

Topological Stabilization of Fullerenes

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Most fullerene isomers are recognized as unstable due to the existence of fused pentagons. However, they can be stabilized by introducing electronegative heteroatoms into molecular skeletons, according to topological charge stabilization (TCS) rules, at sites of highest electron densities for closed-shell structures.

INTRODUCTION

Much attention^{1–3} has been devoted to the relationship between fullerene structures and their properties after the discovery of C₆₀.⁴ There exist 1812 isomers for C₆₀,^{5,6} that provides an interesting problem to explore. How do their stabilities vary? Because one knows all these isomers involve equal numbers of vertices (atoms) and edges (bonds) as well as 12 pentagons and 20 hexagons in different arrangements. So far, only that species without fused pentagons has been synthesized.⁷ Would not some of remaining ones be able to be stabilized?

With the molecular orbital (MO) viewpoint, HOMO–LUMO gaps are widely used to rationalize the stabilities of molecules with half of their magnitude known as “hardness”.^{8,9} The principle of maximum hardness¹⁰ asserts that systems tend to be as hard as possible, namely, the larger the HOMO–LUMO gap, the more stable the system will be. For fullerenes, it has been noticed that a concerted trend exists between the HOMO–LUMO gaps and the signals of photoionization observed.¹¹

The magnitude of HOMO–LUMO gaps depends on the energy level pattern and electron counts (EC) of the molecules. In Hückel framework, those neutral π -electron species that have non-bonding MOs or unequal numbers of bonding and antibonding MOs are recognized to be unstable, because they are either open shell or closed shell structures with small HOMO–LUMO gaps. However, heteroatomic derivatives of them exist very often attributing to topological charge stabilization (TCS). Gimarc¹² and Aihara¹³ pointed out that heteroatoms with high electronegativity prefer to locate at the sites of high electron density, while weakly electronegative atoms would prefer to occupy the low density positions, where electron densities are calculated in reference to the homo-skeleton isoelectronic with the heteromolecule. Both kinds of replacement may change the level pattern index (LPI) and the number sequence of bonding, nonbonding, and antibonding MOs symbolized by $\{n_+, n_0, n_-\}$ ¹⁴ and may enlarge the HOMO–LUMO gap simultaneously in favor of forming a closed-shell, stabilized heteroatomic system. Calculations within the Hückel framework can be easily carried out using parameters for the substituents relative to references.^{15,16} Analogously, the possible modes for the stabilization of C₆₀ isomers via heteroatomic substitution should be capable of being deduced from similar discussions based on TCS and the evaluation of LPI, EC, and HOMO–

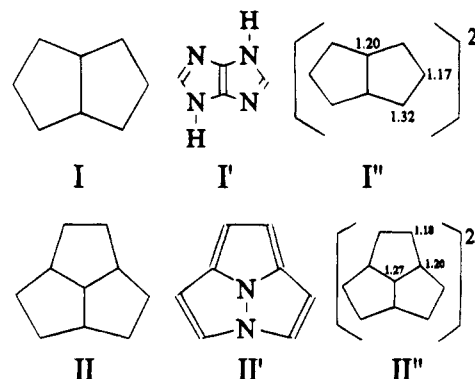


Figure 1. Two nonalternants consisting of fused pentagons.

LUMO gaps appropriate to form stabilized closed-shell structures.

CONJUGATED MOLECULES

For nonalternants, the adjoining of pentagons is one of the factors leading to the instability which has been analyzed in detail.^{17–19} Two typical examples, pentalene (I) and cyclopenta[cd]pentalene (II), are shown (Figure 1). For pentalene, it has been shown that a nonsymmetrical ground state exists due to the second order Jahn–Teller effect^{17,18} and that the Hubbard transition¹⁹ should take place. In practice, pentalene has only been observed as a fugitive species at -196°C .¹⁹ However, their heteroatomic derivatives, I' (imidazo[4,5-d]imidazole) and II', have been known experimentally. Electron densities of the dianions referring to structures I and II as well as isoelectronic heteroderivatives I' and II' can be easily calculated (Figure 1). Obviously, the heteroatoms occupy positions having the highest electron densities in dianions I'' and II''. LPI, EC, and HOMO–LUMO gaps of both groups of molecules are tabulated in Table 1. We immediately see that LPI of heterospecies I' and II' are feasible to accommodate 10 and 12 π -electrons to form closed-shell structures, respectively, and both of the HOMO–LUMO gaps are increased distinctly. In comparison with I and II, heteromolecules I' and II' should be stabilized.

