

Kekulé- and Clar-structure based parameters for hexagonal graphs

Andrej Vodopivec

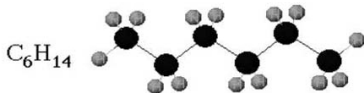
`andrej.vodopivec@fmf.uni-lj.si`

IRMACS
Interdisciplinary Colloquium

March 30, 2006

Hydrocarbons

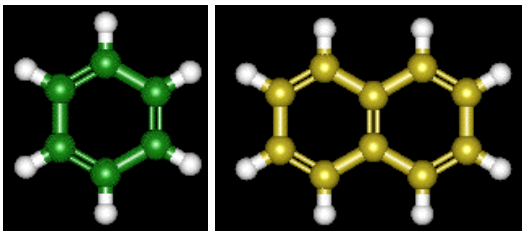
What is a hydrocarbon?



- A molecule with carbon and hydrogen atoms
- Each carbon has 4 bonds to other atoms
- Each hydrogen has one bond to one other atom

Benzenoids

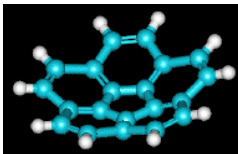
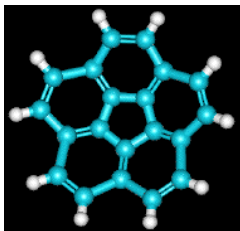
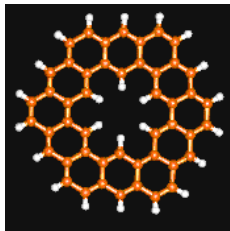
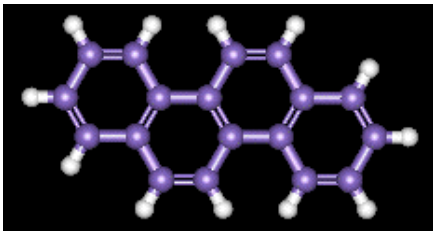
What is a hydrocarbon benzenoid?



- Carbon atoms form rings of length 6
- Double bonds between carbon atoms
- More rings are connected to form a molecule

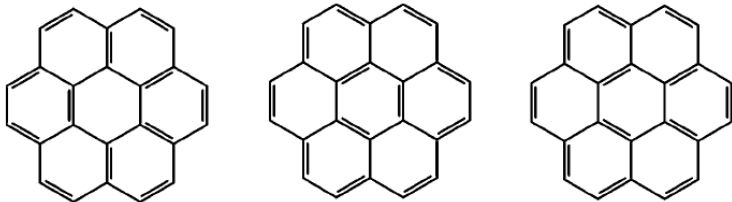
Benzenoids

Bigger examples



Representation of benzenoids 1

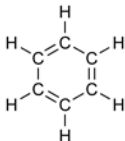
Kekulé structures



- Hexagonal grid representing the carbon structure of benzenoid.
- Double bonds are represented by “double lines” in the grid.

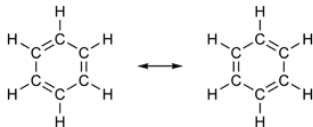
Benzene

A closer look at Benzene



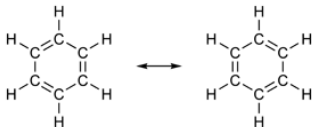
Benzene

A closer look at Benzene



Benzene

A closer look at Benzene

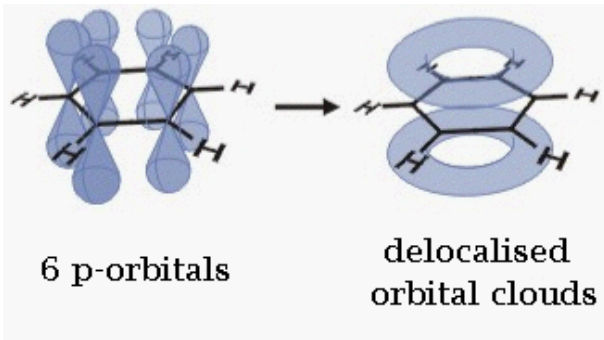


- The double bonds should be shorter than the single bond.
- This representation would imply different chemical properties than observed in nature.

