MATHEMATICAL MODELING OF CHEMICAL PHENOMENA

Ivan Gutman

Faculty of Science
University of Kragujevac
P.O. Box 60, 34000 Kragujevac, Serbia & Montenegro
E-mail: gutman@kg.ac.yu

Summary. *It is pointed out that the number of possible chemical compounds is so enormously large that there is no chance that even a tiny fraction thereof will ever be produced and investigated experimentally. The only way to learn about the properties of a reasonable large number of chemical species is to study them by mathematical models. Such a mathematical model, developed by the author, is presented in detail. This model is essentially nonlinear.*

Total π-electron energy E (as computed within the Hückel molecular orbital approximation) is a quantum chemical characteristic of unsaturated conjugated compounds whose dependence on molecular structure can be deduced and analyzed by means of algebraic graph theory. It is shown that E depends - in a perplexed, but mathematically well-defined manner - on a large number of molecular structural features. The mathematical representations of these structural features are the so-called Sachs graphs. Some of these Sachs graphs correspond to the cycles contained in the underlying molecule. This makes it possible to "extract" the energy-effect of each particular cycle from the total energy and thus to measure the cyclic conjugation in individual cycles of a polycyclic conjugated molecule.

Keywords: *Chemistry, mathematical modeling, conjugated molecules, energy effect of cycle.*

1 INTRODUCTION: A WEIRD VIEW ON CHEMISTRY

Chemistry is a two thousand years old science. Yet, the vast majority of results that chemistry has achieved was obtained in the second half of the 20th century and in the first years of this century. The enormous expansion of chemistry is best reflected in the claim that of all chemists who ever lived, the majority is still alive. Until now about 21

million different chemical compounds were either synthesized in laboratory or isolated from various natural products. Every day dozens of new chemical compounds are obtained and their properties investigated, a remarkable achievement indeed.

Yet, the coin has also another side. Already in the 19th century the basic laws of chemistry were discovered, including those that determine the structure of molecules. Knowing the rules by which atoms are joined to form molecules, chemists are able to predict the possible structures that molecules may possess. It turned out that the number of possible molecular structures (and thus the number of possible chemical compounds) is far beyond what the greatest optimists of the 19th century could imagine. After the theory of isomer enumeration was completed (in the 1930s, for details see the book [1]) we know, for instance, that there may exist 328092 distinct alcohols $C_{15}H_{31}OH$ and 110500 distinct acids $C_{14}H_{29}COOH$, from which 328092 x 110500 different esters could be produced. Cyclic and polycyclic compounds are much more numerous. According to a recently published theoretical enumeration, there are 7×10^{21} possible benzenoid hydrocarbons with up to 35 six-membered rings. Of these only about 1000 have been actually prepared. With biomolecules the situation is even worse: There are 4^{100000} possible DNA-chains consisting of (only!!!) 100,000 base-pairs. There are 20^{100} possible proteins consisting of (only!!!) 100 amino acids. The number of possible chemical compounds is far greater than the number of nucleons in the (known) universe. Therefore the 10^8-10^9 chemical species that will be (perhaps) produced until the end of our civilization is negligibly small compared to the number of possible – virtual – chemical compounds. The vast majority of chemical compounds will never be synthesized. We thus arrive at the conclusion that

Chemistry is the science of virtual objects – chemical compounds

of which only a negligibly small fraction will (ever) be produced in reality and studied experimentally.

The enormous disbalance between the number of existing and possible chemical species has a consequence that the true problem of chemistry is no more to synthesize a given compound, but to decide which compound to synthesize. In order to choose the potentially interesting compounds from combinatorial libraries consisting of millions or billions of imagined (but not yet existent) compounds, one must employ some very fast and computationally inexpensive method, that needs not be exact, but that is required to reproduce the main, chemically relevant, properties of a virtual chemical compound. Such methods must necessarily be based on suitably chosen mathematical models.

Chemistry is a science. Thus, one of its goals must be to discover regularities that are valid for large classes of chemical compounds, so called "laws". Because the objects of chemistry are virtual (with a few exceptions, that exist in reality), the only way in which chemical "laws" can be treated is mathematical reasoning. Today most colleagues will disagree, but in the years ahead of us it will become more and more evident that

the main tool of chemistry is mathematics

and that

mathematical chemistry is the main part of chemistry.

