

Molecular Size and Pyramidalization: Two Keys for Understanding the Reactivity of Fullerenes

Miquel Solà, Jordi Mestres, and Miquel Duran*

Institut de Química Computacional, Universitat de Girona, 17071 Girona, Catalonia, Spain

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The large electron affinity of fullerenes such as C₆₀ or C₇₀ has been rationalized by taking into account the effects of molecular size, the number of five-membered rings, and pyramidalization on their LUMO energy. The study of conjugated cyclopolynes having different size and pyramidalization has shown an enhancement of their electron affinity upon an increase in these two factors and with the presence of pentagonal instead of hexagonal rings. It has also been found that pyramidalization has an effect which is almost constant for all the systems studied, namely, a reduction of the LUMO energy by a similar extent. The stabilization of the LUMO orbital due to an increase in the molecular size is normally more determining than the effect of pyramidalization. The results obtained indicate that fullerenes exhibit enhanced electron-withdrawing character upon increase of their molecular size and pyramidalization.

Introduction

After the discovery¹ and synthesis in macroscopic quantities² of C₆₀ and C₇₀, it was initially assumed that fullerenes exhibited extremely stable aromatic character. This initial hypothesis was soon rejected in the light of the numerous chemical reactions undergone by C₆₀ and C₇₀^{3–8} (see ref 3 for recent reviews on chemical reactivity of fullerenes).

Due to the high symmetry, in these compounds the charges on carbons and the molecular dipole moment are 0 or close to 0. Therefore, it is expected that the reactivity of such systems can be understood and predicted from a consideration of their frontier orbitals, namely, the highest occupied molecular orbital (HOMO) and the lowest unoccupied molecular orbital (LUMO). In fact, the high electron affinity⁹ due to the presence of a low-lying LUMO orbital is the general trend observed in all fullerenes; this fact makes them so reactive, especially with nucleophiles.^{3a,9b} For instance, experimental¹¹ and theoretical studies¹² have demonstrated that C₆₀ acting as an electron-poor dienophile can readily undergo Diels–Alder cycloadditions. The high electron affinity of C₆₀ and other closed-shell fullerenes has been recently explained, using a qualitative molecular-orbital treatment and group theory analysis, by showing that these species always have six low-lying empty orbitals.¹³

On the other hand, the high electron affinity of fullerenes has also been commonly connected to the contribution of the carbon s atomic orbitals to the π molecular orbitals^{3,9,12} as a result of the pyramidalization of carbon atoms in fullerenes. This causes electron delocalization in fullerenes to be poor,^{3a} so they are much more reactive than originally expected. For the sake of comparison, pyramidalized alkenes show larger electron-withdrawing character than nonpyramidalized alkenes. Moreover, it has been recently found¹² that the LUMO energy changes from 0.55 to –0.57 eV when benzene is pyramidalized by 20°, thus enhancing its electron affinity. Further, some authors have pointed out^{9a} that the energy required to force pyramidalization increases the reactivity of fullerenes when compared to normal alkenes.

Pyramidalization has been commonly accepted^{9b,c} as the main reason to justify the low-lying LUMO orbital of fullerenes. This notwithstanding, the molecular size of the chemical system may

also be another important aspect to be considered. However, as far as we know, the effect of molecular size has not been discussed yet, even though it may have a large influence on HOMO and LUMO energies and hence in the HOMO–LUMO energy gap. This HOMO–LUMO energy gap is of paramount importance for the relative abundance of fullerenes and to understand their properties as semiconductors.¹⁴ Interestingly, in such a simple model as the particle in a one-dimensional box of length l , one already finds that the energy gap between states n and $n + 1$ depends on l^{-2} ,¹⁵ the gap being thus reduced as the box lengthens. Extrapolating this result to the π system of conjugated cyclopolynes, one can launch the hypothesis that increasing the molecular size will result in a decrease of the HOMO–LUMO energy gap for those species. Another point worth consideration is the presence of five-membered rings in the compound, which may decrease delocalization and facilitate pyramidalization, thus having an important influence on the HOMO and LUMO energies.

In order to gain more insight into the effect of molecular size, the presence of five-membered rings, and pyramidalization on the HOMO and LUMO energies, and thus into the nature of the reactivity of fullerenes, we have studied a series of 11 conjugated cyclopolynes (Chart 1) of different molecular size constrained to have different pyramidalization angles. The cyclopolynes studied have been selected to have, as fullerenes do, only hexagonal and pentagonal rings. Special attention will be paid to naphthalene, pyracyclene, and corannulene, which can be considered as the structural fragments from which fullerenes may be built. For instance, there are six pyramidalized pyracyclene^{3a} units arranged octahedrally in buckminsterfullerene (C₆₀) and connected to form a pattern of icosahedral geometry. Six naphthalene or three corannulene molecules may also be used to build C₆₀. In fact, it has already been found that C₆₀ may be obtained from six naphthalene molecules by pyrolysis.¹⁶ Although this study is intended to be applicable to any fullerene, we will refer usually to C₆₀ because more experimental and theoretical data are available for this special system than for any other fullerene.