Double bonds

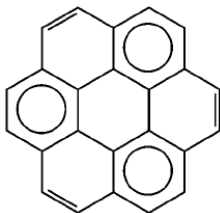
Electrons are shared between all 6 carbons

- π -electrons are shared between all 6 carbon atoms



Representation of benzenoids 2

Clar structures

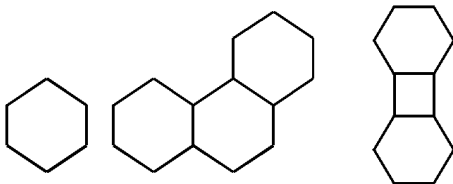


- Hexagonal grid representing the carbon structure of benzenoid.
- Hexagons with shared π -electrons are denoted by inscribed circles.
- Double bonds are represented by “double lines” in the grid.
- We wish to have as many hexagons with shared π -electrons as possible.

Graphs in chemistry

From molecules to graphs

- Graphs which could form a carbon grid of hydrocarbon molecules.



- Hexagonal graphs: start with n hexagons and identify pairs of edges so that no vertex is incident with more than 3 edges.

Kekulé- and Clar-structures

Let G be a graph

- Kekulé structure of G is a collection \mathcal{K} of edges in G such that:
 - every vertex of G is incident with at least one edge in \mathcal{K}
 - no two edges in \mathcal{K} are incident.
- Clar structure of G is a collection \mathcal{C} of edges and hexagons in G such that:
 - every vertex of G is incident with at least one element in \mathcal{C} ,
 - no two elements of \mathcal{C} are incident.
- Clar formula of G is a Clar structure with maximal number of hexagons.

Graph polynomials

Characteristic polynomial

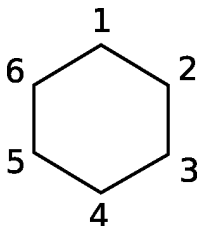
- Label the vertices of graph G with $1, 2, \dots, n$
- Create a $n \times n$ matrix A with

$$A_{i,j} = \begin{cases} 1 & ; \quad i, j \text{ adjacent} \\ 0 & ; \quad \text{otherwise} \end{cases}$$

- The characteristic polynomial of A is called the characteristic polynomial of graph G



$$\lambda^6 - 6\lambda^4 + 9\lambda^2 - 4$$

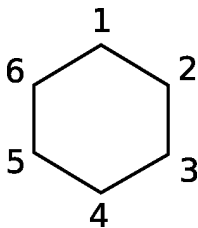


$$\begin{bmatrix} 0 & 1 & 0 & 0 & 0 & 1 \\ 1 & 0 & 1 & 0 & 0 & 0 \\ 0 & 1 & 0 & 1 & 0 & 0 \\ 0 & 0 & 1 & 0 & 1 & 0 \\ 0 & 0 & 0 & 1 & 0 & 1 \\ 1 & 0 & 0 & 0 & 1 & 0 \end{bmatrix}$$

Matchings

What is a matching

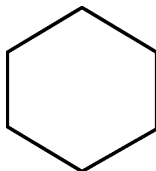
- A set M of edges of a graph G is a matching in G if the edges in M are pairwise independent.
- If $|M| = k$ then M is a k -matching.
- $\{12, 34, 56\}$ and $\{23, 45, 61\}$ are 3-matchings in the 6-cycle.



Matchings

Counting k -matchings

- $m(G, k)$ the number of k -matchings in G .
- An edge in G is a 1-matching in G :
 - $m(G, 1)$ is the number of edges in G .
- If $|V(G)| = 2k$ and M a k -matching, then every vertex of G is incident with an edge in M :
 - M is a perfect matching,
 - counting perfect matchings is a #P-complete problem.
- $m(C_6, 0) = 1, m(C_6, 1) = 6, m(C_6, 2) = 9, m(C_6, 3) = 2$.



Matching polynomial

Definition of matching polynomial

- We define the matching polynomial of G as

$$mp(G, x) = \sum_{k=0}^{\lfloor \frac{n}{2} \rfloor} (-1)^k m(G, k) x^{n-2k}.$$

- We already know the matching polynomial of C_6 :

$$mp(C_6, x) = x^6 - 6x^4 + 9x^2 - 2$$

- **[Godsil, Gutman]:** The zeros of a matching polynomial are real.