Until these days come, we have to aim at much more humble targets. In what follows we describe a mathematical model of cyclic conjugation in polycyclic conjugated molecules. This model makes it possible to calculate the energy-effects arising from cyclic conjugation in individual cycles. After some early attempts [2-5], the model was formulated in 1977 [6,7] and since then extensively studied, elaborated, and applied by the present author and his coworkers [8-46]. A chemist-friendly review has also recently been published [47].

2 SOME CONCEPTS FROM CHEMICAL GRAPH THEORY

It is one of the paradigms of chemistry that molecular structure determines the (physical, chemical, pharmacological, ...) properties of the corresponding substance, provided, of course, that this substance consists of molecules. Thus, from the known molecular structure, the properties of substances should be predictable. Although much success along these lines has been achieved and much knowledge accumulated, we are still very far from the complete solution of the problem. [In contemporary chemical literature two acronyms are often encountered: QSPR = *Quantitative Structure Property Relations* and QSAR = *Quantitative Structure Activity Relations*. Under "property" are meant the physical and chemical properties, whereas "activity" refers to pharmacological, biological, medicinal, toxicological, and similar properties.]

In what follows we consider a special problem in QSPR research, namely the finding of the (quantitative) connection between the structure of a polycyclic conjugated hydrocarbon and its total π-electron energy E. Although E cannot be directly measured, it is known to be reasonably well related to the experimentally accessible thermodynamic data [48-51].

The total π-electron energy considered here is computed by means of the tight-binding Hückel molecular orbital (HMO) approximation and is, as usual, expressed in the units of the carbon-carbon resonance integral β. Within the HMO model it is possible to employ the mathematical apparatus of graph spectral theory. Details on this matter can be found in the books [1,49,52-54].

For the present considerations the actual value of the parameter β is not important, except that its value is negative. We nevertheless mention that for thermochemical purposes the recommended value of β is -137.00 *kJ/mol* and that the heats of atomization computed by the HMO method are accurate to 0.1%, implying that E is accurate up to ± 0.005 β units [48]. Thus, the greater is E, the higher is the thermodynamic stability of the respective compound; structural factors increasing (resp. decreasing) the value of E increase (resp. decrease) the thermodynamic stability.

It is possible the find a direct relation between molecular structure and *E*, and by means of this relation to determine the effect of certain structural details on the numerical value of *E*. Among these structural details are also the cycles contained in the molecules and, consequently, one may speak of the energy effect of these cycles. Such an analysis is performed by means of the mathematical apparatus of graph theory, or more specifically: of graph spectral theory [55]. Therefore, in order to be able to present the results on the structure-dependence of *E*, we must specify a few basic notions of graph theory and graph spectral theory. More details can be found in the books [1,49,55].

A conjugated hydrocarbon is represented by its molecular graph. The construction of such a graph should be evident from the example shown in Fig. 1.
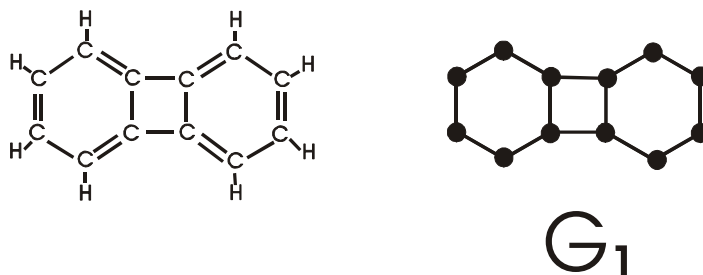

Figure 1. The structural formula of biphenylene and the corresponding molecular graph G_1. The graph G_1 has $n=12$ vertices and $m=14$ edges. The vertices of G_1 represent the carbon atoms, whereas its edges represent the carbon-carbon bonds of biphenylene.

The number of vertices of a molecular graph G is denoted by n. Two vertices connected by an edge are said to be adjacent.

