

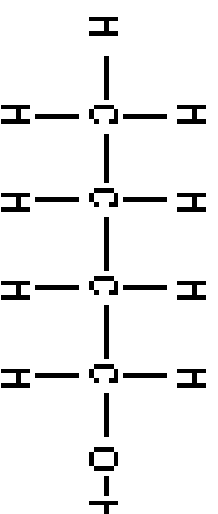
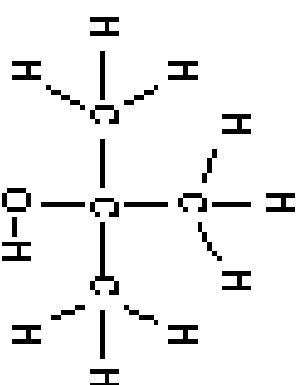
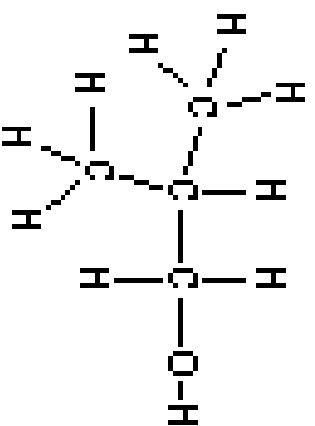
Some Applications of Graph Polynomials in Chemistry

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Graphs in Chemistry

Graphs naturally model molecules:



Graphs in Chemistry - cont.

This modeling provides:

- rules that predict chemical properties
- easy classification of compounds
- computer simulations and computer-assisted design of new compounds

Graphs in Chemistry - cont.

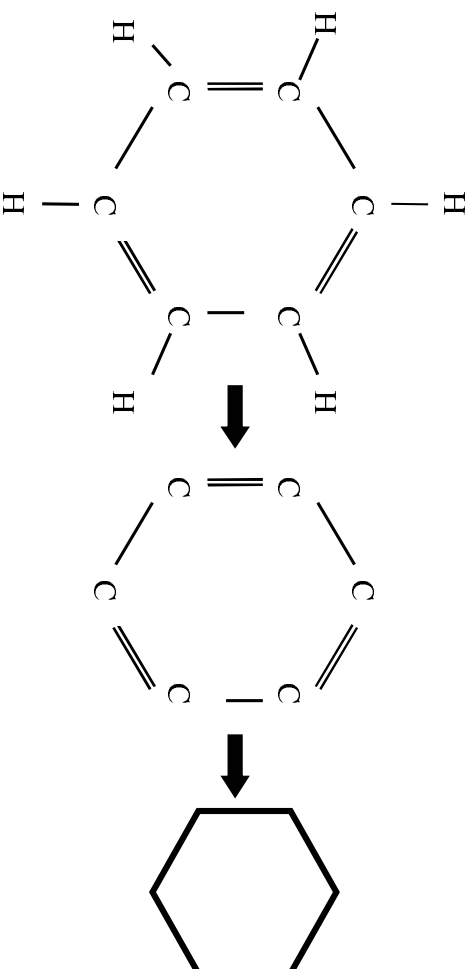
- Chemists manipulate graphs on a daily basis
- Many notions and theorems from graph theory are used in chemistry with a different name

Graph Theory – Chemistry Dictionary

Graph Theory	Chemistry
Graph	Structural formula
Vertex	Atom
Edge	Chemical bond
Degree of vertex	Valency of atom
Tree	Acyclic structure
Bipartite graph	Alternant structure
Perfect matching	Kekule structure
Adjacency matrix	Huckel matrix
Characteristic polynomial	Secular polynomial

Hydrocarbons

- Consist of hydrogen (H) and carbon (C)
- Very suitable for modeling as a graph



Hydrocarbons – cont.

- Trivially, every hydrocarbon has a graph representation.
- But when does a graph represent a real hydrocarbon?
- What properties of the compound can be inferred from its graph?

