and $\mathcal{B}_2$ and their corresponding benzenoid graphs B_1 and B_2 we have:

$\Phi(B_1) > \Phi(B_2) \Longrightarrow \mathcal{B}_1$ is "more stable" than $\mathcal{B}_2$.

Number of perfect matchings in fullerene graphs

C_{60} has 1812 isomers.

$\Phi(C_{60} : 1812(I_h)) = 12500$ (21) – The most stable isomer.

$\Phi(C_{60} : 1(D_{5h})) = 16501$ (1) – The "least stable" isomer.

Candidates

- Independence number

- Second moment of the hexagon signature

- Separator

- The smallest eigenvalue

- Combinatorial curvature

- Bipartite edge frustration

- Bipartivity

- Average hexagon abundance

Stability of benzenoid compounds

5   4   0
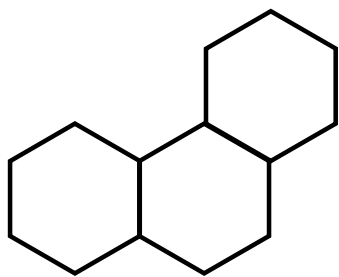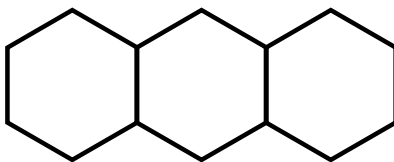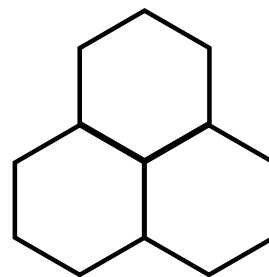
Partition of π-electrons
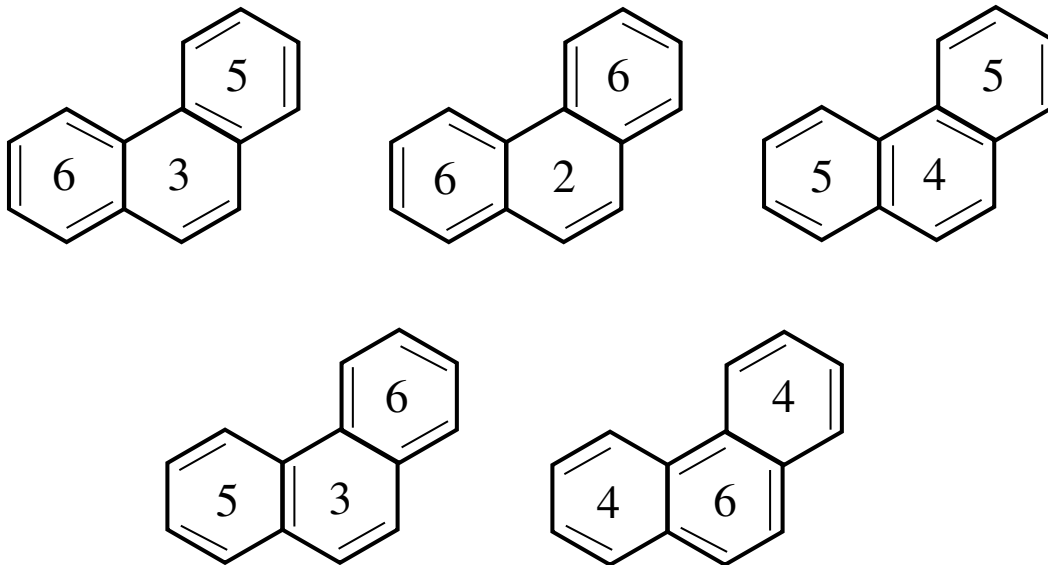
Importance and redundancy of an edge

Let G be a graph with a perfect matching and e an edge of G. Importance of e, denoted by $\iota(e)$, is the number of perfect matchings of G that contain e, while the redundancy of e, denoted by $\rho(e)$, is the number of perfect matchings of G that do not contain e.

$\iota(e) = \Phi(G \backslash e)$

$\rho(e) = \Phi(G - e)$

$\iota(e) + \rho(e) = \Phi(G)$ for every $e \in E(G)$

$\sum_{e=\{u,v\}} \iota(e) = \Phi(G)$ for every $v \in V(G)$

Richness and abundance of a face

Let G be a planar graph with a given plane embedding and F a face of G. The richness of F with respect to a perfect matching M is the number of electrons given to F by M.