If the vertices of the graph G are labeled by v_1, v_2,..., v_n, then the structure of G can be represented by the adjacency matrix $A = A(G) = ||A_{ij}||$. This is a square matrix of order n, whose elements A_{ij} are defined so that $A_{ij}=A_{ji}=1$ if the vertices v_i and v_j are adjacent, and $A_{ij}=0$ otherwise. For an example see Fig. 2.

The characteristic polynomial of the graph G, denoted by $\Phi(G,x)$ is equal to the determinant $det(xI\text{-}A)$ where I is the unit matrix. It can be shown that $\Phi(G,x)$ is a monic polynomial in the variable x, of degree n. For an example see Fig. 2.

The numbers x_1, x_2,...,x_n, obtained by solving the equation $\Phi(G,x)=0$, are the eigenvalues of the graph G. These eigenvalues form the spectrum of G. For an example see Fig. 2.

It can be shown that, in the majority of chemically interesting cases, the HMO total π-electron energy is related to the eigenvalues of the molecular graph as

$$E = 2\sum x_i \tag{1}$$

where the summation goes over the positive-valued eigenvalues of the molecular graph. Another neat way in which Eq. (1) can be written is

$$E = \sum_{i=1}^{n} |x_i| \tag{2}$$

where now the summation embraces all graph eigenvalues.

$$A(G_2) = \begin{Vmatrix} 0 & 1 & 0 & 0 & 0 \\ 1 & 0 & 1 & 0 & 1 \\ 0 & 1 & 0 & 1 & 0 \\ 0 & 0 & 1 & 0 & 1 \\ 0 & 1 & 0 & 1 & 0 \end{Vmatrix}$$
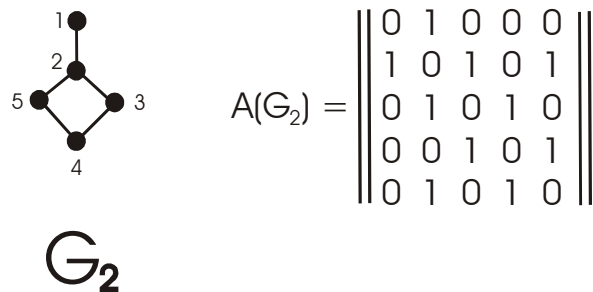
G_2

Figure 2. A graph G_2 and its adjacency matrix $A(G_2)$. It can be computed (but not easily) that the characteristic polynomial of G_2 is $\Phi(G_2,x) = x^5 - 5 x^3 + 2 x$. The solutions of the equation $x^5 - 5 x^3 + 2 x = 0$ are $x_1=[(5 + \sqrt{17})/2]^{1/2} = 2.13578$, $x_2=[(5 - \sqrt{17})/2]^{1/2} = 0.66215$, $x_3=0$, $x_4=-[(5 - \sqrt{17})/2]^{1/2} = -0.66215$ and $x_5=-[(5 + \sqrt{17})/2]^{1/2} = -2.13578$. These five numbers are the eigenvalues of the graph G_2 and form the spectrum of G_2.

Thanks to the symmetric form of Eq. (2), the HMO total π-electron energy E is particularly suitable for mathematics-based investigations; for details and an exhaustive list of references see in the recent review [51]. The first significant result in this area was obtained by the British mathematician and theoretical chemist Charles Coulson, as early as in 1940. Coulson found a connection between E and the characteristic polynomial of the molecular graph:

$$E = \frac{1}{\pi} \int_{-\infty}^{+\infty} \left[n - \frac{ix\,\Phi'(G,ix)}{\Phi(G,ix)} \right] dx \tag{3}$$

In formula (3), Φ' stands for the first derivative of the characteristic polynomial, and i for the imaginary unit, $i=\sqrt{-1}$.

A quarter of century later, the German mathematician Horst Sachs discovered the way in which the characteristic polynomial of a graph depends on its structure. His result, nowadays referred to as the Sachs theorem [1,55,56], reads as follows:

$$\Phi(G,x) = x^n + \sum_{S} (-1)^{p(S)} 2^{c(S)} x^{n-n(S)} \tag{4}$$

where the summation goes over all so-called Sachs graphs of the graph G. These Sachs graphs, essential for the present considerations, are defined below.

