

On the HOMO-LUMO Separation in Fullerenes*

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The isomers of a given fullerene C_n could be divided into subsets, each characterized by two numbers, p and q . The former denotes the number of bonds shared by two fused pentagons and the latter denotes the number of vertices being common to the triplets of pentagons.

The HOMO-LUMO separation, $\Delta\epsilon$, and π -electron energy per electron, EPE, have been studied from the graph-theoretical point of view. The dependence of $\Delta\epsilon$ and EPE on p , q and n in fullerenes from C_{24} to C_{60} is presented and discussed.

INTRODUCTION

The electronic and steric factors/effects are in a fine balance in fullerenes.¹ The celebrated »pentagon rule«²⁻³ refers to electronic effects and it has played a crucial role in the first attempts to explain the stability of some fullerenes.⁴

Attention has been also paid to other electronic effects that increase the stability, such as closed electronic shell structure⁵ and the large HOMO-LUMO (the highest occupied – lowest unoccupied molecular orbital) separation.⁶

The HOMO-LUMO separation, $\Delta\epsilon$, is studied here from the graph-theoretical point of view for all fullerenes from C_{24} to C_{60} .

As, generally, many isomers could be generated for a given fullerene, a reliable and efficient algorithm for their generation is urgently needed. A few algorithms has been published so far,⁶⁻⁸ but only the algorithm of Klein *et al.*⁷ is complete. However, it requires a large amount of time, and for this reason we adhered to our algorithm,⁸ which is more efficient but needs yet to be proven as complete.

The role of fused pairs (pentalene motif in a fullerene) and symmetrically fused triplets (triquinacene motif) of pentagons in the destabilization of fullerenes is well described in the literature.³ Accordingly, two numbers could be attached to a fullerene

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isomer, p and q , the former denoting the number of bonds shared by two adjacent/fused pentagons and the latter denoting the number of vertices common to triplets of pentagons.

All isomers of a given fullerene could be now divided into the distinct subsets of isomers marked by p and q . The HOMO-LUMO separation Δx in each subset is studied in the present paper. Besides p , q , and n , Δx , of course, also depends on further structural details of isomers within the subsets. For the sake of compression of data, only the first few maximal Δx are presented, with their corresponding p and q values indicated.

The dependence of Δx on p , q and n is discussed and its chemical consequences are pointed out as well as the limitations of such a graph-theoretical approach.

The importance of Δx in predicting the stability and reactivity of molecules is well known.⁹ Another graph-theoretical quantity – the total π -electron energy per electron, EPE, has found rather limited applications in predicting chemical stability.¹⁰ However, for completeness, the dependence of EPE on p , q and n in fullerenes is also presented here.

METHOD

The graph-theoretical approach to the chemistry of conjugated systems¹⁰ is based on a few simplifying assumptions. The basis atomic orbitals (AO) in this approach are π -orbitals located on carbon atoms. If their interactions are modeled by only two parameters, α and β , the former (Coulomb integral) denoting the on-site energy and the latter (resonance integral) standing for the interactions between two adjacent (*i.e.* connected by a chemical bond) π -orbitals, and other possible interactions are neglected, the simple Hückel molecular orbital (HMO) model of chemistry (or its equivalent in physics: the tight-bonding approximation, TBA) is obtained.

When π -orbitals are depicted by vertices and chemical bonds by edges, a graph G of a conjugated molecule is obtained. The adjacency matrix $\mathbf{A} = \mathbf{A}(G)$ of the order $n \times n$ (with the matrix elements being either 1 or 0) describes the connectivity of vertices in G , where n is the number of π -AO's in a molecule.

Therefore, the interaction matrix \mathbf{H} of the HMO model can be written as: $\mathbf{H} = \alpha \mathbf{I} + \beta \mathbf{A}$, where \mathbf{I} is the unit matrix. The eigenvalues, ε , of \mathbf{H} – the molecular orbital (MO) energies – are simply related to the eigenvalues, x , of \mathbf{A} by:

$$\varepsilon = \alpha + \beta x \quad (1)$$

Because of $\beta < 0$, the ordering: $x_1 \geq x_2 \geq \dots \geq x_n$ implies the increasing order of MO energies: $\varepsilon_1 \leq \varepsilon_2 \leq \dots \leq \varepsilon_n$.