The abundance $\pi(F)$ of a face F is the richness of F averaged over all perfect matchings of G.

Randić, Balaban, Gutman, *et al* considered $\pi-$electron content of rings in polycyclic conjugated hydrocarbons.

Theorem

$$\pi(F) = \frac{\sum_{e \in \partial F} \iota(e)}{\Phi(G)}.$$

Average n-gon abundance

Let G be a fullerene graph on n vertices.

$$\overline{\pi}_6(G) = \frac{1}{n/2-10} \sum_H \pi(H)$$

$$\overline{\pi}_5(G) = \frac{1}{12} \sum_P \pi(P)$$

Prisms
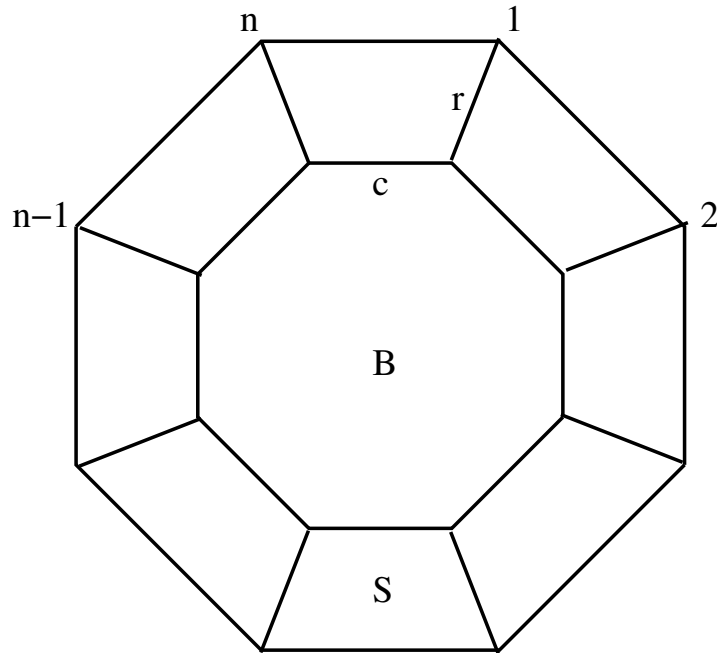
$$\iota(r) = F_n, \qquad \iota(c) = F_{n-1} + \frac{1+(-1)^n}{2}$$

$$\Phi(Z_n) = \iota(r) + 2\iota(c) = F_{n+1} + F_{n-1} + 1 + (-1)^n$$

Prisms

$$\pi(B) = \frac{n \cdot \iota(c)}{\Phi(Z_n)}, \qquad \pi(S) = 2\frac{\iota(r) + \iota(c)}{\Phi(Z_n)}$$

$$\lim_{n\to\infty} \pi(B) = \frac{n}{\phi^2 + 1}, \qquad \lim_{n\to\infty} \pi(S) = 2 - \frac{2}{\phi^2 + 1}$$

Here $\phi = \frac{1+\sqrt{5}}{2}$ is the Golden Section.

Under uniform distribution, a face with n vertices receives $n/3$ electrons. Hence, the bases are poorer, and the sides are richer in π-electrons than under the uniform distribution.

