Theoretical Study of the Regioselectivity of Successive 1,3-Butadiene Diels−Alder Cycloadditions to C_{60}

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Abstract: The possibility of successive Diels−Alder cycloadditions of 1,3-butadiene to C_{60} has been studied theoretically by means of the AM1 semiempirical method. The nine unique possible reaction pathways leading to the experimentally observed T_h-symmetric hexakisadduct have been described, and the most thermodynamically favored has been analyzed in more detail. The enthalpy barrier for the cycloaddition changes from 16.2 kcal/mol in the formation of the monoadduct to 17.8 kcal/mol for the hexakisadduct, increasing slightly with successive attacks. However, once the hexakisadduct is reached, addition of a new 1,3-butadiene has an enthalpy barrier as high as 35.5 kcal/mol, in agreement with the fact that experimentally the heptakisadduct has not yet been observed.

1. Introduction

At the initial stages after the discovery of the most abundant fullerenes (C_{60} and C_{70}),[1] researchers worldwide focused their efforts in determining the physical properties of this new emerging family of carbon clusters.[2] However, the exploration of their chemical reactivity did not occur until fullerenes became commercially available.[3,4] Since then, the interest in the chemical possibilities of these peculiar carbon ensembles has continued to increase, in part due to the fact that the emptiness of the cavity of these carbon cages offers the possibility of both an endohedral and an exohedral chemistry, which expands their chemical potential.[5,6]

Pioneering theoretical calculations[7] provided a first clue to the kind of reactivity trends of these compounds. In particular, the electronic structure of C_{60} was characterized by the presence of an energetically low-lying, 3-fold degenerate lowest unoccupied molecular orbital, which suggested that fullerenes should readily act as electron-deficient species by accepting up to six electrons and, thus, revealed their preference to react with electron-rich reagents (nucleophiles).[8] This ability of fullerenes to accept electrons has been widely confirmed by the electronic nature of the organic and organometallic C_{60} adducts reported so far.[9,10]

One step forward in the comprehension of the chemistry of fullerenes emerged from the possibility of multiple additions on the carbon surface. Formation of higher adducts was first manifested when the metal chemistry of fullerenes was studied.[11−14] For example, Fagan *et al.*[11a] were able to exclusively synthesize the T_h-symmetric regioisomer of $[Pt(P(C_2H_5)_3)_2]_6C_{60}$. In these processes, the very pronounced regioselectivity of these adducts is possible because metal additions are reversible, thus yielding the thermodynamically most stable isomer. *Ab initio* theoretical calculations[15] have recently provided additional information on the electronic characteristics and structure of the $[Pt(PH_3)_2]_nC_{60}$ species (n = 1, 2, and 6). However, in order to synthesize stable and stereochemically different adducts with a variable degree of addition, irreversible reactions have to be employed.

For this purpose, cyclopropanations[16,17] and [4 + 2] Diels−Alder cycloadditions[18−24] to C_{60} have been employed to control the regioselectivity during the formation of higher adducts.

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Multiadditions with benzyne[25] and cycloadditions of disilirane[26] to C_{70} have also been reported. As can be extracted from the number of studies performed recently, special attention has been paid to multiple Diels−Alder cycloadditions. This reaction has been found to evolve through a remarkable regiocontrol,[23] although a reasonable explanation for this fact is not clear yet.

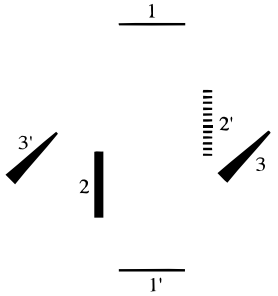
Despite the growing number of experimental works being recently reported on this topic, theoretical studies on successive additions to C_{60} and C_{70} are still scarce. Hirsch *et al.*[16] analyzed the thermochemistry of the eight possible bisadducts using the semiempirical AM1 method. In a subsequent work,[17] these authors were able to rationalize the preferred sites for nucleophilic attack on the basis of enhanced orbital coefficients of low-lying unoccupied molecular orbitals. Four out of the eight different bisadducts were studied by Chikama *et al.*[27] at the *ab initio* level using a minimal STO-3G basis set. These authors also located the transition state (TS) for the addition of 1,3-butadiene to C_{60}. However, the kinetics of the addition for more than a single addend has not been discussed yet from a theoretical point of view.