Fullerenes are all-carbon molecules C_n ($n \geq 24$) where n is an *even* number.⁴ They are conjugated molecules composed of n sp^2 -hybridized carbon atoms closed in a cage that contains only pentagons and hexagons. Euler's law requires 12 pentagons for a closure.

There are n π -AO orbitals in a fullerene C_n and by summing up the first $n/2$ occupied MO's (each doubly occupied), the total π -electron energy, E_π , of the ground state of fullerene C_n is obtained:

$$E_\pi = 2 \sum_{j=1}^{n/2} \varepsilon_j = n\alpha + \beta E \quad (2)$$

where E is a purely graph-theoretical quantity defined by:

$$E = 2 \sum_{j=1}^{n/2} x_j \quad (3)$$

E is some measure of thermodynamical stability and, in order to apply it to conjugated molecules of different size, the (π -electron) energy per electron, EPE, is defined:

$$\text{EPE} = E/n \quad (4)$$

When considering the stability and reactivity in the ground state of conjugated molecules, the following quantity:

$$\Delta\varepsilon = \varepsilon_{n/2+1} - \varepsilon_{n/2} \quad (5)$$

has found the widest application. It is called the HOMO-LUMO (the highest occupied – lowest unoccupied MO) separation and its large value points to the kinetic stability of the conjugated molecule considered. It can be written as:

$$\Delta\varepsilon = |\beta| \Delta x \quad (6)$$

where $\Delta x = x_{n/2} - x_{n/2+1}$ is a graph-theoretical analogue of the HOMO-LUMO separation.

The results of Δx and EPE in fullerenes from C_{24} to C_{60} are given in the next chapter.

RESULTS

A given fullerene C_n has generally many isomers. They could be divided into subsets characterized by two numbers, p and q .^{3,7} The number of isomers in a subset of given p and q is denoted by $n(p,q)$ and by summing up all $n(p,q)$'s the total number, $N = N(n)$, of the isomers of C_n is obtained. These numbers in fullerenes C_{24} to C_{60} are calculated by our own algorithm⁸ and given in Table I.

TABLE I

The number of isomers with given p and q (see text) and the total number, $N = N(n)$, of isomers in fullerenes C_n , $n = 24, 26, \dots, 60$.

$n = 24, N = 1$	
	q
p	12
24	1

$n = 26, N = 1$	
	q
p	7
21	1

$n = 28, N = 2$		
	q	
p	4	8
18	1	
20		1

TABLE III

*A few largest HOMO-LUMO separations, $\Delta X(p,q)$, in fullerenes C_n , $n = 24, 26, \dots, 60$.
The numbers p and q (see text) indicate to which subset of isomers ΔX belongs.*