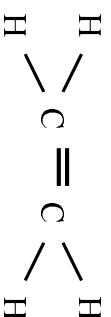
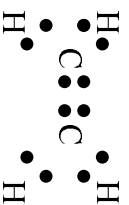
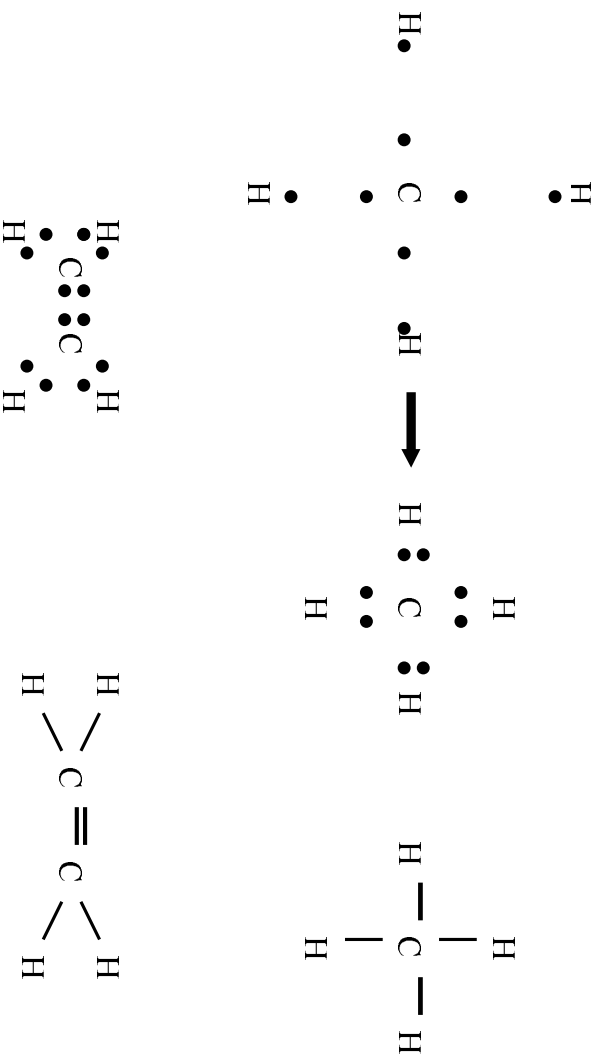
Basics of Chemical Bonding

- Each chemical element is composed of a nucleus and electrons.
- Carbon has 6 electrons and hydrogen has only 1 electron.
- *Valence electrons* of an element are its electrons that participate in chemical bonds.
- For now, we can assume that these are electrons in the outer shell (the farthest from the nucleus).

Basics of Chemical Bonding – cont.

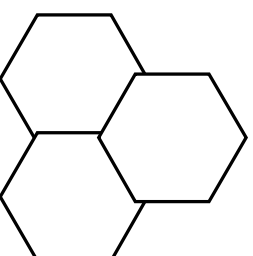
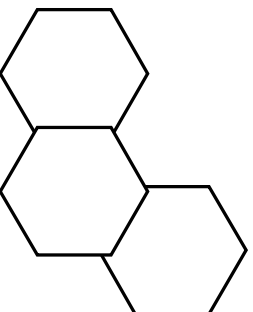
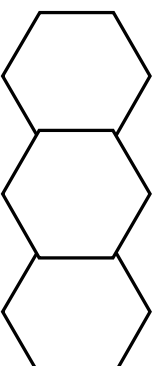
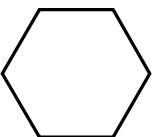
- Carbon has 4 valence electrons, hydrogen has 1.
- Atoms are most stable when their outer shell of electrons is “complete”. For carbon “complete” means 8 electrons and for hydrogen 2 electrons.
- Elements share electrons in order to complete their outer shell of electrons, thus forming *covalent* chemical bonds.

