CHEMICAL GRAPH THEORY
-a pictorial introduction
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Chemical Graph Theory is an important branch of Theoretical Chemistry.

Its basic element is the so-called molecular graph $G$. Vertices $V(G)$ of this graph denote molecular atoms and edges $E(G)$ are the bonds of the molecule.

Normally, $G$ corresponds the carbon atom skeleton of the molecule. This is the hydrogen-depleted representation of the molecular graphs. Atomic valence is the vertex degree $r$. 
Example Let’s consider a connected graph $G$ like this one with $n$ nodes and $m$ edges:

$n = 10; \ m = 11$

Chemically, $G$ represents Naphtalene molecule with $n$ carbon atoms and $m$ bonds.

Vertex degree $r = 2$ or $3$ corresponds to atomic valence. For carbon, silicon compounds $r \leq 4$. 
Graph Theory properties are transferred to molecular structures like the following: The First Theorem of Graph Theory:

Any graph contains an even number of vertices of odd degree $r$

which becomes: *Every molecule contains an even number of atoms of odd valence*

→ Then $C_{61}$ fullerene and others with odd carbon atoms are forbidden also by topology.
In Chemical Graph Theory *graph invariants* or *topological indices* are used to correlate the properties of molecules to their chemical structure.

A topological index is defined by a map from a graph \( G \) into a number or a finite string of numbers:

\[
\rho : G(V,E) \rightarrow \{x_i | i = 1, ..., n \}
\]

Topological indices should be graph invariant, i.e. isomorphic graphs lead to the same topological index.
**Isomorphic graphs**

**Definition.** Two graphs $G$ and $H$ are isomorphic, denoted by $G \cong H$, if there exists a bijection $\alpha : V_G \rightarrow V_H$ such that

$$uv \in E_G \iff \alpha(u)\alpha(v) \in E_H$$

for all $u, v \in G$.

Hence $G$ and $H$ are isomorphic if the vertices of $H$ are renaminings of those of $G$. Two isomorphic graphs enjoy the same graph theoretical properties, and they are often identified.
Isomorphic graphs

EXERCISE are these graphs isomorphic?

See: Lecture Notes on GRAPH THEORY
Tero Harju (2007), Department of Mathematics
University of Turku, FIN-20014 Turku, Finland
e-mail: harju@utu.fi
Let $V_G = \{v_1, \ldots, v_n\}$ be ordered. The adjacency matrix of $G$ is the $n \times n$-matrix $M$ with entries $M_{ij} = 1$ or $M_{ij} = 0$ according to whether $v_iv_j \in E_G$ or not. For instance, the graphs of Example 1.1 has an adjacency matrix on the right. Notice that the adjacency matrix is always symmetric (with respect to its diagonal consisting of zeros).

\[
\begin{pmatrix}
0 & 1 & 1 & 0 & 1 \\
1 & 0 & 0 & 1 & 1 \\
1 & 0 & 0 & 1 & 0 \\
0 & 1 & 1 & 0 & 0 \\
1 & 1 & 0 & 0 & 0
\end{pmatrix}
\]

A graph has usually many different adjacency matrices, one for each ordering of its set $V_G$ of vertices. The following result is obvious from the definitions.

**Theorem 1.1.** Two graphs $G$ and $H$ are isomorphic if and only if they have a common adjacency matrix. Moreover, two isomorphic graphs have exactly the same set of adjacency matrices.
An important topological graph invariant the Graph Energy

Let $A(G)$ be the adjacency matrix of $G$, and let $\lambda_1, \lambda_2, \ldots, \lambda_n$ be its eigenvalues.

Let $G$ be a graph on $n$ vertices, and let $\lambda_1, \lambda_2, \ldots, \lambda_n$ be its eigenvalues. The energy of $G$ is defined

$$E = E(G) = \sum_{i=1}^{n} |\lambda_i|.$$ 

These eigenvalues form the (ordinary) spectrum of the graph $G$

See: Ivan Gutman, Bo Zhou and Boris Furtula
The Laplacian–energy Like Invariant is an Energy Like Invariant
ISSN 0340 - 6253 AND RELATED REFERENCES
Properties of the Graph Energy

McClelland inequality  \( E \leq \sqrt{2mn} \)

empirically determined fitting

\[ E \approx a_1 \sqrt{2mn} \quad E \approx a_2 \sqrt{2mn} + b_2 \]

For the usually employed standard set of 106 benzenoid hydrocarbons, one gets \( a_1 = 0.908 \pm 0.002 \), \( a_2 = 0.898 \pm 0.002 \), \( b_2 = 0.44 \pm 0.07 \), correlation coefficient \( R = 0.99982 \), and average relative error equal to 0.30%
Properties of the Graph Energy for regular graphs, i.e. with vertices with the same number of bonds (degree) \( r \)

\[ G \text{ possesses } m = \frac{1}{2} nr \text{ edges} \quad E(G) \leq n \sqrt{r} \quad \text{regular graph} \]

**Theorem 6.** The energy \( E \) of the molecular graph of a fullerene or a nanotube with \( n \) carbon atoms is bounded as:

\[
\frac{3}{\sqrt{5}} n < E < \sqrt{3} n .
\]

or, what is the same, \( 1.34 n \leq E \leq 1.73 n \).