Barrels
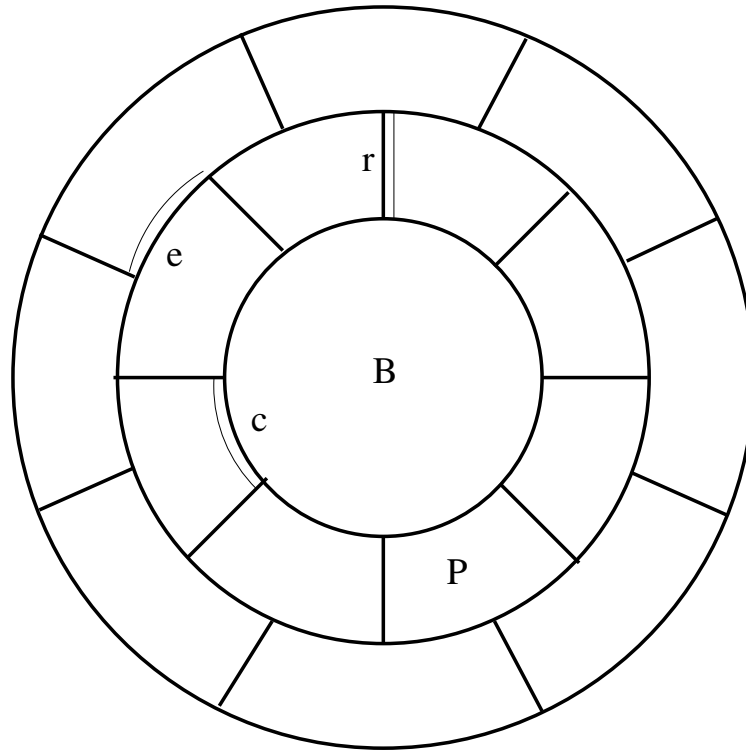
$$\Phi(B_n) = \iota(r) + 2\iota(c) = \iota(r) + 2\iota(e) \implies \iota(c) = \iota(e)$$

$$\pi(B) = \frac{n \cdot \iota(c)}{\Phi(B_n)}, \qquad \pi(P) = 2 - \frac{\iota(c)}{\Phi(B_n)}$$

Barrels

For $\iota(c)$ one obtains

$$\iota(c) = r_{n-1} + s_{n-3},$$

where r_k and s_k satisfy following recurrences:

$r_k = r_{k-1} + 2r_{k-2} - r_{k-4}$ for $k \geq 5$
$r_1 = 1, r_2 = 3, r_3 = 5, r_4 = 10.$

$s_k = 2s_{k-2} + s_{k-3} - s_{k-4}$ for $k \geq 7$
$s_3 = 1, s_4 = 3, s_5 = 4, s_6 = 5.$

Asymptotic behavior of r_n and s_n is given by

$$r_n \sim \gamma^n, \qquad s_n \sim \delta^n,$$

where $\gamma \approx 1.905$ and $\delta \approx 1.490$ are obtained by solving the characteristic
equations $x^4 - x^3 - 2x^2 + 1 = 0$ and $x^4 - 2x^2 - x + 1 = 0$, respectively.

Barrels

Now

$$\lim_{n \to \infty} \frac{\iota(c)}{\Phi(B_n)} = \frac{2\gamma^2 - 2}{\gamma^3 + 4\gamma^2 - 4} \approx 0.302 = \tau_\infty.$$

Hence,

$$\lim_{n \to \infty} \pi(B) = n \cdot \tau_\infty, \qquad \lim_{n \to \infty} \pi(P) = 2 - \tau_\infty.$$

Again, the bases are poorer, and the side faces richer in π-electrons than under the uniform distribution.

Tubular fullerenes $C_{10n} : 1$
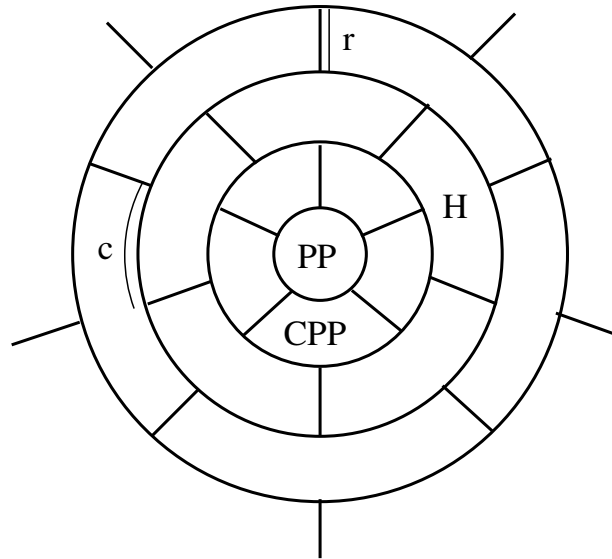
Again, all circular edges are equally important.