Method of Calculation

To reach the main goal of this work, which is to understand the reactivity of fullerenes in terms of their HOMO and LUMO

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CHART 1

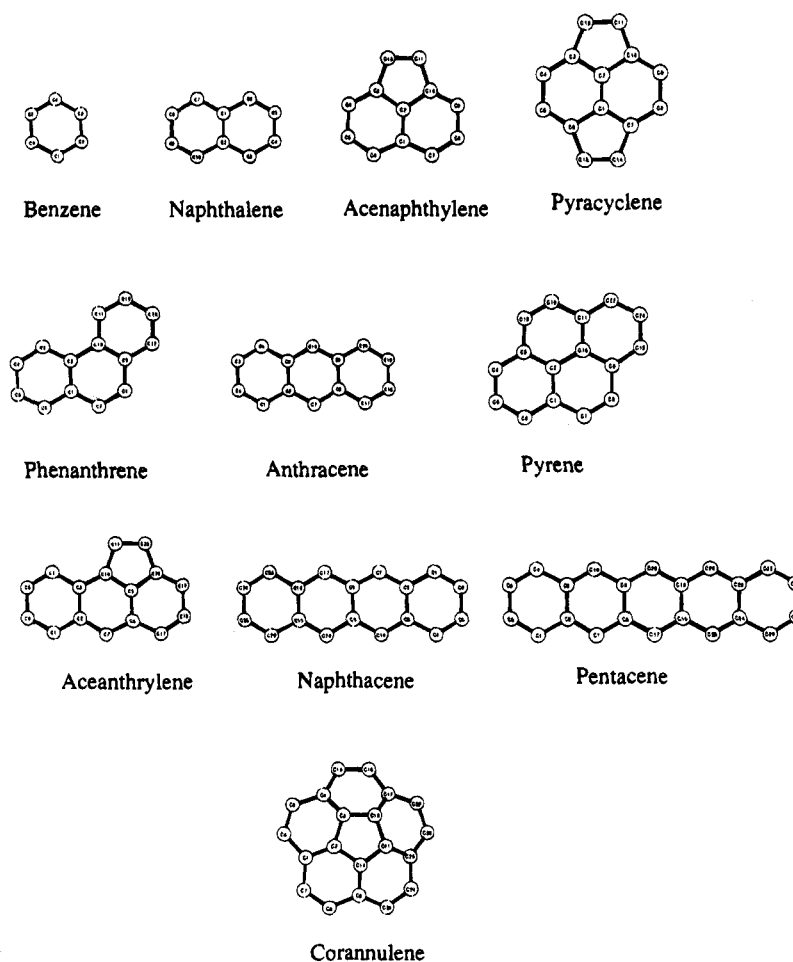
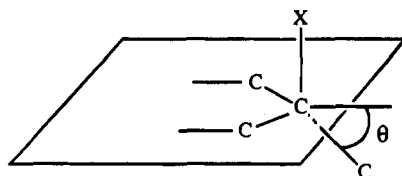


CHART 2



energies, one is faced with an important problem: unfortunately, the size of fullerene molecules prevents the use of current *ab initio* quantum mechanical methods for studying most chemical reactions they undergo. On the contrary, the AM1 molecular-orbital semiempirical method¹⁷ is usually suitable for the study of fullerene reactivity.¹² For this reason, we have preferred to perform our study within the AM1 methodology as implemented in the AMPAC 5.0 program,¹⁸ rather than using an *ab initio* method.

Full geometry optimizations have been carried out at the RHF level, using the Davidson–Fletcher–Powell¹⁹ conjugated-gradient technique. The only constraints to full optimizations have been imposed on pyramidalized cyclopolyenes. In this case we have considered that, as in C_{60} , the different hexagonal and pentagonal cycles are planar, while we have imposed angles of θ° (see Chart 2 and Figure 1 for a definition of the θ angle) between the planes defined by the cycles and also between these planes and attached hydrogens. For instance, Figure 1 depicts the naphthacene molecule pyramidalized by $\theta = 30^\circ$. This definition of θ does not correspond to the common definition of the pyramidalization angle.^{9a,10} For instance, the AM1-optimized geometry of C_{60} yields $\theta = 37.4$, whereas for the same structure the pyramidalization angle is found to be 11.6° .

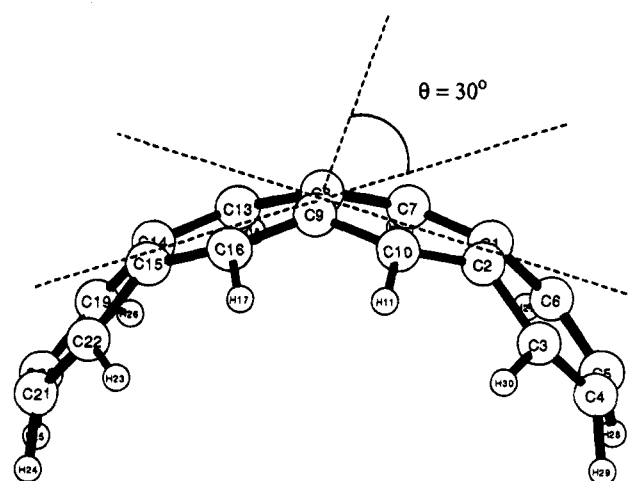


Figure 1. AM1-optimized geometry for naphthacene when $\theta = 30^\circ$.