→ Then the total \( \pi \)-electron energy of fullerenes and nanotubes is determined solely by their carbon atom content and depends very little on other structural features.
Given two vertices $u$ and $v$ in $V(G)$, we denote by $d(u,v)$ or $d_{u,v}$ the distance between $u$ and $v$, i.e. the length of the shortest path connecting $u$ and $v$ by traveling along the graph edges (or molecular bonds).

This distance belongs to the invariants of the graphs conveying crucial information about the structure.

**TECHNICALLY AND COMPUTATIONALLY THIS IS ONE OF SPECIALTIES OF Prof.PUTZ’s LAB**
After an arbitrarily numbering of the nodes we calculate the length $d_{ij}$ of the shortest path connecting pair wise the $n$ atoms.

$n=10; \ m=11$

Some cases: $d_{11}=0 \quad d_{12}=d_{21}=1$

$d_{16}=d_{19}=2 \quad .. \ Etc..$

$d_{max}=d_{14}=5$
... composing - with all $d_{ij}$ entries - the Matrix $D$ of the chemical distances of $G$:
**Topological Wizard Provides**

1) Some info about Symmetry

- \( D \) contains interesting structural information. Let’s zoom in it first by sorting its rows:

\[
\begin{array}{cccccc}
1 & 5 & 9 & 7 & 3 \\
2 & 6 & 10 & 8 & 4
\end{array}
\]

<table>
<thead>
<tr>
<th></th>
<th>( D )</th>
<th></th>
<th>( w_i )</th>
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<tbody>
<tr>
<td>1</td>
<td>0 1 1 2 2 3 3 4 4 5</td>
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<td>13</td>
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<td>2</td>
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<td>6</td>
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<tr>
<td>7</td>
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<td>11</td>
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<td>8</td>
<td>0 1 1 2 2 2 3 4 4 4</td>
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<td>11</td>
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<tr>
<td>9</td>
<td>0 1 1 1 2 2 2 3 3 3</td>
<td>8,5</td>
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<tr>
<td>10</td>
<td>0 1 1 1 2 2 2 2 3 3</td>
<td>8,5</td>
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TOPOLOGICAL WIZARD PROVIDES
1) SOME INFO ABOUT SYMMETRY

... the action of D in possibly grouping structurally-equivalent atoms emerges:
Row half-sum $w_i$ invariant provides atom-$i$ contribution to Wiener index $W$ of $G$:

$$W = \frac{1}{2} \sum_{ij} d_{ij}$$

$$W = \sum w_i$$

$w_1 = 13$, $w_5 = 11$

$w_9 = 8.5$

We call $w_i$ the Wiener weight of atom-$i$; let’s zoom again in $D$ by sorting by $w_i$ ....
TOPOLOGICAL WIZARD PROVIDES 2) SOME INFO ABOUT STABILITY

... the action of \( w_i \) in suggesting possible most-stable atoms emerges:

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<td>5</td>
<td>13</td>
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Exercise (HOMEWORK): for any (or all) of the below PAH structures:
- Write the ADJACENCY MATRIX
- Write the DISTANCE (BONDING) MATRIX
- Calculate the Wiener index

*by making use of molecular symmetry*
Much attention is devoted on FULLERENES.

Luckily they admit a representation with planar molecular graphs the Schlegel diagram.
Planar connected graphs fulfil Euler’s theorem

\[ n_v + n_f - n_e = 2 \]

\[ n_v = 20; \quad n_e = 20 \times 3/2 = 30 \]

\[ n_f = 12 \] where is the 12th face? 20 + 12 - 30 = 2

\[ W = 500 = 20 \times w_1 \]
Wiener index computation of $C_{20}$ fullerene

$$W = 500 = 20 \times w_1$$
$$w_1 = 25$$

<table>
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<tr>
<th>Shell s</th>
<th>Atoms k</th>
<th>s*k</th>
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<tbody>
<tr>
<td>1</td>
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</tr>
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<td>2</td>
<td>6</td>
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<td>3</td>
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<td>12</td>
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<tr>
<td>5</td>
<td>1</td>
<td>50</td>
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</table>