One should note that the Sachs theorem played (and still plays) a very important role in the theory of conjugated molecules and in theoretical chemistry in general. After this theorem was made known to the chemical community [57], more than a thousand publications followed, in which the theorem was applied to chemical problems. Also the results outlined in this article belong to the applications of the Sachs theorem. In a recent review [56], an extensive (but far from complete) bibliography of the chemical applications of the Sachs theorem can be found.

By K_2 is denoted the graph consisting of two vertices, connected by an edge. By C_n is denoted the cycle possessing n vertices, $n=3,4,5,...$, see Fig. 3.
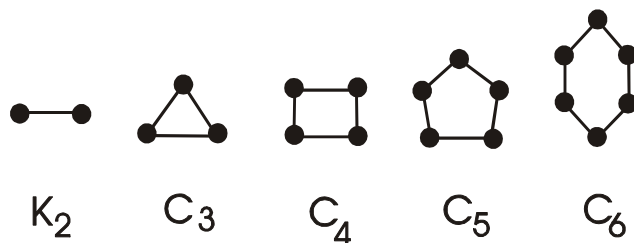

$$K_2 \qquad C_3 \qquad C_4 \qquad C_5 \qquad C_6$$

Figure 3. Components of the Sachs graphs. Any Sachs graph consists of components that are K_2 and/or C_3 and/or C_4 and/or ... , see Fig. 4.

A graph in which each component is K_2 or C_3 or C_4 or C_5 or ... is called a Sachs graph. Some of these Sachs graphs are contained in the molecular graph; examples are found in Fig. 4.

$$S_1 \qquad S_2 \qquad S_3$$

$$S_4 \qquad S_5 \qquad S_6$$

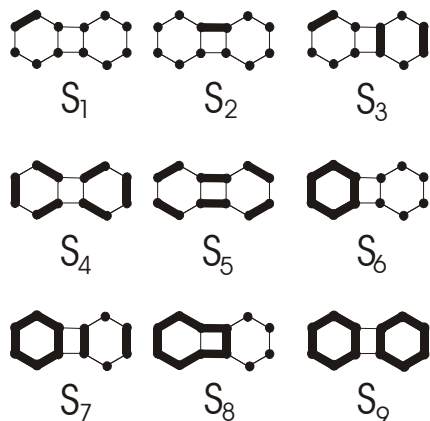$$S_7 \qquad S_8 \qquad S_9$$

Figure 4. Examples of Sachs graphs (indicated by tick lines) contained in the biphenylene graph G_1. The biphenylene graph contains a total of 514 Sachs graphs. Each of these graphs can be understood as representing a structural feature of the respective molecule.

In formula (4), *p(S), c(S),* and *n(S)* are the number of components, cyclic components and vertices, respectively, of the Sachs graph *S*. For instance, the Sachs graphs S_1, S_4, S_7, and S_9 (depicted in Fig. 4), have, respectively, 1, 6, 3, and 2 components, 0, 0, 1, and 2 cyclic components, and 2, 12, 10, and 12 vertices.

When formulas (3) and (4) are combined, one arrives at an explicit expression, connecting the total π-electron energy with molecular structure:

$$E = \frac{1}{\pi} \int\limits_{-\infty}^{+\infty} x^{-2} \ln \left| 1 + \sum_{S} (-1)^{p(S)} 2^{c(S)} x^{n(S)} \right| dx \tag{5}$$

Each Sachs graph can be understood as representing a particular structural detail of the underlying molecule. Some of these structural details are those familiar to every chemist. For instance, S_1 and S_2 in Fig. 4 pertain to two distinct carbon-carbon bonds of biphenylene, S_6 corresponds to one of its six-membered rings, S_4 and S_5 can be viewed as representing two of its Kekulé structural formulas. However, most Sachs graphs have no usual chemical interpretation. Yet, all such structural details play role in determining the magnitude of the total π-electron energy, and thus are responsible for the thermodynamic stability of the respective molecule.

Formula (5) represents the mathematically complete solution of the structure-dependence problem of a molecular property, in this particular case - of the HMO total π-electron energy. There exist very few QSPR results of this kind.

What can we learn from formula (5)?