The aim of the present theoretical work is to extend the knowledge of this kind of process from the kinetic point of view by locating the TSs of the successive Diels−Alder cycloadditions of 1,3-butadiene to C_{60} leading to the T_h-symmetric hexakisadduct. Furthermore, the thermodynamic and kinetic possibilities of a heptakisadduct to be formed will also be discussed.

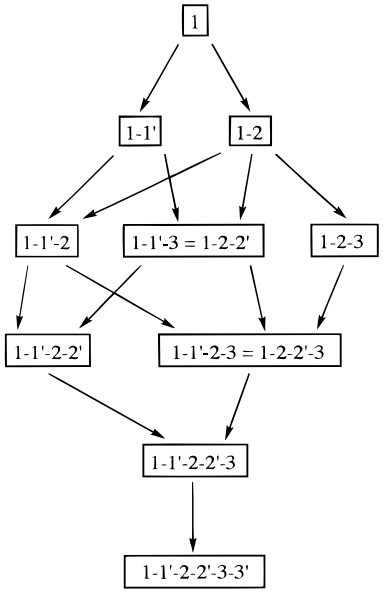
2. Computational Details

The size of the systems studied prevents the use of *ab initio* molecular quantum mechanical methods. Therefore, we have employed the AM1 semiempirical method[28] as implemented in AMPAC 5.0.[29] This method has been preferred over other semiempirical methods because it has been proven in previous studies to yield reliable results for the geometries and energetics of C_{60}[30] and C_{70}[31] Diels−Alder adducts. Further, the AM1 method reproduces high-level *ab initio* calculations and experimental results for a number of Diels−Alder cycloadditions,[32] including the ethylene + butadiene cycloaddition, for which this method yields better energy barriers that are closer to experiment than those provided by some correlated *ab initio* and density functional methods.[33] Moreover, Dewar's group encourages the use of the AM1 method among other semiempirical methods for the study of pericyclic reactions.[34] All zero-gradient structures have been fully optimized without symmetry constraints using the eigenvector following algorithm, continued by a vibrational analysis to characterize the stationary points. Pyramidalization angles have been calculated using the π-orbital axis vector approach (POAV1)[8] as implemented in the POAV3 program.[35] Even though different methods to define the degree of pyramidalization exist,[8,31,36] we have chosen the POAV1 method because it is conceptually simple and widely used.[37] In this method the local curvature of any carbon atom is defined by constructing a vector that makes equal angles to the three attached σ-bonds assuming these bonds lie along the internuclear axes. For planar sp^2 centers this angle ($\theta_{\sigma\pi}$) is 90° while for tetrahedral sp^3 carbons this angle is 109.47°. The pyramidalization angle is then defined as $\theta_{\sigma\pi} - 90°$. Using this definition, the pyramidalization angle for a sp^2 carbon atom is 0°, 19.47° for sp^3 carbon atoms, and 11.64° for carbon atoms in C_{60}. Cartesian coordinates for all reactants, TSs, and adducts are available from the authors upon request.

Chart 1



Scheme 1



3. Results and Discussion

We shall begin our discussion by describing the different possible ways to reach the centrosymmetric hexakisadduct. After that, the adducts obtained with the successive additions are examined: for each new addition we consider the thermodynamics of the possible adducts and the kinetics for the formation of the most stable adduct. Finally, a global discussion on the evolution of the reactivity of the system as the multiaddition proceeds is performed by analyzing the changes with successive addition in reaction enthalpies, enthalpy barriers, the hardness parameter, HOMO and LUMO energies, charge transfers, and pyramidalization angles.

A. Outline of the Study. C_{60} possesses only one type of carbon atom and two types of C−C bonds: 30 bonds at the 6−6 ring fusions and 60 bonds at the 6−5 ring fusions.

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Experimental works[6,18−24] indicate that in Diels−Alder cycloadditions the diene shows a clear preference to attack the 6−6 ring fusions of the fullerene core over the 6−5 ring fusions. Furthermore, theoretical calculations[27,30] have revealed that for the 6−5 Diels−Alder cycloaddition, the energy barrier is about 16 kcal/mol larger than for the 6−6 attack, thus confirming the experimental fact. Thus, it seems evident that the formation of a T_h-symmetric hexakisadduct will proceed through multiple cycloadditions to 6−6 bonds, as confirmed by the ^{13}C NMR data.[17] For the sake of clarity, Chart 1 depicts the six possible sites of 6−6 attack in order to finally reach the experimentally observed centrosymmetric hexakisadduct.[23]