C₆₀ ISOMERS

It is reasonable to think that the 1811 isomers of C₆₀ not yet synthesized is due to the existence of fused pentagons. These isomers have LPI with $n_+ > n_-$ or $n_0 > 0$ with less stable neutral structures. In this paragraph, we will first

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Table 1. LPI, EC, and HOMO–LUMO Gaps of Two Conjugated Molecules and Heteroderivatives

molecule	LPI	EC	HOMO–LUMO gap
I	{4,1,3}	8	0.471
I'	{5,0,3}	10	1.334
II	{6,0,4}	10	0.000
II'	{6,0,4}	12	1.325

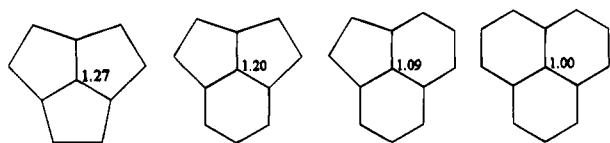
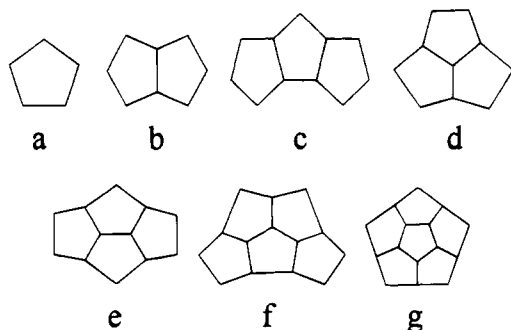

Figure 2. Electron densities at the central points in four planar conjugated molecules.

Figure 3. Seven kinds of pentagon segments in C_{60} isomers.

Table 2. Point Distribution of Segments a–g

segment	$v(5^3)$	$v(5^{2,6})$	$v(5,6^2)$
a			5
b		2	6
c		4	7
d	1	3	6
e	2	4	6
f	3	5	6
g	5	5	5

present some model discussion. In fullerenes, all vertices are triconnected and can be characterized by their neighboring pentagons and hexagons.²⁰ They are abbreviated as $v(5^3)$, $v(5^{2,6})$, $v(5,6^2)$, and $v(6^3)$, where the upper corner numerals signify the number of pentagons and hexagons neighboring the vertex considered (see Figure 2). One can find the four typical conjugated molecules in which the central atoms mimic the connectivity of these four categories of vertices, respectively (Figure 2), where electron densities calculated via Hückel scheme show a tendency corresponding to the order of site reactivity below

$$v(5^3) > v(5^{2,6}) > v(5,6^2) > v(6^3)$$

In C_{60} isomers, pentagons can doubly, triply, or even multiply adjoin, and we are limited to consider typical structures in which only isolated pentagons (a), doubly fused pentagons (b), triply fused pentagons (c) and (d), and quadruply fused pentagons with two inner points (e) exist. Two other pentagon segments (f and g) are also tabulated (Figure 3) where a central pentagon neighbors with four or five pentagons. The number of different kinds of points in these segments are easy to count by inspection, listed in Table 2, which are useful to characterize C_{60} isomers in terms of a sequence of the point counts.

For illustrations, we select four isomers of C_{60} for discussions. They are symbolized by A, B, C, and D and

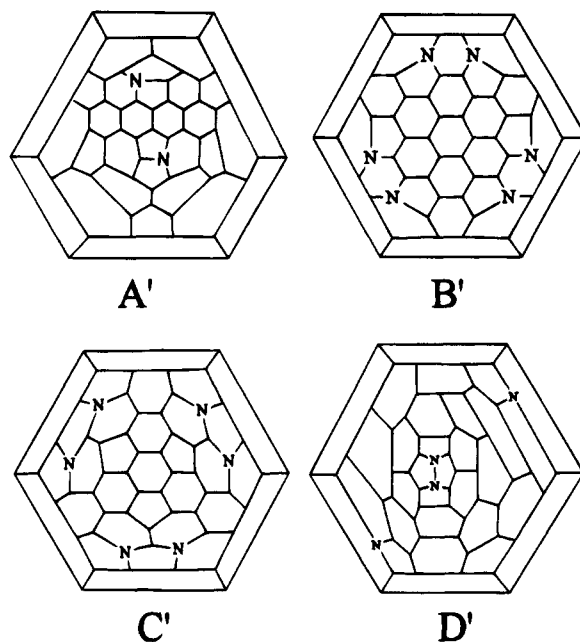

Figure 4. The most probable modes of nitrogen substitution for four C_{60} isomers.