Bonding Examples



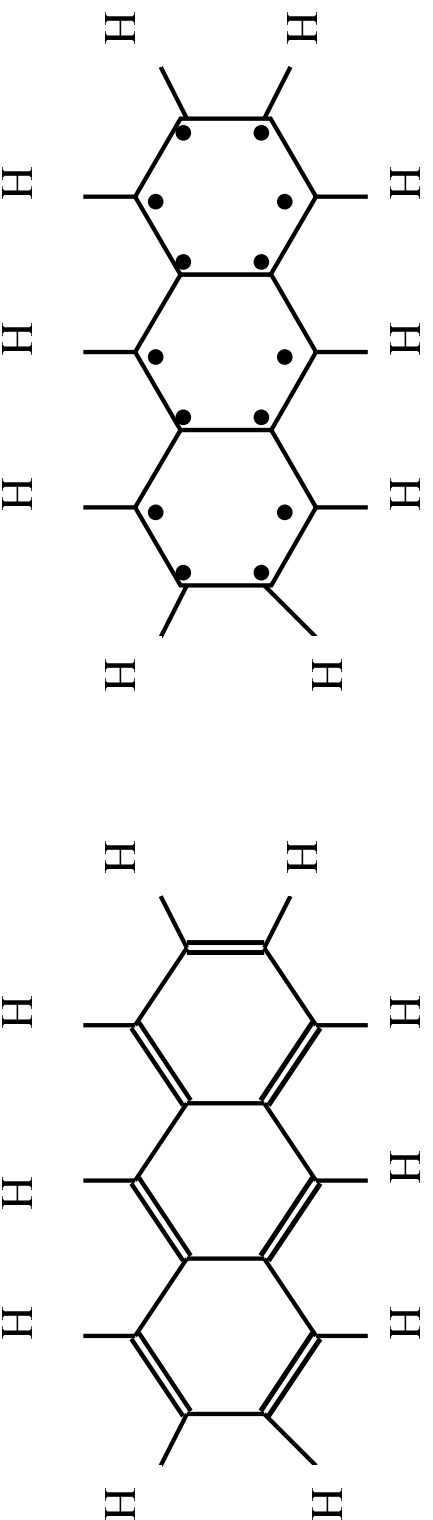
Benzenoids

The graphs of benzenoids consist of hexagons arranged in the plane, such that any two hexagons are either point-disjoint or possess exactly one common line.



Benzenoids – cont.

From the graph of a benzenoid we see the bonds of 3 valence electrons of each carbon. To get a stable compound the 4th electron needs to participate in a double bond ($C=C$). Therefore the compound is stable (has a valid *Kekule structure*) iff a perfect matching exists in the graph.



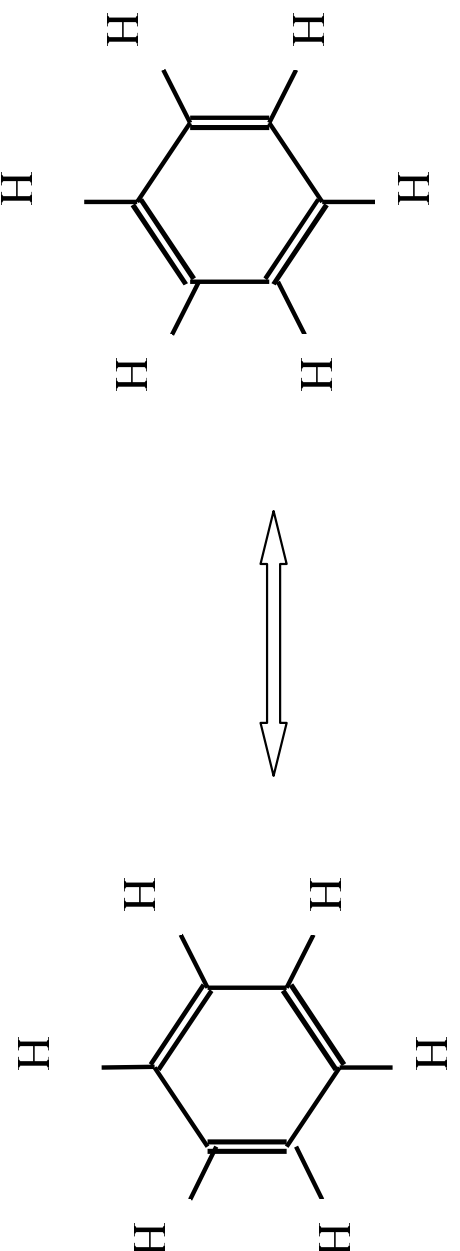
The Need for a New Theory

The classical theory that pictures compounds as atoms with single or multiple bonds between them doesn't explain several experimental observations. Take benzene, for example.

- All the bonds of benzene are of equal length. The length is *between* the length of a single bond and the length of a double bond. This contradicts the representation of benzene as having alternating single and double bonds.
- Benzene is more stable than we might expect from a compound with alternating single and double bonds.

The Need for a New Theory – cont.

Kekule (19th century) proposed that benzene is constantly shifting between 2 possible structures:



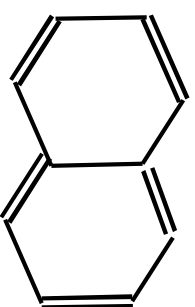
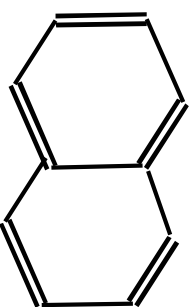
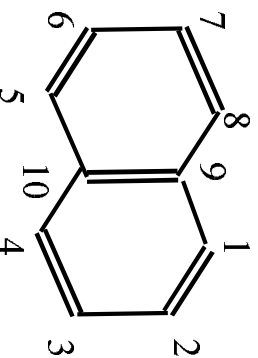
This still doesn't explain, however, the stability of benzene...

The Need for a New Theory – cont.

