The McClelland Number of Conjugated Hydrocarbons*

Ivan Gutman,[a,**] Lemi Türker,[b] Boris Furtula,[a] and Veselin Vučković[a]

[a]*Faculty of Science, University of Kragujevac, P.O. Box 60, 34000 Kragujevac, Serbia & Montenegro*

[b]*Department of Chemistry, Middle East Technical University, 06531 Ankara, Turkey*

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The McClelland number of a conjugated hydrocarbon is the integer k, satisfying the condition $2^{-(1/2)^k} \sqrt{2nm} \leq E < 2^{-(1/2)^{k+1}} \sqrt{2nm}$, where E is the HMO total π-electron energy, n the number of carbon atoms, and m the number of carbon-carbon bonds. If $k = 3$, then the respective conjugated system is said to be energy-regular. If $k \leq 2$ and $k \geq 4$, then one speaks of energy-poor and energy-rich π-electron systems, respectively. We found that all polycyclic Kekuléan hydrocarbons, possessing condensed rings, are energy-regular, with only three exceptions: naphthalene, phenanthrene, and triphenylene (which are energy-rich). Energy-poor π-electron systems are some (but not all) non-Kekuléans, whereas many of the polycyclic Kekuléan hydrocarbons with non-condensed rings (polyphenyls, phenyl-substituted polyenes and similar) are energy-rich.

INTRODUCTION

In the theory of conjugated molecules the total π-electron energy plays an outstanding role.[1-4] In this paper we are concerned with the total π-electron energy of conjugated hydrocarbons, as computed by means of the Hückel molecular-orbital (HMO) model. In what follows, this quantity is denoted by E; as usual,[1–4] E is expressed in the units of the HMO carbon-carbon resonance integral β.

An important result on E was obtained by McClelland,[5] who showed that

$$E \leq \sqrt{2nm} \qquad (1)$$

where n is the number of carbon atoms and m the number of carbon-carbon bonds of the underlying conjugated hydrocarbons (Recall that the formula of this hydrocarbon is C_nH_{3n-2m}).

The importance of McClelland's upper bound (1) lies in the fact that it provides a reliable approximate expression for E, namely

$$E = a\sqrt{2nm} \qquad (2)$$

with $a \approx 0.9$. The high quality of the approximation (2) was confirmed by means of several extensive comparative studies.[4,6,7]

From the inequality (1) itself, the approximation (2) cannot be deduced. To arrive at (2) one would need also McClelland-type lower bounds for E, namely a lower bound of the form: $E \geq g\sqrt{2nm}$ with g being some constant. Initially,[8] it was found that $g = \sqrt{16/27} \approx 0.77$ holds for benzenoid hydrocarbons. This result was later improved. First, one of the present authors[9] arrived at $g = 1/2$, and then the other present author[10] showed that $g = \sqrt{4/15} \approx 0.52$ if $n \geq 2$, $g = \sqrt{3/10} \approx 0.55$ if $n \geq 3$,

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** Author to whom correspondence should be addressed. (E-mail: gutman@kg.ac.yu)

$g = \sqrt{8/25} \approx 0.57$ if $n \geq 4$, and $g = \sqrt{1/3} \approx 0.58$ if $n \geq 5$. These g-values hold provided the number of three-membered rings plus twice the number of four-membered rings is less than the number of carbon atoms, a condition satisfied by all chemically sound π-electron species. Additional improvements were: $g = \sqrt{32/81} \approx 0.63$, valid for all conjugated molecules,[11] and $g = \sqrt{32/49} \approx 0.70$, valid for conjugated molecules with no four-membered rings.[12]

In what follows we employ the simplest among these McClelland-type lower bounds,[9] *i.e.*,

$$E \geq \frac{1}{2} \sqrt{2nm} \qquad (3)$$

A METHOD FOR SHARPENING THE McCLELLAND ESTIMATES

As explained in the preceding section, the HMO total π-electron energy is estimated by McClelland-type expressions as

$$\frac{1}{2} \sqrt{2nm} \leq E \leq \sqrt{2nm} \qquad (4)$$

Formula (4) is, of course, just a combination of (1) and (3).

We now show how the estimates (4) can be improved.