First of all, the dependence of *E* on various (precisely determined) structural details of the underlying molecule is nonlinear. In particular, *E* is not equal to the sum of the effects of individual structural details. (The author experienced on many occasions the dissatisfaction of chemists because of this fact. Evidently, linear models are more popular among chemists, and scholars who design linear chemical models get a greater and sooner recognition. This author's reply to such "criticism" was always that we just model a natural phenomenon, and that we are not responsible for the nonlinearity of the phenomenon itself.)

Next, formula (5) shows that the relation between total π-electron energy and molecular structure is extremely complicated. [In our opinion, the true relation between any molecular property and molecular structure is extremely complicated, only usually we are not aware of this fact.] Formula (5) precisely identifies all structural details that influence the total π-electron energy. As already mentioned, some of these are familiar: bonds, rings, Kekulé structures. Most of them are exotic, never anticipated by "intuitively thinking" chemists. Formula (5) reveals the plenitude of (relevant) information contained in a molecular structure, most of which chemist would never recognize without utilizing graph spectral theory.

Formula (5) shows the precise mathematical form by which each structural feature influences the value of *E*. Thus from it we could make quantitative inferences. In particular, it is possible to express the effect of an individual cycle (contained in the

molecular graph) on E.

3   ENERGY EFFECTS OF CYCLIC CONJUGATION

Long time ago chemists have recognized that cyclic π-electron systems exhibit very large stabilization or destabilization relative to their acyclic analogs. The pairs benzene vs. hexatriene (stabilization) and cyclobutadiene vs. butadiene (destabilization) are textbook examples. Already in the 1930s Hückel formulated his *4m+2* rule, claiming that monocyclic conjugated systems are stable if they possess *4m+2* (i. e., 2, 6, 10, 14, ...) π-electrons, and are unstable if the number of π-electrons is *4m* (i. e., 4, 8, 12, ...). That this is an energy-based effect was demonstrated in the 1960s [58].

Extending the Hückel rule to polycyclic conjugated molecules became possible only after graph theory was applied in molecular orbital theory, more precisely: after Eq. (5) was discovered.

Using the fortunate fact that the total π-electron energy depends on Sachs-graph-type structural features, and that (some) Sachs graphs consist of cycles, it was possible to express the effect of a particular cycle C, contained in the molecular graph G, on the respective E-value [3,5,6,7,12,13,23].

Denote the set of all Sachs graphs of the molecular graph G by $\mathbf{S} = \mathbf{S}(G)$. Formula (5) can be understood as an expression showing how the elements of the set $\mathbf{S}$ determine E. We may write formula (5) in an abbreviated form as:

$E = f(\mathbf{S})$.

Denote by $\mathbf{S}_C$ the subset of $\mathbf{S}$, consisting of only those Sachs graphs which contain the cycle C, and consider the expression $f(\mathbf{S} \setminus \mathbf{S}_C)$. This expression contains the effects of all Sachs graphs on E, except the effects coming from the cycle C. In other words, $f(\mathbf{S} \setminus \mathbf{S}_C)$ is an energy-like quantity resulting from the effects of all relevant structural details of the underlying molecule, except from the effects of the cycle C. Consequently, the difference

$ef = f(\mathbf{S}) - f(\mathbf{S} \setminus \mathbf{S}_C)$

may be interpreted as the effect of the cycle C on the HMO total π-electron energy. It can be shown that [6,7]:
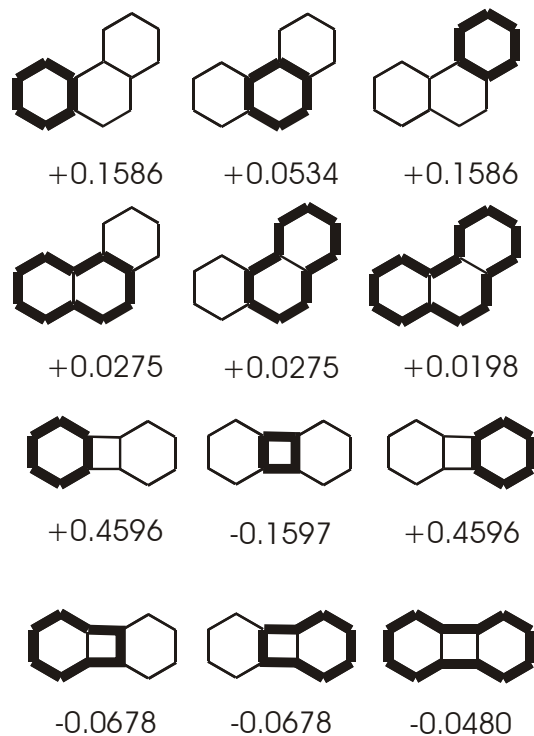
Figure 5. The energy-effects of the cycles of phenanthrene and biphenylene, expressed in the units of the HMO resonance integral β.