To explain the bond length of molecules Pauling proposed the following theory. If several Kekule structures are possible for a molecule, the molecule is actually a *hybrid* of these structures. The *relative double bond character* of two atoms is defined as the number of Kekule structures with a double bond between the atoms divided by the total number of Kekule structures.

The Need for a New Theory – cont.

For example, in naphthalene 3 Kekule structures are possible:



We predict that the bonds 1-2, 3-4, 5-6, 7-8 are shorter than the bonds 2-3, 6-7, 9-10, 1-9, 8-9, 5-10, 10-4, since the first group has relative double bond character of $2/3$ and the second group has relative double bond character of $1/3$. This specific prediction is correct, but the theory is still very inaccurate...

Quantum Mechanics

- In reality electrons don't stand still in octets around the nucleus.
- According to quantum mechanics a *wave function* ψ is used to calculate the *probability* of finding the electron in a particular point in space. The probability density is given by $|\psi|^2$.
- The wave function ψ contains a lot of information about the system it describes.

The Schrödinger Equation

- The wave function for a particular system (e.g. atom or molecule) is obtained by solving the Schrödinger equation:

$$\hat{H}\psi = E\psi,$$

where \hat{H} is the Hamiltonian operator (we don't need the exact definition of \hat{H} for now).

- The Schrödinger equation is a partial differential equation.
- The wave function ψ is an eigenfunction of \hat{H} with the eigenvalue E (which specifies the energy).

Quantum Chemistry

- In order to understand the nature of bonds and the properties of molecules chemists need to solve the Schrödinger equation for various systems and obtain the wave function ψ for the system.
- The wave functions for atoms are called *atomic orbitals* and the wave functions for molecules are called *molecular orbitals*.
- Each orbital can accommodate 2 electrons of the opposite *spin* (let's just say that the spin is some property of the electron).

Quantum Chemistry – cont.

- The Schrödinger equation is solvable only for very simple systems, like the hydrogen atom (that has only one electron).
- Therefore many theories use different techniques to try and approximate the wave function ψ .
- *Semiempirical* methods use a simpler Hamiltonian than the correct one and also use parameters whose values are adjusted to fit experimental data.

Hückel Theory

- This is a semiempirical method for calculating molecular orbitals for conjugated molecules (molecules with alternating single and double carbon-carbon bonds, like benzene).
- It turns out that Hückel theory and graph-spectral theory (for planar connected undirected graphs with maximum degree 3) are isomorphic theories.

Hückel Theory – cont.

- The Hückel molecular orbitals are approximated as a linear combination of atomic orbitals.
- The Hückel molecular orbitals (viewed as vectors) are in fact the eigenvectors of the adjacency matrix.
- The eigenvalues of the adjacency matrix (the roots of the characteristic polynomial) are the energies corresponding to the Hückel molecular orbitals.

Hückel Theory – cont.

- Let N_- be the number of negative roots of the characteristic polynomial, N_0 be the number of zero roots and N_+ be the number of positive roots.
- N_- , N_0 and N_+ contain important information about the molecule. For example, stable molecules always have $N_+ = N_-$ and $N_0 = 0$.
- The molecular orbitals with energy 0 are called *non-bonding molecular orbitals* (NBMOs).

Hückel Theory – cont.

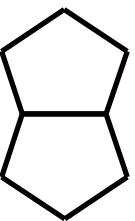
N_- , N_0 and N_+ can be calculated by just looking at the characteristic polynomial. Denote the characteristic polynomial by $P(G, x) = a_0x^N + a_1x^{N-1} + \dots + a_N$. It holds that:

$$\begin{aligned} a_N &= a_{N-1} = \dots = a_{N-N_0+1} = 0 \\ a_{N-N_0} &\neq 0 \\ Ch(a_0, a_1, \dots, a_{N-1}, a_N) &= N_+, \end{aligned}$$

where Ch denotes the number of sign changes in the sequence it operates on.

Hückel Theory – cont.

Example: pentalene (C_8H_6):



The characteristic polynomial is $P(G, x) = x^8 - 9x^6 + 24x^4 - 4x^3 - 16x^2 + 8x$. We see that $a_8 = 0$, but $a_7 \neq 0$. Therefore $N - N_0 + 1 = 8$ yielding $N_0 = 1$. We can also calculate $N_+ = Ch(1, -9, 24, -4, -16, 8) = 4$ and $N_- = 8 - N_+ - N_0 = 3$.

Since $N_+ > N_-$ and $N_0 > 0$ we predict that the compound is unstable, which is correct.