We have chosen the θ angle instead of the pyramidalization angle to characterize pyramidalized cyclopolyenes because its definition is unique for the different carbons of the cyclopolyene, as opposed to the pyramidalization angle, which may vary for each carbon depending on angles of attached atoms. This notwithstanding, for all systems considered, we have included the average value of the pyramidalization angle computed using the POAV3 program.²⁰

Results and Discussion

This section is organized as follows: first, we analyze the effect of molecular size on the reactivity of fully optimized

TABLE 1: Experimental Ionization Potentials, HOMO and LUMO Orbital Energies and the Corresponding Energy Gap for the Different Cyclopolynes Studied and Also for C₆₀, C₅₅C₅, C₅₄C₆, and C₇₀ at Their AM1-Optimized Geometry (Energies in eV)

| compound | IP ^a | HOMO | LUMO | gap |
|---|-----------------|-------|-------|-------|
| benzene (C ₆ H ₆) | -9.24 | -9.65 | 0.55 | 10.20 |
| naphthalene (C ₁₀ H ₈) | -8.15 | -8.71 | -0.27 | 8.44 |
| acenaphthylene (C ₁₂ H ₈) | -8.22 | -8.94 | -0.94 | 8.00 |
| pyracyclene (C ₁₄ H ₈) | | -8.49 | -1.38 | 7.11 |
| phenanthrene (C ₁₄ H ₁₀) | -7.86 | -8.62 | -0.41 | 8.20 |
| anthracene (C ₁₄ H ₁₀) | -7.47 | -8.12 | -0.84 | 7.28 |
| pyrene (C ₁₆ H ₁₀) | -7.41 | -8.13 | -0.89 | 7.24 |
| aceanthrylene (C ₁₆ H ₁₀) | | -8.22 | -1.34 | 6.88 |
| naphthacene (C ₁₈ H ₁₂) | -7.04 | -7.74 | -1.23 | 6.51 |
| corannulene ^b (C ₂₀ H ₁₀) | | -8.92 | -0.90 | 8.02 |
| pentacene (C ₂₂ H ₁₄) | -6.74 | -7.49 | -1.52 | 5.97 |
| C ₆₀ | -7.61 | -9.64 | -2.95 | 6.69 |
| C ₅₅ C ₅ | | -9.41 | -2.61 | 6.80 |
| C ₅₄ C ₆ | | -9.12 | -2.83 | 6.29 |
| C ₇₀ ^c | -7.61 | -9.14 | -3.27 | 5.87 |

^a Ionization potentials from ref 31 for cyclopolynes and from ref 23 for fullerenes. ^b Values corresponding to a planar molecule. The AM1 fully optimized corannulene is nonplanar. ^c Data from ref 30.

cyclopolynes; second, for selected cyclopolynes, we study the effect of pyramidalization on their HOMO and LUMO energies; and third, we draw some conclusions and discuss their implications on the chemistry of fullerenes.

The Effect of the Molecular Size. Table 1 gathers the HOMO and LUMO orbital energies and the corresponding energy gaps for the 11 conjugated cyclopolynes depicted in Chart 1, together with those of fullerenes C₆₀ and C₇₀. Experimental and calculated HOMO energies differ by only 0.5–0.8 eV in cyclopolynes. For the cases where HOMO energies are available, AM1 results are closer to experimental data than the PM3 HOMO energies reported by Matsuzawa and Dixon.²¹ The only two exceptions correspond to the HOMO energies of C₆₀ and C₇₀, which are calculated to be too high by 2.0 and 1.5 eV with the AM1 method, and also too high by 1.9 and 1.4 eV with the PM3 method,²¹ respectively. Moreover *ab initio* calculations by Scuseria²² report HOMO energies of 8.0 and 7.6 eV for the C₆₀ and C₇₀ molecules, respectively. Despite these values being much more closer to the experimental value of 7.6 eV for the two molecules,²³ the HOMO energy of C₆₀ is found to be larger than that of C₇₀, both at the semiempirical and *ab initio* levels.

The effect of increasing the molecular size can be assessed first by following the series benzene, naphthalene, anthracene, naphthacene, and pentacene (hereafter named linear cyclopolynes), which can be successively obtained by adding four carbon atoms to benzene in order to build new hexagonal cycles. These systems follow the well-known $4n + 2$ Hückel rule for aromatic compounds; furthermore, in all these systems the π electrons are completely delocalized over the entire molecule. Traditionally, the large stability of these cyclopolynes has been related to π delocalization, although some authors have raised rational doubts about the importance of delocalization of π electrons as a driving force of molecular stability and geometry.²⁴ Anyway, the effect of delocalization on the energy of the π orbitals, and in particular on HOMO and LUMO energies, is indeed undeniable.

The results gathered in Table 1 show that, as expected from elementary quantum mechanics, the HOMO–LUMO energy gap decreases with the increase in the molecular size, as a result of the destabilization of the HOMO and the stabilization of the LUMO. The energy gap of 10.20 eV for benzene is reduced to 5.97 eV for pentacene: the larger the delocalization of the π

system, the smaller the energy gap. In particular, naphthacene and pentacene have an energy gap which is even smaller than that corresponding to C₆₀. This fact provides a first hint of the poor delocalization in fullerenes, which yields larger energy gaps than those expected from their dimensions. As a matter of fact, one can predict that a hypothetical planar C₆₀ fullerene would have an energy gap smaller than that of real pyramidalized C₆₀, although probably it would also have a more destabilized LUMO because of pyramidalization (*vide infra*). Lüthi and Almlöf have discussed the difference between spheroidal and single-layer graphite-like C₆₀ in terms of energy and found that spheroidal C₆₀ is more stable, although they have not reported HOMO and LUMO energies for these two systems.²⁵