$w_i = 25$

$W = n \times w_i = 500$
Ri-prediction of the magic LEM: C\textsubscript{28}H\textsubscript{4}

**Table 8.** Topologically deduced reactivity scale for atoms of C\textsubscript{28}(T\textsubscript{d}); highly reactive sites (c) allow this structure to act as a tetravalent carbon cage

<table>
<thead>
<tr>
<th>Set</th>
<th>{b\textsubscript{im}}</th>
<th>\ell</th>
<th>WW</th>
<th>Reactivity</th>
</tr>
</thead>
<tbody>
<tr>
<td>(a)</td>
<td>3 6 7 6 5</td>
<td>12</td>
<td>85</td>
<td>Min</td>
</tr>
<tr>
<td>(b)</td>
<td>3 6 7 7 3 1</td>
<td>12</td>
<td>85</td>
<td>↓</td>
</tr>
<tr>
<td>(c)</td>
<td>3 6 6 6 6</td>
<td>4</td>
<td>87</td>
<td>Max</td>
</tr>
</tbody>
</table>
Some Simple Results

- Topological prediction of saturn like-fullerene $\text{C}_{50}\text{H}_{10}$ from $\text{C}_{50}D_{5h}$ 10 equatorial reactive nodes (maximal $w_i$):

- NOT BAD AT ALL FOR A PURE TOPOLOGICAL WIENER BASED CALCULATIONS OF A MILLISECOND!

- Ri-prediction of the SATURN: $\text{C}_{50}\text{H}_{10}$
Let’s focus on the minimal vertices in green giving the minimal contribution \( w \) to wiener index \( W \)

\[ w = 8.5 \]

Minimal vertices are distinguished atoms in a graph, they are in fact the most compactly embedded in the structure.

Now a question naturally arises: how to “measure” the ability of the remaining atoms in contributing to the overall compactness of graph \( G \)?
A possible solution consists in computing the following invariant $\rho$:

$$\rho = \frac{W}{N_w}$$

$\rho \geq 1$  
$\rho = 1.282$

TOPOLOGICAL EFFICIENCY INDEX

- It is very interesting noticing that for the buckminsterfullerene $C_{60} I_h$ we have:

$$\rho = 1$$

- $C_{60}$ is in fact a very round hollow cage showing, for any of the $N=60$ nodes, the same $\{b_{im}\} = \{3 6 8 10 10 10 8 3 1\}$ coordination shells with $M=9$; $w_i=139=w$ and therefore $W=N*w=8340$. In this stable structure any node works as *minimal node.*
Assuming $\rho$ as a measure of sphericity it gives interesting (and sometime unexpected) results:
- Benzene is spherical $\rho = 1$;
- Closed square lattice (torus) is spherical
- Closed graphene lattice is spherical
- Sodalite closed zeolitic lattice is spherical $\rho = 1$ too and so on....
Spheriality of a Graph

- Assuming \( \rho \) to determine sphericity produces interesting (and sometime unexpected) results:
  - \( C_{60} \) is spherical \( \rho = 1 \) as we said;
  - \( C_{20} \) polyhedron is also spherical \( \rho = 1 \)
  - Other fullerenes \( C_n \) have \( \rho > 1 \) so less spherical than \( C_{20} \) but surely more stable

→ Warning: better we try correlating \( \rho \) and relative stability only among isomers of the same \( C_n \) fullerene.
ρ is then the topological sphericity of a chemical graph

The lower is ρ the more spherical and stable the structure will be.

So we adopted for invariant ρ the new alias topological sphericity index.
The minimum principle works BETTER on **topological efficiency index** $\rho \geq 1$ as it has been successfully tested on $C_{66}$ fullerene 4478 isomers, see **Topological efficiency of $C_{66}$ fullerene**, D. Vukicevic, F. Cataldo, O. Ori, A. Graovac, Chemical Physics Letters 501 (2011) 442-445.
Topological Anisotropy of Stone-Wales Waves in Graphenic Fragments
Ottorino Ori, Franco Cataldo and Mihai V. Putz
 Indices \( W \) and \( \rho \) tool quickly sieve interesting candidates for stable chemical structures (molecules, 1-2-3D lattices, fractals...)

- Index \( \rho \) has been put in FULLERENE generator program by Prof. Peter Schwerdtfeger


- free DOWNLAOD PLS USE IT
MANY THANKS FOR YOUR ATTENTION

Questions?

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