Matching polynomial

Computing the matching polynomial

- Another formula:

$$mp(G, x) = \sum_{M \text{ matching}} (-1)^{|M|} x^{|G|-2|M|}$$

- Let $e = uv$ be an edge in G . Then

$$mp(G, x) = mp(G - e, x) - mp(G - \{u, v\}, x).$$

- Let G and H be two graphs:

$$mp(G \cup H, x) = mp(G, x)mp(H, x).$$

Matching polynomial

How to compute the matching polynomial

- Use recursion formula until all vertices have degree less than 3.
- Each component is a cycle or a path - computing matching polynomials is easy.
- Multiply matching polynomials of components.

Clar-cover polynomial

Zhang-Zhang Clar-cover polynomial

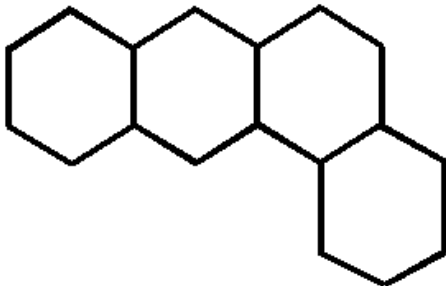
- $z(G, k)$ the number of Clar covers of G with precisely k hexagons.
- Clar-cover polynomial:

$$\zeta(G, x) = \sum_{k \geq 0} z(G, k) x^k$$

- $\zeta(G, 0) = KeSC$
- $\zeta(G, 1) = CISC$

Clar-cover polynomial

Clar-cover polynomial of benzoanthracene

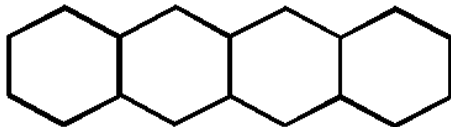


$$\zeta(G, x) = 7 + 8x + 2x^2$$

Clar-cover polynomial

Another example

- Let L_n be a linear hexagonal chain



- $\zeta(L_n, x) = nx + n + 1.$

Clar-cover polynomial

Computing clar-cover polynomial

- $\zeta(G \cup H, x) = \zeta(G, x)\zeta(H, x)$
- Let S_1 and S_2 be two hexagons having a common edge $e = xy$. Then

$$\zeta(G, w) = w \sum_{i=1}^2 \zeta(G - s_i, w) + \zeta(G - e, w) + \zeta(H - x - y, w).$$

- Let $e = xy$ be an edge in precisely one hexagon s of G . Then

$$\zeta(G, w) = w\zeta(G - s, w) + \zeta(G - x - y) + \zeta(G - e).$$

- If $e = xy$ is in no hexagon of G then

$$\zeta(G, w) = \zeta(G - x - y, w) + \zeta(G - e, w)$$

Kekulé- and Clar-structure base parameters

Counting the number of structures

- Theoretical chemistry tries to deduce physical properties and chemical behavior of hydrocarbon benzenoids using properties of hexagonal graphs.
- We investigate properties of hexagonal graphs which depend on Kekulé and Clar structures of graphs:
 - *KeSC*: the number of Kekulé structures
 - *CISC*: the number of Clar structures

- E_π holds the information about thermodynamic stability of conjugated molecules.
- $E_\pi > 0$.
- In the class of molecules with the same number of atoms and bonds: higher E_π implies higher thermodynamic stability.
- Hückel molecule orbits model:

$$E = 2E_+$$

$$E = \sum_{i=1}^n |\lambda_i|$$

- In interesting cases we get

$$E_{\pi} \approx a\sqrt{2nm}$$

- Resonance energy: compare the total π -electron energy of a conjugated molecule with the energy of a reference system

$$RE = E_{\pi} - E$$

- By choosing different reference we get different resonance energies.

- Choose a set of possible bond types $E_{i,j}$ and for each type select a parameter $n_{i,j}$. Then

$$DRE = E_{\pi} - \sum n_{i,j} E_{i,j}$$

- Hess-Schaad model defines 8 types of bonds

For a graph G let

- $x_1^c \leq x_2^c \leq \dots \leq x_n^c$ be the zeros of characteristic polynomial,
- $x_1^m \leq x_2^m \leq \dots \leq x_n^m$ be the zeros of matching polynomial.