The HOMO and LUMO energy shifts upon increasing molecular size can be easily understood by paying attention to the changes in the shape of the HOMO and LUMO orbitals for the different linear cyclopolynes. For instance, the degenerate HOMO orbitals corresponding to benzene have a unique nodal plane, whereas the HOMO orbital of naphthalene has two nodal planes. Thus, increasing the number of nodal planes destabilizes the HOMO orbital and explains the destabilization of this orbital upon increase of the molecular size. Another example concerns LUMOs: one of the two degenerate LUMO orbitals of benzene contains two nodal planes, whereas the LUMO of naphthalene has three, although this latter molecule has two pairs of carbons bonded by the LUMO π orbital, which results in an additional energy stabilization, thus explaining the LUMO stabilization upon increase of the molecular size. All in all, changes in the HOMO and the LUMO energies give rise to smaller energy gaps as more carbon 2p_z atomic orbitals are involved in the molecular π orbital and π delocalization becomes more important. Therefore, reactivity of conjugated cyclopolynes increases with the increase in the molecular size. Actually, both the electron-withdrawing and electron-donating character of the cyclopolynes increase with enlarged dimensions.

The HOMO and LUMO energies of phenanthrene have values intermediate between those of naphthalene and anthracene, yet somewhat closer to those of naphthalene, despite being structurally more similar to anthracene. The reason is found in the smaller π delocalization in phenanthrene as compared to anthracene caused by its “nonlinearity”.

Pyrene can be constructed from phenanthrene by adding a new six-membered ring, and in this case the evolution of the HOMO and LUMO energies is the same as that followed by linear cyclopolynes. Due to its molecular structure, pyrene is poorly delocalized as compared to linear cyclopolynes; therefore, despite having two carbon atoms more than anthracene does, the energies of the HOMO and LUMO are almost the same in both compounds.

Interestingly, the effect of setting up an additional pentagonal ring to naphthalene, yielding acenaphthylene, turns out to be a reduction of the HOMO–LUMO energy gap by 0.44 eV, which is smaller than that one could expect from the fact that two carbon atoms have been added to naphthalene. This fact can be attributed to the smaller delocalization in pentagonal cycles as compared to the benzene-like hexagonal cycles. Furthermore, when a pentagonal cycle is added to naphthalene to yield acenaphthylene, the LUMO is stabilized to a larger extent (0.67 eV) than when a hexagonal cycle is appended to naphthalene to build anthracene (0.57 eV). Thus, acenaphthylene (having a pentagonal ring) exhibits a larger electron affinity than anthracene, despite the latter having a smaller energy gap. This is because, in contrast with what happens when a hexagonal cycle is added to naphthalene, the HOMO of acenaphthylene is stabilized with respect to the HOMO of naphthalene by 0.23

eV. This effect is especially noticeable in pyracylene, which has two pentagonal rings. As compared to anthracene, having the same number of carbon atoms, the HOMO is more stabilized, yet the main difference corresponds to the LUMO energy, which is much more stabilized, thus resulting in a larger electron affinity for pyracylene as compared to anthracene.

It is also interesting to compare acenaphthylene and pyracylene, which differ only by the presence of an additional pentagonal cycle. This new cycle has a large effect on the energy gap (with a reduction of 0.89 eV) as a result of a destabilization of the HOMO and a stabilization of the LUMO. This large effect is due to the fact that π delocalization in pyracylene is more important than in acenaphthylene. Therefore, adding a new pentagonal cycle to acenaphthylene gives rise to a quite more reactive cyclopolyene.

Comparison of the HOMO and LUMO energies of pyrene and aceanthrylene, which are structural isomers, again shows the effect of changing a hexagonal ring to a pentagonal one: the HOMO and LUMO orbitals are both stabilized. We must emphasize here that stabilization of the HOMO when changing benzene-like cycles to five-membered rings is consistent with the notion that the π system in benzene disfavors the symmetric structure^{24,26} and that, therefore, a reduction in the symmetry stabilizes the π orbitals like the HOMO. The HOMO and LUMO energy stabilization when changing from anthracene to aceanthrylene is similar to that of changing from naphthalene to acenaphthylene and shows the effect of adding a five-membered ring in the molecular structure. Likewise, the differences in the HOMO and LUMO energies between acenaphthylene and aceanthrylene are almost the same as those found between naphthalene and anthracene, since in both cases the differences amount to adding a new six-membered ring in the molecular structure. Finally, we must remark that the HOMO and LUMO energies of a planar corannulene are almost the same as those of acenaphthylene, despite the fact that corannulene has 10 additional carbon atoms. The reason must be found in the fact that delocalization in the latter is quite poor due to the presence of the pentagonal ring.

To sum up, we have found that the larger the delocalization, the smaller the energy gap. For the systems where π delocalization is poorer, the energy gap increases. This fact does not always imply that the frontier orbital interactions are less favorable and the system is going to be less reactive, because in some cases the LUMO is, in fact, stabilized. This effect is particularly remarkable in conjugated cyclopolyenes with pentagonal cycles like pyracylene, which has an electron affinity larger than anthracene. It is found that the presence of pentagonal rings decreases π delocalization and stabilizes the HOMO and LUMO orbitals, so they increase the electron affinity with respect to adding hexagonal rings.