Explicit formulas for $C_{10n} : 1$

$$\iota(r) = 5^{n-1} + 3\left[\left(\tfrac{5+\sqrt{5}}{2}\right)^{n-2} + \left(\tfrac{5-\sqrt{5}}{2}\right)^{n-2}\right] + 1$$

$$\iota(c) = 2 \cdot 5^{n-1} + \left(\tfrac{5+\sqrt{5}}{2}\right)^{n-2} + \left(\tfrac{5-\sqrt{5}}{2}\right)^{n-2}$$

$$\pi(PP) \to 2, \quad \pi(CPP) \to 1.6, \quad \pi(H) = 2$$

$$\Phi(C_{10n} : 1) = \iota(r) + 2\iota(c)$$

$$\Phi(C_{10n} : 1) = 5^n + 5\left[\left(\tfrac{5+\sqrt{5}}{2}\right)^{n-2} + \left(\tfrac{5-\sqrt{5}}{2}\right)^{n-2}\right] + 1$$

Average abundances in C_{60}

$$\overline{\pi}_6(C_{60} : 1812(I_h)) = 2.16, \quad \overline{\pi}_5(C_{60} : 1812(I_h)) = 1.40$$

$$\overline{\pi}_6(C_{60} : 1(D_{5h})) = 2.00, \quad \overline{\pi}_5(C_{60} : 1(D_{5h})) = 1.67$$

Observation

$$\overline{\pi}_6(C_{60} : 1(D_{5h})) < \overline{\pi}_6(C_{60} : p) < \overline{\pi}_6(C_{60} : 1812(I_h))$$

The same pattern is observed for C_{70}.

Hypothesis

$$\overline{\pi}_6(C_n : p) > \overline{\pi}_6(C_n : q) \Longrightarrow C_n : p \text{ is more stable than } C_n : q.$$

Test space

IPR isomers – experimentally verified

- $C_{60} : 1(I_h)$

- $C_{70} : 1(D_{5h})$

- $C_{76} : 1(D_2)$

- $C_{78} : 1(D_3), 2(C_{2v}), 3(C_{2v})$

- $C_{80} : 1(D_{5d}), 2(D_2)$

- $C_{82} : 3(C_2)$

- $C_{84} : 22(D_2), 23(D_{2d})$

Non-IPR isomers – energy calculations

- $C_{32} : 6(D_3)$

- $C_{36} : 15(D_{6h})$

- $C_{40} : 38(D_2), 39(D_{5d})$

Results

n (# of isomers)	Isomer no.	$\overline{\pi}(C_n)$
60 (1)	1	1
70 (1)	1	1
76 (2)	1	1
78 (5)	1	3
	2	2
	3	4
80 (7)	1	1
	2	2
82 (9)	3	3
84 (24)	22	16
	23	15
32 (6)	6	1
36 (15)	15	15
40 (40)	38	2
	39	1

Comments and conclusions

Stability of fullerenes is likely to depend on both local and global properties in an intricate way.

Fullerene graphs are all very much alike.

No indicator considered so far seems to be perfect.

"Law of Small Numbers"

Further search for more sensitive generic indicators is needed.

Indicators based on pentagon and hexagon abundances are promising, since they offer a possibilty of quantifying local effects.

Further developments

Bi-indices
(M. Randić, Bled 2007)

Generalized combinatorial curvature
(T. Reti, E. Bitay, Prediction of Fullerene Stability Using Topological Descriptors,
Materials Science Forum 537–538 (2007) 439–448)

Locally sensitive indicators based on partitons of π-electrons

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References

[1] P.W. Fowler, D.E. Manolopoulos, *An Atlas of Fullerenes*, Clarendon Press, Oxford, 1995.

[2] I. Gutman, Ž. Tomović, K. Müllen, J.P. Rabe, On the distribution of π-electrons in large polycyclic aromatic hydrocarbons, *Chem. Phys. Lett.* 397 (2004) 412–416.

[3] A.T. Balaban, M. Randić , D. D. Vukičević , Partition of π -electrons between faces of polyhedral carbon aggregates, *J. Math. Chem.*, 43 (2008) 773–779.

[4] M. Randić, H.W. Kroto, D. Vukičević, Numerical Kekulé Structures of Fullerenes and Partitioning of π-Electrons to Pentagonal and Hexagonal Rings, *J. Chem. Inf. Model.* 47 (2007) 897–904.

Hyperindex