Computation of the Characteristic Polynomial of Some Simple Hydrocarbons

- Chains (e.g. linear polyenes and n -alkanes):

$$P(L_n, x) = xP(L_{n-1}, x) - P(L_{n-2}, x)$$

- Trees (e.g. branched alkanes): the strategy is to break the tree into constituting chains and to use the formula

$$P(T, x) = P(T - e, x) - P(T - u - v, x)$$

- Cycles (e.g. cycloalkanes):

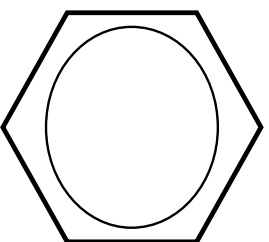
$$P(C_n, x) = P(L_n, x) - P(L_{n-2}, x) - 2$$

Bipartite Graphs: Alternant Hydrocarbons (AHs)

- AHs can be even or odd, depending on the number of vertices.
- The *pairing theorem* states that for bipartite graphs if x_i is a root of the characteristic polynomial, then $-x_i$ is also a root.
- This means that for even AHs the number of NBMOs is even and for odd AHs the number of NBMOs is at least 1.
- The pairing theorem has some more chemical consequences which we will not cover here...

Another Application of Graph Polynomials in Chemistry: Aromaticity

- Aromaticity is a set of properties of some conjugated structures, the main property being the unusual stability of the compound.
- The classical example of an aromatic compound is benzene.



Aromaticity – cont.

Benzene is more stable than expected, this means that it has lower energy than expected. This difference in energy is called *resonance energy*:

$$RE = E_{\text{actual compound}} - E_{\text{reference structure}}$$

The choice of the reference structure is not rigorously defined...

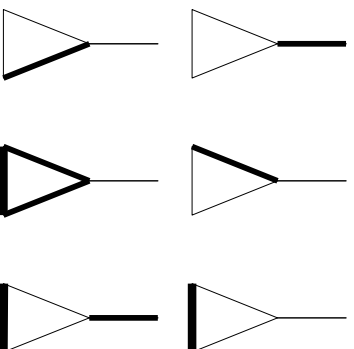
Topological Resonance Energy

- The goal is to define resonance energy in a way that will predict the aromaticity of compounds.
- The reason for aromaticity is the cyclic structure of the aromatic compounds.
- Therefore the goal is to calculate the energy of a reference structure that is similar to our molecule but is *acyclic*.
- How can we find such a reference structure?

Topological Resonance Energy – cont.

- The topology of our molecule is described by its characteristic polynomial. Denote the characteristic polynomial by $P(G, x) = a_0x^N + a_1x^{N-1} + \dots + a_N$.

- A *Sachs graph* of a graph G is a subgraph of G whose connected components are only K_2 or C_m ($m \geq 3$).



Topological Resonance Energy – cont.

The coefficients of the characteristic polynomial can be computed via *Sachs formula*:

$$a_n = \sum_{s \in S_n} (-1)^{p(s)} 2^{c(s)},$$

where S_n denotes the set of all Sachs graphs of G with n vertices, $p(s)$ denotes the number of connected components in s and $c(s)$ denotes the number of cycles in s . It is agreed that $a_0 = 1$ and if $S_n = \emptyset$, then $a_n = 0$.

Topological Resonance Energy – cont.

- To capture the topology of the molecule *without* the cycles it contains, the following adaptation of Sachs formula is considered:

$$a_n^{ac} = \sum_{s \in S_n^{ac}} (-1)^{p(s)},$$

where S_n^{ac} denotes the *acyclic* Sachs graphs of G with n vertices. This is actually the set of $n/2$ -matchings in G .

- We actually got the coefficients of the *acyclic polynomial* of G !

Topological Resonance Energy – cont.

- Denote the roots of the characteristic polynomial by x_i and the roots of the acyclic polynomial by x_i^{ac} .
- Our reference structure can be approximated as having the acyclic polynomial as its characteristic polynomial. We saw in Hückel theory that the roots of the characteristic polynomial correspond to the energies of the molecular orbitals. Therefore the energies of the orbitals of the reference structure can be approximated with the roots of the acyclic polynomial.

Topological Resonance Energy – cont.

- The energy of the system is defined as:

$$E = \sum_{i=1}^N g_i x_i,$$

where g_i is the number of electrons that occupy the i th orbital ($g_i \in \{0, 1, 2\}$).

- Therefore we can define the Topological Resonance Energy as:

$$TRE = E_{\text{actual compound}} - E_{\text{reference structure}} = \sum_{i=1}^N g_i (x_i - x_i^{ac}).$$

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