$n = 24$	$\Delta X(24,12) = 0.000$			
$n = 26$	$\Delta X(21,8) = 0.067$			
$n = 28$	$\Delta X(20,8) = 0.093$	>	$\Delta X(18,4) = 0.000$	
$n = 30$	$\Delta X(18,6) = 0.404$	>	$\Delta X(17,4) = 0.058$	>
				$\Delta X(20,10) = 0.000$
$n = 32$	$\Delta X(18,6) = 0.394$	>	$\Delta X(15,2) = 0.364$	>
				$\Delta X(16,4) = 0.253$
				$\Delta X(17,6) = 0.012$
$n = 34$	$\Delta X(15,3) = 0.122$	>	$\Delta X(15,4) = 0.114$	>
				$\Delta X(17,6) = 0.023$
				$\Delta X(14,2) = 0.002$
$n = 36$	$\Delta X(12,0) = 0.300$	>	$\Delta X(16,4) = 0.148$	>
				$\Delta X(14,4) = \Delta X(18,8) = 0.137$
$n = 38$	$\Delta X(11,0) = 0.300$	>	$\Delta X(14,4) = 0.207$	>
				$\Delta X(15,6) = 0.197$
				$\Delta X(12,2) = 0.150$
$n = 40$	$\Delta X(10,0) = 0.373$	>	$\Delta X(13,3) = 0.243$	>
				$\Delta X(11,0) = 0.243$
				$\Delta X(14,4) = 0.206$
$n = 42$	$\Delta X(9,0) = 0.280$	>	$\Delta X(11,2) = 0.260$	>
				$\Delta X(13,3) = 0.224$
				$\Delta X(13,4) = 0.221$
$n = 44$	$\Delta X(9,2) = 0.424$	>	$\Delta X(12,4) = 0.406$	>
				$\Delta X(10,0) = 0.382$
				$\Delta X(14,4) = 0.284$
$n = 46$	$\Delta X(8,0) = 0.335$	>	$\Delta X(9,0) = 0.330$	>
				$\Delta X(9,1) = 0.260$
				$\Delta X(10,1) = 0.245$
$n = 48$	$\Delta X(8,0) = 0.384$	>	$\Delta X(9,0) = 0.319$	>
				$\Delta X(11,2) = 0.258$
				$\Delta X(7,0) = 0.247$
$n = 50$	$\Delta X(6,0) = 0.468$	>	$\Delta X(7,0) = 0.328$	>
				$\Delta X(9,1) = 0.277$
				$\Delta X(8,0) = 0.252$
$n = 52$	$\Delta X(6,0) = 0.352$	>	$\Delta X(10,0) = 0.349$	>
				$\Delta X(14,4) = 0.298$
				$\Delta X(8,0) = 0.286$
$n = 54$	$\Delta X(8,1) = 0.324$	>	$\Delta X(9,0) = 0.318$	>
				$\Delta X(8,0) = 0.309$
				$\Delta X(10,0) = 0.247$
$n = 56$	$\Delta X(5,0) = 0.393$	>	$\Delta X(4,0) = 0.373$	>
				$\Delta X(8,0) = 0.329$
				$\Delta X(6,0) = 0.309$
$n = 58$	$\Delta X(7,0) = 0.340$	>	$\Delta X(10,1) = 0.296$	>
				$\Delta X(9,2) = 0.293$
				$\Delta X(6,0) = 0.290$
$n = 60$	$\Delta X(0,0) = 0.757$	>	$\Delta X(6,0) = 0.414$	>
				$\Delta X(3,0) = 0.384$
				$\Delta X(4,0) = 0.370$

An inspection of Table IV shows that the dispersion of EPE within a given subset is very small, typically of the order of 5×10^{-3} .

DISCUSSION

The results presented above show that the variation of the π -electron energy per electron, EPE, against p and q is low in the isomers of C_{60} . However, by increasing p and q , there is a tendency of isomers to become less stable as measured by their EPE's. A similar low dispersion of the EPE's is noticed in other fullerenes, as well. Therefore, EPE alone is of low predictive power in finding the most stable isomers of fullerenes. However, in the case of C_{60} , the maximal EPE correctly points to the icosahedral isomer, buckminstefullerene, as the most stable one.

On the other hand, the HOMO-LUMO separation is of a much higher discriminative power. In the case of C_{60} , the icosahedral isomer ($p = q = 0$) has a very pronounced peak in Δx , which is almost twice larger than the next Δx , which belongs to an isomer from the subset with $p = 6$ and $q = 0$, followed by Δx of an isomer from the subset with $p = 3$ and $q = 0$. Regardless of some interruptions, a slight tendency of the HOMO-LUMO separations in C_{60} to decrease with an increase of p and q should be noticed. These interruptions, as well as the dispersion of Δx for isomers within a given subset, show that besides p and q other structural details influence Δx .

From C_{36} on, all maximal HOMO-LUMO separations are characterized by $q = 0$, except in C_{44} ($q = 2$) and C_{54} ($q = 1$). In the case of C_{60} , the first four largest Δx 's belong to the subsets with $q = 0$.

The results presented in this paper show that the HOMO-LUMO separation should be a valuable guide for indicating the most stable isomers of fullerenes.

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SAŽETAK

O HOMO-LUMO separaciji u fullerenima

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Izomeri fullereena C_n mogu se podijeliti u skupine od kojih je svaka karakterizirana sa dva broja, p i q . Prvi broj označava broj veza koje su zajedničke parovima dodirujućih se peteročanih prstenova, a drugi predstavlja broj atoma zajedničkih trojkama peteročanih prstenova.

HOMO-LUMO separacija, $\Delta\epsilon$, i π -elektronska energija po elektronu, EPE, proučavane su s graf-teorijskog stajališta. U radu je prikazana i raspravljena ovisnost $\Delta\epsilon$ i EPE o p , q i n za fullerene od C_{24} do C_{60} .