Topological resonance energy of G is defined as

$$TRE(G) = \sum_{i=1}^n (|x_i^c| - |x_i^m|).$$

- Classes of graphs
 - isomers: equal number of carbon atoms and carbon-carbon bonds
 - catacondensed benzenoids, pericondensed benzenoids
 - [h]-phenylenes

Comparing parameters

Known results

- Within classes of isomeric benzenoid molecules, E_π and $KeSC$ are linearly correlated.
- Within classes of benzenoid molecules DRE and $\log KeSC$ are linearly correlated.
- Within classes of benzenoid molecules TRE and $\log CISC$ are linearly correlated.

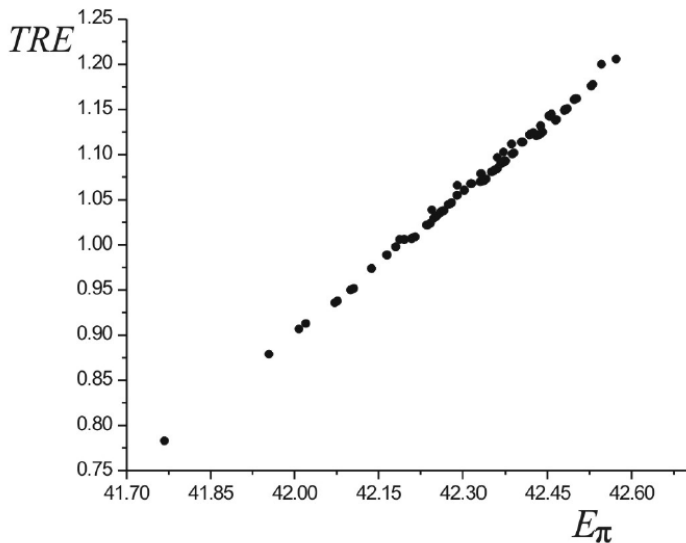
Comparing TRE to E_{π}

benzenoids

- Computation for 4 classes of pericondensed isomers and 4 classes of catacondensed isomers.
- Catacondensed benzenoids
- Pericondensed benzenoids