The Effect of Pyramidalization. As mentioned above, in order to analyze the effect of pyramidalization, we have defined the angle θ , and we have constrained to different θ values the angles between (a) planes defined by the pentagonal and hexagonal cycles and (b) between cycles and attached hydrogens. Therefore, strictly speaking, we will not pyramidalize the cyclopolyenes; instead, we will distort them by a certain amount θ . Nevertheless, because these two processes are almost equivalent, we will continue to use the term pyramidalization throughout this work. As a matter of fact, it is found that a change of 10° in the θ angle corresponds approximately to a variation of 3.3° in the average pyramidalization angle. (see Tables 2–8). The enthalpy of formation, the HOMO and

TABLE 2: HOMO and LUMO Orbital Energies (in eV) and the Corresponding Energy Gap (in eV) for Pyramidalized Benzene at Different θ Angles (in deg) in Their AM1-Optimized Geometry^a

| θ | pyr | ΔH_f | E_π | E_{HOMO} | E_{LUMO} | $\Delta E_{HOMO-LUMO}$ |
|----------|------|-------------------|---------|------------|------------|------------------------|
| 0 | 0 | 22.0 ^b | -65.4 | -9.65 | 0.55 | 10.20 |
| 10 | 3.3 | 26.8 | -65.3 | -9.65 | 0.52 | 10.17 |
| 20 | 6.6 | 41.3 | -65.2 | -9.63 | 0.41 | 10.04 |
| 30 | 9.9 | 65.6 | -64.9 | -9.61 | 0.24 | 9.85 |
| 40 | 13.1 | 99.8 | -64.7 | -9.59 | 0.02 | 9.61 |

^a The pyramidalization angle corresponding to each value of the θ angle is also given. Calculated enthalpy of formation (in kcal/mol) and energy corresponding to the π system (in eV) are also included. ^b Experimental value is 19.8 kcal/mol.³²

TABLE 3: HOMO and LUMO Orbital Energies (in eV) and the Corresponding Energy Gap (in eV) for Pyramidalized Naphthalene at Different θ Angles (in deg) in Their AM1-Optimized Geometry^a

| θ | av pyr | ΔH_f | E_π | E_{HOMO} | E_{LUMO} | $\Delta E_{HOMO-LUMO}$ |
|----------|--------|-------------------|---------|------------|------------|------------------------|
| 0 | 0 | 40.6 ^b | -109.9 | -8.71 | -0.27 | 8.44 |
| 10 | 3.3 | 48.7 | -109.9 | -8.72 | -0.29 | 8.43 |
| 20 | 6.6 | 73.4 | -109.8 | -8.74 | -0.37 | 8.37 |
| 30 | 9.8 | 115.7 | -109.8 | -8.78 | -0.50 | 8.28 |
| 40 | 12.9 | 177.9 | -109.8 | -8.84 | -0.68 | 8.16 |

^a Calculated enthalpy of formation (in kcal/mol) and energy corresponding to the π system (in eV) are also included. The average value of the pyramidalization angle corresponding to each value of the θ angle is also given. ^b Experimental value is 35.9 kcal/mol.³²

TABLE 4: HOMO and LUMO Orbital Energies (in eV) and the Corresponding Energy Gap (in eV) for Pyramidalized Acenaphthylene at Different θ Angles (in deg) in Their AM1-Optimized Geometry^a

| θ | av pyr | ΔH_f | E_π | E_{HOMO} | E_{LUMO} | $\Delta E_{HOMO-LUMO}$ |
|----------|--------|-------------------|---------|------------|------------|------------------------|
| 0 | 0 | 80.7 ^b | -131.9 | -8.94 | -0.94 | 8.00 |
| 10 | 3.4 | 89.2 | -132.0 | -8.95 | -0.96 | 7.99 |
| 20 | 6.8 | 115.1 | -132.3 | -8.98 | -1.03 | 7.95 |
| 30 | 10.1 | 160.1 | -132.8 | -9.04 | -1.14 | 7.90 |
| 40 | 13.1 | 228.9 | -133.6 | -9.11 | -1.29 | 7.82 |

^a Calculated enthalpy of formation (in kcal/mol) and energy corresponding to the π system (in eV) are also included. The average value of the pyramidalization angle corresponding to each value of the θ angle is also given. ^b Experimental value is 62.0 kcal/mol.³²

TABLE 5: HOMO and LUMO Orbital Energies (in eV) and the Corresponding Energy Gap (in eV) for Pyramidalized Pyracylene at Different θ Angles (in deg) in Their AM1-Optimized Geometry^a

| θ | av pyr | ΔH_f | E_π | E_{HOMO} | E_{LUMO} | $\Delta E_{HOMO-LUMO}$ |
|----------|--------|--------------|---------|------------|------------|------------------------|
| 0 | 0 | 135.6 | -154.2 | -8.49 | -1.38 | 7.11 |
| 10 | 3.4 | 142.8 | -154.2 | -8.50 | -1.40 | 7.10 |
| 20 | 6.9 | 166.3 | -154.4 | -8.54 | -1.48 | 7.06 |
| 30 | 10.2 | 209.2 | -154.9 | -8.62 | -1.60 | 7.02 |
| 40 | 13.3 | 279.8 | -155.7 | -8.74 | -1.76 | 6.98 |

^a Enthalpy of formation (in kcal/mol) and energy corresponding to the π system (in eV) are also included. The average value of the pyramidalization angle corresponding to each value of the θ angle is also given.