Construct a sequence $E_0, E_1, E_2, \ldots$ in the following manner. Let $E_0 = \frac{1}{2} \sqrt{2nm}$ and let E_i, $i = 1, 2, \ldots$, be recursively defined as $E_i = \sqrt{E_{i-1} \sqrt{2nm}}$. In other words, E_i is equal to the geometric mean of E_{i-1} and the McClelland upper bound (1). As a consequence of this, it must be

$$E_0 < E_1 < E_2 < E_3 < \cdots \qquad (5)$$

and

$$\lim_{i \to \infty} E_i = \sqrt{2nm} \qquad (6)$$

By direct calculation we obtain

$$E_i = 2^{-(1/2)^i} \sqrt{2nm} \qquad (7)$$

Bearing in mind (4), the relations (5) and (6) imply that there must exist an integer k, such that $E_k \leq E < E_{k+1}$, *i. e.*, by taking into account relation (7),

$$2^{-(1/2)^k} \sqrt{2nm} \leq E < 2^{-(1/2)^{k+1}} \sqrt{2nm} \qquad (8)$$

Evidently, the estimates (8) are better (narrower) than the starting estimates (4), and their quality increases with the increasing value of k. Furthermore,

$$E(G) \approx \sqrt{E_k E_{k+1}} = 8^{-(1/2)^{k+1}} \sqrt{2nm} \qquad (9)$$

should be a reasonably good approximation for the total π-electron energy, especially if k is large enough.

For obvious reasons we call the parameter k *the Mc-Clelland number*. Because the actual value of k depends on the conjugated system considered, we speak of *the McClelland number of a particular conjugated molecule*. Each conjugated molecule has its McClelland number.

Numerical values of the multipliers $2^{-(1/2)^k}$ and $8^{-(1/2)^{k+2}}$ for the first few values of k are given in Table I.

TABLE 1. The multipliers occurring in the lower bound in (8) and in the approximate formula (9), pertaining to the McClelland number k. Note that the multiplier in the upper bound in (8) is equal to the lower-bound-multiplier for $k+1$.

k	$2^{-(1/2)^k}$	$8^{-(1/2)^{k+2}}$
0	0.5000	0.5946
1	0.7071	0.7711
2	0.8409	0.8781
3	0.9170	0.9371
4	0.9576	0.9680
5	0.9786	0.9839
6	0.9892	0.9919
7	0.9946	0.9959
…	…	…
∞	1.0000	1.0000

ENERGY-REGULAR, ENERGY-POOR, AND ENERGY-RICH CONJUGATED HYDROCARBONS

As explained in the subsequent section, the McClelland number of practically all polycyclic conjugated molecules that are of interest in both experimental and theoretical chemistry is equal to 3. This means that the respective HMO total π-electron energies may be reproduced by means of the expression (2) for some value of the multiplier a belonging to the narrow interval (0.9170, 0.9576). We refer to these molecules as *energy-regular*.

If the McClelland number is less than 3, then the parameter a in Eq. (2) is less than 0.917 and, consequently, the respective conjugated systems have E-values smaller than their »regular« mates. Such conjugated systems may be classified as *energy-poor*.

In a fully analogous manner, if the McClelland number of a conjugated molecules is greater than 3, we may include this molecule into the class of *energy-rich* π-electron species.

NUMERICAL WORK

In order to be able to apply the estimates (8) and the approximation (9) to a particular conjugated hydrocarbon,

one must know the actual value of the corresponding McClelland number k. In the general case, various conjugated species have different values of the McClelland number. In view of this, for the practical applicability of Eqs. (8) and (9) it is essential that all (or, at least, the majority) of conjugated molecules have equal McClelland numbers. In order to test this requirement, we have undertaken extensive numerical studies.

We computed the McClelland numbers of all benzenoid hydrocarbons from the books,[13,14] all catacondensed benzenoid hydrocarbons with 8 and fewer hexagons (employed in the paper[15]), all pericondensed benzenoids with 7 and fewer hexagons (from the book[16]), all phenylenes with 8 and fewer hexagons (also from the paper[15]), all non-alternant hydrocarbons from the book,[17] all acyclic polyenes with 10 and fewer carbon atoms, the maximal-energy uni-, bi-, tri-, and tetracyclic conjugated hydrocarbons,[18] as well as a variety of other polycyclic conjugated species. Thus a total of about 2000 conjugated π-electron systems was examined.

The main result of our quest is surprisingly simple:

Rule 1. *All, except three, polycyclic Kekuléan conjugated hydrocarbons, the rings of which are condensed, are energy-regular. There exist only three exceptions: naphthalene, phenanthrene, and triphenylene, whose McClelland numbers are equal to 4.*

Rule 2. *All Kekuléan acyclic polyenes are energy-regular.*

With regard to the conjugated species having McClelland numbers different from 3, we have established the following:

Rule 3a. *Some, but far not all, polycyclic non-Kekuléan conjugated hydrocarbons, the rings of which are condensed, are energy-poor (with McClelland numbers usually equal to 2).*

Rule 3b. *Some, but not all, non-Kekuléan acyclic polyenes are energy-poor (usually having McClelland numbers equal to 2).*

Rule 4. *Some, but not all, polycyclic Kekuléan hydrocarbons with non-condensed rings (polyphenyls, phenyl-substituted polyenes and similar) are energy-rich (usually having McClelland numbers equal to 4). To these belong also the monocyclic conjugated species, including benzene.*

In Figure 1 are depicted some characteristic representatives of energy-poor and energy-rich conjugated hydrocarbons, as well as the three exceptions mentioned in Rule 1.