$$ef(G,C) = \frac{1}{\pi} \int_{-\infty}^{+\infty} \ln\left|\frac{\Phi(G,ix)}{\Phi(G,ix) + 2\Phi(G-C,ix)}\right| dx \ . \tag{6}$$

In Eq. (6) *G-C* denotes the subgraph obtained by deleting the cycle *C* from the graph *G*. Whenever *ef(G,C)* is positive, the cycle *C* stabilizes the molecule; negative *ef*-values imply destabilization.

In Fig. 5 are given the energy-effects of two typical polycyclic conjugated systems.

The examples shown in Fig. 5 illustrate some basic properties of cyclic conjugation.

(a) Not only rings, but also larger cycles (often ignored by chemists) have their energy contributions.

(b) The energy-effect usually decreases with increasing size of the cycle, but has a non-negligible value also for cycles of larger size.

(c) Cycles of the same size may have significantly different energy-effects.

(d) In the examples shown in Fig. 5, the 6-, 10- and 14-membered cycles have a stabilizing effect, and the 4-, 8- and 12-membered cycles a destabilizing effect. This is in full agreement with the Hückel *4m+2* rule.

(e) However, contrary to what chemists may expect based on their "intuition", the Hückel *4m+2* rule is not generally obeyed. Surprisingly, only the following result could be rigorously proven [9]:

(f) In all alternant polycyclic conjugated hydrocarbons, cycles of size 4, 8, 12, 16, ... always have a negative *ef*-value and thus always destabilize the respective molecule. (This is just one half of the Hückel *4m+2* rule.)

(g) In the majority of cases, cycles of size 6, 10, 14, 18, ... have a stabilizing effect. However, there exist exceptions, namely alternant polycyclic conjugated hydrocarbons in which some of the *(4m+2)*-membered cycles have a destabilizing energy-effect and thus violate the Hückel *4m+2* rule [28].

* * *

Although the results (f) and (g) can be stated and made understandable without any mathematical formalism, they hardly could have been deduced without use of mathematical reasoning. These results could be viewed as examples of what chemistry may gain from mathematics:

Over half a century, chemists believed that a certain regularity holds and is generally valid. Only a couple of years after a couple of mathematical chemists started to apply graph theory, it could be shown that one half of the regularity is generally valid (and is thus a law on Nature), whereas the other half is not.

* * *

Almost at the same time when Eq. (6) was discovered [5-7] and applied to various chemical problems, the Japanese chemist Jun-ichi Aihara proposed a similar, yet not equivalent, approach [59]. According to it, the energy-effect of a cycle C is computed as

$$ef_A = f(\mathbf{S}_{ac} \cup \mathbf{S}_C) - f(\mathbf{S}_{ac})$$

where $\mathbf{S}_{ac}$ is the set of all Sachs graphs (of the molecular graph G), which do not contain any cycle. This would lead to the expression:

$$ef_A(G,C) = \frac{1}{\pi} \int\limits_{-\infty}^{+\infty} \ln\left|\frac{\alpha(G,ix) - 2\alpha(G-C,ix)}{\alpha(G,ix)}\right| dx$$

where $\alpha(G,x)$ is the matching polynomial of the graph G. For details on the matching polynomial see [1,49]. As a curiosity we mention that Aihara needed about 30 years to realize (and publicly announce [60]) that his method (based on ef_A) is inferior to our (based on ef). In the paper [60] he demonstrated that the ef-values are in good agreement with local magnetic properties of benzenoid molecules. This sheds a new light on the physical meaning and chemical applicability of our theory of cyclic conjugation, outlined in this paper.

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