LUMO energies, and the HOMO–LUMO energy gap for some selected cyclopolyenes constrained to different θ angles are gathered in Tables 2–8. As one can see in cases where experimental enthalpy of formation is known, the error in calculated heats of formation increases with the increase in the number of carbons. AM1 heats of formation, like those from PM3,²¹ are too large when compared to experimental data.

As one can expect from elementary orbital considerations, the HOMO and LUMO orbitals are stabilized by pyramidalization. Contributions of the carbon 2p_x and 2p_y atomic orbitals

TABLE 6: HOMO and LUMO Orbital Energies (in eV) and the Corresponding Energy Gap (in eV) for Pyramidalized Anthracene at Different θ Angles (in deg) in Their AM1-Optimized Geometry^a

| θ | av pyr | ΔH_f | E_π | E_{HOMO} | E_{LUMO} | $\Delta E_{\text{HOMO-LUMO}}$ |
|----------|--------|-------------------|---------|-------------------|-------------------|-------------------------------|
| 0 | 0 | 62.9 ^b | -154.4 | -8.12 | -0.84 | 7.28 |
| 10 | 3.3 | 74.4 | -154.5 | -8.14 | -0.87 | 7.27 |
| 20 | 6.6 | 109.4 | -154.7 | -8.19 | -0.94 | 7.25 |
| 30 | 9.8 | 170.0 | -155.0 | -8.27 | -1.07 | 7.20 |
| 40 | 12.8 | 260.5 | -155.5 | -8.39 | -1.26 | 7.13 |

^a Calculated enthalpy of formation (in kcal/mol) and energy corresponding to the π system (in eV) are also included. The average value of the pyramidalization angle corresponding to each value of the θ angle is also given. ^b Experimental value is 55.4 kcal/mol.³²

TABLE 7: HOMO and LUMO Orbital Energies (in eV) and the Corresponding Energy Gap (in eV) for Pyramidalized Naphthalene at Different θ Angles (in deg) in Their AM1-Optimized Geometry^a

| θ | av pyr | ΔH_f | E_π | E_{HOMO} | E_{LUMO} | $\Delta E_{\text{HOMO-LUMO}}$ |
|----------|--------|-------------------|---------|-------------------|-------------------|-------------------------------|
| 0 | 0 | 87.0 ^b | -199.0 | -7.74 | -1.23 | 6.51 |
| 10 | 3.3 | 101.8 | -199.1 | -7.77 | -1.26 | 6.51 |
| 20 | 6.6 | 147.2 | -199.7 | -7.84 | -1.35 | 6.49 |
| 30 | 9.7 | 226.0 | -200.7 | -7.96 | -1.49 | 6.47 |
| 40 | 12.7 | 345.0 | -202.2 | -8.15 | -1.71 | 6.44 |

^a Calculated enthalpy of formation (in kcal/mol) and energy corresponding to the π system (in eV) are also included. The average value of the pyramidalization angle corresponding to each value of the θ angle is also given. ^b Experimental value is 69.8 kcal/mol.³²

TABLE 8: HOMO and LUMO Orbital Energies (in eV) and the Corresponding Energy Gap (in eV) for Pyramidalized Corannulene at Different θ Angles (in deg) in Their AM1-Optimized Geometry^a

| θ | av pyr | ΔH_f | E_π | E_{HOMO} | E_{LUMO} | $\Delta E_{\text{HOMO-LUMO}}$ |
|----------------|--------|--------------|---------|-------------------|-------------------|-------------------------------|
| 0 ^b | 0 | 173.4 | -222.9 | -8.92 | -0.90 | 8.02 |
| 10 | 3.5 | 178.4 | -223.2 | -8.94 | -0.95 | 7.99 |
| 20 | 7.0 | 198.6 | -224.3 | -8.98 | -1.09 | 7.89 |
| 30 | 10.2 | 255.5 | -226.3 | -9.07 | -1.27 | 7.80 |
| 40 | 13.0 | 415.6 | -227.2 | -9.16 | -1.52 | 7.64 |

^a Enthalpy of formation (kcal/mol) and energy corresponding to the π system (eV) are also included. The average value of the pyramidalization angle corresponding to each value of the θ angle is also given. ^b This does not correspond to the optimized value for corannulene.

to the HOMO and LUMO molecular orbitals are usually larger than that of the carbon 2s atomic orbital. In particular, the HOMO is stabilized by combination with the carbon 2s, 2p_x, and 2p_y atomic orbitals. Further interaction with the valence atomic orbitals of attached C and H destabilizes this molecular orbital. Altogether the HOMO orbital is in most cases slightly stabilized. There is only one exception, corresponding to the HOMO of benzene, which is destabilized as θ increases, due to large contributions of the attached hydrogen 1s atomic orbitals. With regards to LUMO, it is especially stabilized by pyramidalization, because of contributions of the valence atomic orbitals of attached carbon and hydrogen atoms.