DISCUSSION

The fact that all (except three) chemically sound polycyclic conjugated hydrocarbons, and in particular, all (ex-
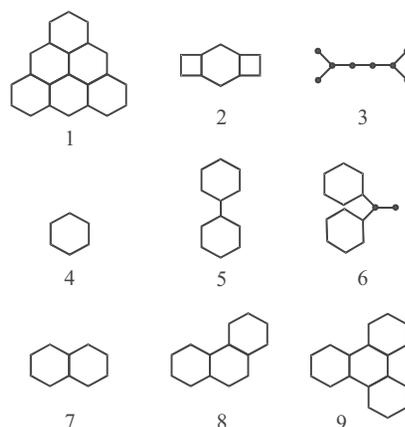

Figure 1. Examples of energy-poor (1-3) and energy-rich (4-9) conjugated hydrocarbons. The energy-poor systems 1 and 3 are non-Kekuléan. The Kekulé structure count of 2 is equal to four, but its algebraic structure count[1] is zero. Compounds 5 and 6 are characteristic representatives of energy-rich conjugated hydrocarbons. These have highly non-planar geometries and are therefore not suitable for the application of HMO theory (including the McClelland-number-concept). Compounds 7- 9 seem to be the only stable planar polycyclic conjugated hydrocarbons with McClelland number different from 3.

cept three) Kekuléan benzenoid hydrocarbons, have the same McClelland numbers, shows that the McClelland-number-concept was well chosen. At this moment our main discovery, formulated above as Rules 1 and 2, is based only on an extensive numerical testing. It remains a task for the future to find a mathematically rigorous proof of these Rules or, perhaps, to show that they can be violated.

The classification of conjugated hydrocarbons as energy-regular, energy-poor, and energy-reach is not something that deserves great attention. Namely, almost all polycyclic conjugated hydrocarbons belong to the energy-regular category (which, thus, embraces both »aromatic«, »non-aromatic« and »anti-aromatic«species). The majority of conjugated molecules classified as energy-rich are non-planar and neither their HMO total π-electron energies nor their McClelland numbers should be considered as physically meaningful. The majority (or all?) of conjugated molecules classified as energy-poor are non-Kekuléans or have zero algebraic structure count. Such π-electron systems are known to be non-existent (at least in a planar or nearly-planar conformation).

Bearing the above in mind, one of the interesting conclusions that follow from our considerations is that the three benzenoid hydrocarbons mentioned in Rule 1 (plus, if one prefers, benzene) are the true and unique chemically realistic conjugated hydrocarbons that are not energy-regular, *i. e.*, that have a truly exceptional energetics.

The present version of the McClelland-number-concept is applicable only to conjugated hydrocarbons. Its extension to heteroconjugated molecules is possible and we intend to do it in the future.

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SAŽETAK

McClellandov broj konjugiranih ugljikovodika

Ivan Gutman, Lemi Türker, Boris Furtula i Veselin Vučković

McClellandov broj konjugiranoga ugljikovodika cijeli je broj k, koji zadovoljava uvjet $2^{-(1/2)^k} \sqrt{2nm} \leq E < 2^{-(1/2)^{k+1}} \sqrt{2nm}$, gdje je E ukupna HMO π-elektronska energija, n broj ugljikovih atoma, a m broj ugljik-ugljik veza. Ako je $k = 3$, onda se za odgovarajući konjugirani sustav kaže da je energijski regularan. Ako je $k \leq 2$ odn. $k \geq 4$, onda govorimo o energijski siromašnome odn. energijski bogatome π-elektronskom sustavu. Našli smo da su svi policiklički Kekuléovski ugljikovodici s kondenziranim prstenima energijski regularni, uz jedina tri izuzetka: naftalen, fenantren i trifenilen (koji su energijski bogati). Energijski siromašni su neki (ali ne svi) ne-Kekuléovski π-elektronski sustavi, dok su mnogi policiklički Kekuléovski ugljikovodici bez kondenziranih prstenova (polifenili, fenil-substituirani polieni i slični) energijski bogati.