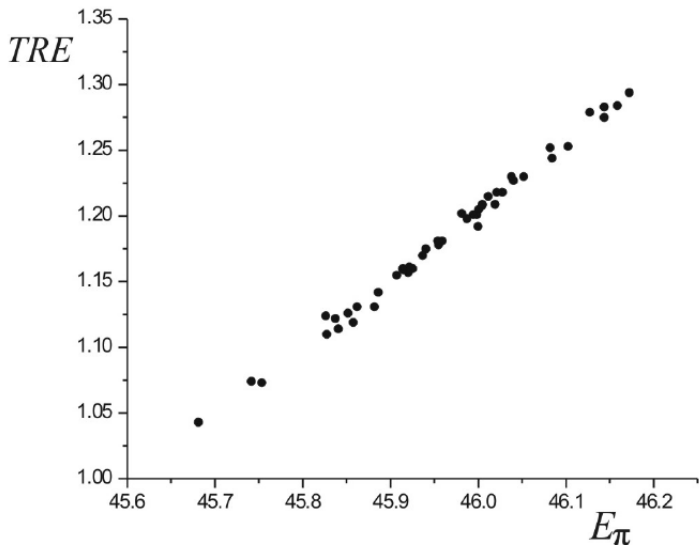
Comparing TRE to E_{π}

Catacondensed benzenoids $C_{30}H_{18}$



Comparing TRE to E_{π}

Pericondensed benzenoids $C_{32}H_{16}$



Comparing TRE to E_{π}

Results for catacondensed and pericondensed benzenoids

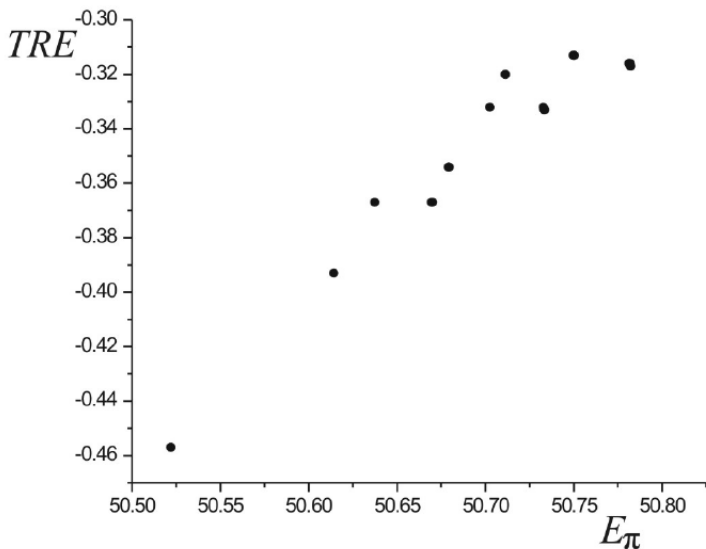
- Linear dependence

$$TRE \approx aE_{\pi} + b$$

$$(a \approx 0.52)$$

Comparing TRE to E_{π}

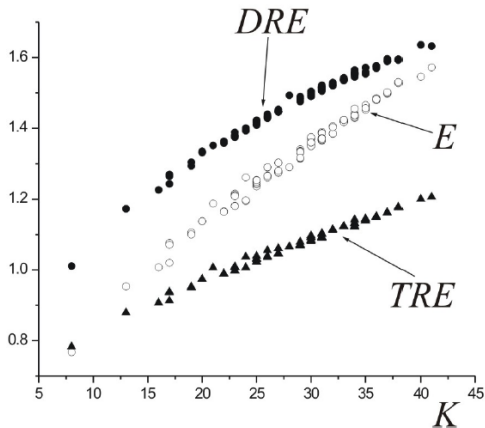
[h]-phenylenes



Comparing Energies with *KeSC*

Catacondensed benzoids $C_{30}H_{18}$

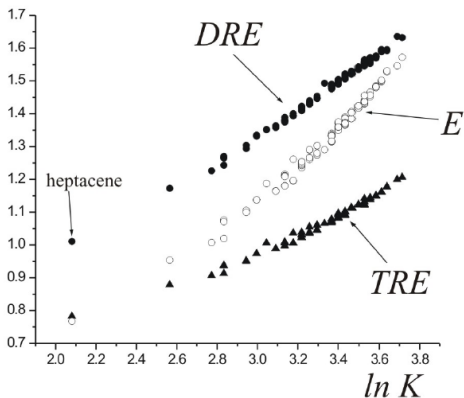
Correlation with *KeSC* (E_{π} is shifted downwards).



Comparing Energies with $\log KeSC$

Catacondensed benzoids $C_{30}H_{18}$

Correlation with $KeSC$ (E_{π} is shifted downwards).



Comparing Energies with Clar-cover polynomial

- Instead of *KeSC* ($= \zeta(G, 0)$) we compare Energies to $\zeta(G, x)$ for x close to 0.

$$E \approx a\zeta(G, x) + b$$

$$TRE \approx a'\zeta(G, x) + b'$$

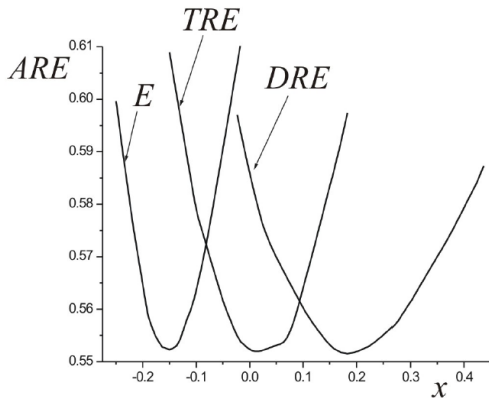
$$DRE \approx a'' \log(G, x) + b''$$

- We are looking for x which gives the best approximation.

Comparing Energies with Clar-cover polynomial

Catacondensed benzenoids $C_{30}H_{18}$

ARE = average relative error (multiplied by 25 and 1.3 for E and DRE).



Comparing TRE with Clar-cover polynomial

Within the class of isomeric benzenoid molecules

- $TRE \approx a\zeta(G, 0) + b$
- $TRE \approx a' \log \zeta(G, 1) + b'$
- $TRE \approx a'' \sqrt{\zeta(G, \frac{1}{2})} + b''$

THANK YOU!