In benzene, destabilization of the HOMO orbital as θ increases is small; on the contrary, the stabilization of the LUMO orbital is important, which gives rise to a smaller HOMO-LUMO energy gap and to a benzene molecule having an increased electron-withdrawing character. Interestingly, stabilization of the LUMO oscillates within a quite small range for all systems considered, the energy reduction changing from 0.35 to 0.62 eV when the θ angle is modified from 0° to 40°. Therefore, one can conclude that in all cases the electron affinity is enhanced to a similar extent because of pyramidalization.

The variation in the HOMO-LUMO energy gap when θ changes from 0° to 40°, which is quite important (0.59 eV) in benzene (Table 2), is reduced when the molecular size is increased. In particular, for naphthalene the HOMO-LUMO energy gap is almost unchanged with increasing pyramidalization, as a result of the HOMO and LUMO energies being reduced to the same extent.

A fundamental question in organic chemistry relates to the net energy change traditionally associated with aromaticity. A potential procedure to measure the stabilization of a chemical system due to aromaticity may be defined from the energy difference between the planar system ($\theta = 0$) and the pyramidalized system ($\theta = 40$). Values gathered in Tables 2-8 show the pyramidalization is a process having a high energetic cost. Comparison of the energies needed to pyramidalize from $\theta = 40^\circ$ two C₁₄H_n cyclopolynes, namely, anthracene ($n = 10$, 197.6 kcal/mol) and pyracyclene ($n = 8$, 144.2 kcal/mol), shows that pyramidalization is easier in pyracyclene, which contains pentagonal cycles, than in anthracene. The reason is found in the large loss of aromaticity due to pyramidalization in systems like anthracene as compared to pyracyclene. This fact can be easily related to the so-called Mills-Nixon effect,²⁷⁻²⁹ which states that the fusion of a small ring compound to a benzene molecule induces a partial π localization and, therefore, a loss of symmetry and aromaticity.

In conflict with traditional belief, it is remarkable that localization due to pyramidalization does not change the energy of the π system (this energy, E_π in Tables 2-8, is obtained as the sum of the energies of electrons occupying π orbitals), so it can be concluded that destabilization arises mainly from σ electrons. This fact was already pointed out by Shaik and Hiberty,²⁴ who in their own words reported that "much of what we think about benzene may well originate in its stiff hexagonal σ framework, that buttresses the delocalized π system". The fact that the energy of the π system of pyracyclene and anthracene (two molecules with a quite different aromaticity) differs by only 0.2 eV reinforces the assertion of Shaik and Hiberty.

Another interesting system worth analyzing is corannulene, whose optimized geometry is nonplanar; in fact, planar corannulene is 16.8 kcal/mol less stable than the AM1 fully optimized system. This notwithstanding, pyramidalization of corannulene from $\theta = 0^\circ$ to 40° has an energetic cost of 242.2 kcal/mol. This cost is higher than that of anthracene because in corannulene there are more bonds to distort. In this particular case, the LUMO energy is reduced by as much as 0.62 eV.

Final Remarks and Implications to the Chemistry of Fullerenes. So far we have analyzed the effect of molecular size and pyramidalization on the reactivity of conjugated cyclopolynes. In this section we draw some final conclusions and extrapolate them to rationalize the HOMO and LUMO energies of fullerenes.

It has been shown above that in cyclopolynes the larger the π delocalization, the more the HOMO is destabilized and the LUMO is stabilized, thus enhancing both the electron-donating and electron-withdrawing character of the conjugated cyclopolylene. The presence of pentagonal rings reduces π delocalization (Mills-Nixon effect)²⁷⁻²⁹ and further stabilizes the LUMO orbital, so the electron affinity of the conjugated cyclopolynes with pentagonal rings is increased. In agreement with the Shaik and Hiberty findings,¹⁸ the HOMO orbital is also stabilized with π localization. Poor delocalization and the presence of five-membered rings partially explain the fact that the HOMO of C₆₀ (a fullerene which has 12 pentagonal rings) has almost the same energy as that of some cyclopolynes, thus

TABLE 9: AM1 6–6 and 5–6 Bond Lengths (in Å) in C₆₀ and Pyramidalized Corannulene at Different θ Values

| species | 5–6 distance | 6–6 distance |
|----------------------------------|--------------|--------------|
| corannulene, $\theta = 0^\circ$ | 1.41 | 1.37 |
| corannulene, $\theta = 10^\circ$ | 1.42 | 1.37 |
| corannulene, $\theta = 20^\circ$ | 1.42 | 1.37 |
| corannulene, optimized | 1.43 | 1.38 |
| corannulene, $\theta = 30^\circ$ | 1.44 | 1.39 |
| corannulene, $\theta = 40^\circ$ | 1.46 | 1.42 |
| C ₆₀ | 1.46 | 1.39 |

being far more stable than expected from its molecular size. Furthermore, Matsuzawa and Dixon²¹ have pointed out that the degeneracy of the HOMO orbital could make this orbital more negative.

The main effect of pyramidalization turns out to be the stabilization of the LUMO orbital, which gives rise to an increase of the electron affinity of the system considered. The effect on the HOMO–LUMO energy gap becomes smaller as the molecular size of the system increases. The presence of pentagonal rings reduces the aromaticity and increases the π localization in the conjugated cyclopolyene; as a consequence, the energetic cost of pyramidalization is smaller.