Table 3. Distribution of Pentagons and Various Points in Isomers A, B, C, and D

molecule	a	b	c	d	e	$v(5^3)$	$v(5^{2,6})$	$v(5,6^2)$	$v(6^3)$
A	8	2					4	52	4
B		6					12	36	12
C	3		3				12	36	12
D	2			2	1	4	10	28	18

Table 4. Calculated Electron Densities of Various Points for C_{60} Isomers

molecule	vertex	electron density
A^{2-}	$v(5^{2,6})$	1.153
	$v(5,6^2)$	1.000–1.103
	$v(6^3)$	0.981
B^{6-}	$v(5^{2,6})$	1.207
	$v(5,6^2)$	1.061–1.123
	$v(6^3)$	1.048
C^{6-}	$v(5^{2,6})$	1.165–1.204
	$v(5,6^2)$	1.020–1.128
	$v(6^3)$	1.007–1.036
D^{4-}	$v(5^3)$	1.220–1.235
	$v(5^{2,6})$	1.057–1.172
	$v(5,6^2)$	1.008–1.112
	$v(6^3)$	0.977–1.054

displayed (Figure 4). The distribution of 12 pentagons specified by numbers of segments a, b, c, d, and e and the sequence of point counts, i.e., numbers of points classified to $v(5^3)$, $v(5^{2,6})$, $v(5,6^2)$, and $v(6^3)$ for all 60 points in these isomers, are listed in Table 3. In addition, electron densities of each kind of points for these four isomers in appropriate ionic state are calculated and listed in Table 4.

We notice that isomer A has two doubly fused pentagons, 2b, and eight isolated pentagons, 8a. Since $n_+ = 31$, electron density should be calculated for dianion A^{2-} . While for isomer B, pentagons adjoin to 6b, and $n_+ = 33$, so B^{6-} is used for the calculation of electron densities. Similar analysis tells us one should calculate the electron densities for C^{6-} and D^{4-} . The results of Table 4 indicate that the order of electron density is as follows

Table 5. LPI, EC, and HOMO–LUMO Gaps of C₆₀ Isomers Before and After the Replacement of Heteroatoms

molecule	LPI	EC	HOMO–LUMO gap
A	{31,0,29}	60	0.318
A'	{31,0,29}	62	0.380–0.433
B	{31,2,17}	60	0.103
B'	{33,0,27}	66	0.731–0.847
C	{33,0,27}	60	0.414
C'	{33,0,27}	66	0.670–0.802
D	{32,0,28}	60	0.055
D'	{32,0,28}	64	0.365

$$v(5^2,6) > v(5,6^2) > v(6^3)$$

which consists with the trend of planar molecules shown in Figure 2. According to Gimarc,¹² points with the highest electron densities would be the most apposite sites for heteroatomic replacement.

The most proper heteroatom for replacement is N (nitrogen atom), whose electronegativity is larger than C (carbon atom), offering two π -electrons. Hence, after replacing the reactive points of A, B, C, and D with two, six, six, and four N atoms respectively, the heterofullerenes of closed-shell electronic structure would be likely to be stabilized. We have calculated the LPI, EC, and HOMO–LUMO gaps of variously replacing modes of N at those reactive sites for these isomers before and after replacement. The most probable modes of nitrogen substitution for these four isomers are displayed (Figure 4), and the calculated results are tabulated in Table 5 for comparison. These nitrogen substituted carbon cages are obviously of closed-shell electronic structures with apparently increased HOMO–LUMO gaps. In consequence, the appropriate replacement of heteroatoms should lead to more stable isoskeletal analogues of unknown C₆₀ fullerenes.

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