As mentioned above, one of the effects of pyramidalization in the HOMO orbital is that the carbon 2p_z atomic orbital is combined with the carbon 2s, 2p_x, and 2p_y atomic orbitals. This fact is of utmost importance in fullerenes, since it increases the electron density outside the cage and reduces it inside the cage, thus likely leading to a different chemistry for the inner and outer faces of the cage.

Interestingly, among all systems studied, pyracyclene pyramidalized by $\theta = 40^\circ$ (see Table 5) turns out to be the most appropriate among the considered systems to be used as a model for studying the reactivity of C₆₀. This molecule is well suited because (a) the HOMO and LUMO energies are those closest to C₆₀ HOMO and LUMO energies and (b) because of resembling C₆₀ by having two kinds of bonds: a 6–5 bond in the ring junction between a pentagonal and hexagonal ring and a 6–6 bond in the ring junction between two hexagonal rings. The values provided by the AM1 method for the bond lengths associated with the 6–5 and 6–6 bonds are 1.46 and 1.39 Å, respectively, in pyramidalized pyracyclene at $\theta = 40^\circ$. It is noteworthy that these two values are almost the same as those found in the AM1 fully optimized C₆₀ fullerene.

We have shown above that three molecules of corannulene may be used to build up C₆₀. We have studied the effects of pyramidalization on the 6–5 and 6–6 bond lengths in corannulene and compared them to those in C₆₀. The results, gathered in Table 9, indicate clearly that the 6–6 and 6–5 bond lengths increase with the value of θ . For a value of θ within 30–40° the values of the 6–5 and 6–6 bond lengths in corannulene become very close to those in C₆₀. In this sense, corannulene pyramidalized to θ angles of 30–40° appears also to be a good model to study the reactivity of C₆₀, besides pyracyclene.

The effects of cage closure in fullerenes have not been assessed yet by our calculations. For this reason, in Table 1 we have also included the HOMO and LUMO energies of AM1-optimized open C₆₀ from a five-membered ring (C₅₅C₅) and from a six-membered ring (C₅₄C₆). These two systems have been depicted in parts a and b of Figure 2, respectively. As can be seen, going from an open C₆₀ to the icosahedral C₆₀, there is a stabilization of both the HOMO and LUMO energies. However, the most interesting point turns out to be the fact that, despite C₅₅C₅ and C₅₄C₆ being greatly destabilized with respect to the C₆₀ cage (412.2 and 525.5 kcal/mol for the C₅₅C₅ and C₅₄C₆

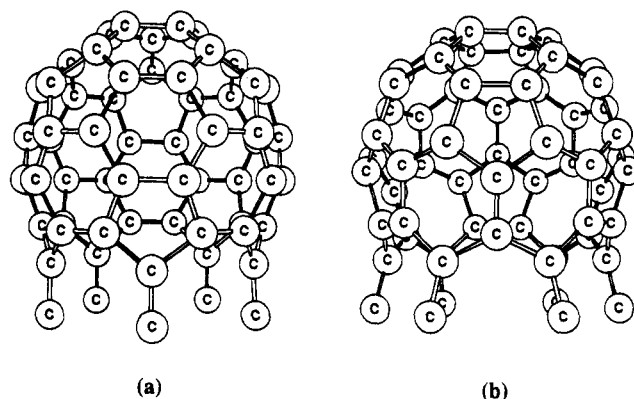


Figure 2. AM1-optimized geometry for the open C₅₅C₅ and C₅₄C₆ species.

open systems, respectively), only small changes in the HOMO–LUMO energy gap are obtained, reinforcing the fact that molecular size is a key factor to stabilize the HOMO and LUMO orbitals.

All in all, both pyramidalization and molecular size increase the electron-withdrawing character of the conjugated cyclopolyenes, especially when pentagonal cycles are present. These three factors allow one to rationalize the large electron affinity of fullerenes. The stabilization of the LUMO orbital due to the increase in the molecular size seems more determining than the effect of pyramidalization. In C₆₀, the large molecular size, the presence of pentagonal rings, and the pyramidalization angle of 11.6° help to substantially stabilize its LUMO, thus leading to a molecule which behaves as a poorly conjugated electron-deficient polyene.

The present AM1 calculations and predictions based on HOMO and LUMO energies of cyclopolyenes reinforce the fact noted earlier^{3a} that C₇₀ is more reactive than C₆₀ as a result of its large molecular size. The changes in HOMO and LUMO energies going from C₆₀ to C₇₀ follow the same trend as that found in linear cyclopolyenes. The larger molecular size in C₇₀ as compared to C₆₀, without modifying the number of five-membered rings or the pyramidalization (the average pyramidalization angle in C₇₀ is 10.8°^{9a}), leads to larger π delocalization and to a smaller energy gap as a result of destabilization of the HOMO orbital and stabilization of the LUMO.

Here it is predicted that, as a general tendency, an increase in the number of carbon atoms in fullerenes will usually imply a more stabilized LUMO and hence a larger reactivity with nucleophiles. This notwithstanding, the molecular topology and symmetry of the fullerene may also largely affect the final HOMO–LUMO energy gap, as recently found for the C₈₄ fullerene.¹⁴ Not only the molecular size will determine the HOMO–LUMO gap but also other factors, such as the number of five- and six-membered cycles and how cycles are joined together to form the fullerene, may be of great importance.

Finally, it has been shown that pyramidalized pyracyclene and corannulene molecules may be used to model chemical reactions of fullerenes. More research on this point is underway in our laboratory.

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