Following bonding labels in Chart 1, Scheme 1 depicts the different possibilities for successive formation of multiadducts toward the hexakisadduct species. From this scheme, the multiple additions can proceed through nine unique reaction paths due to symmetry considerations:[38]

1 1 → 1−1′ → 1−1′−2 → 1−1′−2−2′ → 1−1′−2−2′−3 → 1−1′−2−2′−3−3′

2 1 → 1−1′ → 1−1′−2 → 1−1′−2−3 → 1−1′−2−2′−3 → 1−1′−2−2′−3−3′

3 1 → 1−1′ → 1−1′−3 → 1−1′−2−2′ → 1−1′−2−2′−3 → 1−1′−2−2′−3−3′

4 1 → 1−1′ → 1−1′−3 → 1−1′−2−3 → 1−1′−2−2′−3 → 1−1′−2−2′−3−3′

5 1 → 1−2 → 1−1′−2 → 1−1′−2−2′ → 1−1′−2−2′−3 → 1−1′−2−2′−3−3′

6 1 → 1−2 → 1−1′−2 → 1−1′−2−3 → 1−1′−2−2′−3 → 1−1′−2−2′−3−3′

7 1 → 1−2 → 1−1′−3 → 1−1′−2−2′ → 1−1′−2−2′−3 → 1−1′−2−2′−3−3′

8 1 → 1−2 → 1−1′−3 → 1−1′−2−3 → 1−1′−2−2′−3 → 1−1′−2−2′−3−3′

9 1 → 1−2 → 1−2−3 → 1−1′−2−3 → 1−1′−2−2′−3 → 1−1′−2−2′−3−3′

These nine unique paths leading to the centrosymmetric hexakisadduct appear as a consequence of, for symmetry reasons, having one possible monoadduct (**1**), two possible bisadducts (**11′** and **12**), three possible trisadducts (**11′2**, **11′3**, and **123**), two possible tetrakisadducts (**11′22′** and **11′23**), one possible pentakis adduct (**11′22′3**), and one possible hexakisadduct (**11′22′33′**). The AM1-calculated standard enthalpies of formation of all these adducts are gathered in Table 1. Of these possible nine reaction paths leading to the hexakisadduct, only the TSs corresponding to the path connecting the thermodynamically most stable adducts have been located in this work (path number *9*). In spite of the kinetic study being restricted to this single path, the discussion of the effect of the successive additions on reaction enthalpies and enthalpy barriers is still possible. Table 2 gathers the standard enthalpy of formation of these TSs, as well as the enthalpy barriers for the Diels−Alder and the retro-Diels−Alder reactions.

B. From C_{60} to $C_{60}(C_4H_6)_6$: The Successive Additions. The monoadduct formation has been studied by theoretical means in previous works.[27,30,31] In particular, the *ab initio* STO-3G study of Chikama *et al.*[27] reported an activation barrier of 29.1 kcal/mol for the attack of 1,3-butadiene to the 6−6 ring junction of C_{60}, a value which is too large if one considers the standard experimental conditions used in Diels−Alder cycloadditions of dienes to fullerenes.[6,18−24] For the same reaction, the AM1 method gives an enthalpy barrier of 16.2 kcal/mol.[31] From the structural point of view, it has been observed that the 1,3-butadiene cycloaddition to C_{60} lengthens the 6−6 carbon bond between the two carbon atoms of C_{60} being attacked. Experimentally this bond length changes from 1.401 Å in free C_{60} to 1.592 Å in the Diels−Alder adduct,[39] which represents a distance increase (ΔR) of 0.191 Å. Theoretically, the STO-3G results[27] give 1.376 Å for the free C_{60} and 1.608 Å for the monoadduct (ΔR=0.232 Å) and the AM1 method[31] yields 1.385 Å for C_{60} and 1.573 Å for the monoadduct (ΔR = 0.188 Å). The excellent agreement obtained between experimental and AM1 results for this structural trend may serve to justify the use of the semiempirical AM1 method for studying this kind of process.

Of the eight possible isomeric bisadducts, no more than two, the so-called antipodal (**11′**) and orthogonal (**12**), actually lead to the formation of the hexakisadduct. However, experimentally, seven out of eight possible bisadducts have been observed by Hirsch *et al.*[16] in a cyclopropanation addition reaction. In the same work, the authors have also performed a thermody-

Table 1. Calculated Standard Enthalpy of Formation ($\Delta H_f°$) of Reactants and Adducts at 25 °C, Together with the Average of the Pyramidalization Angle of the Fullerene Core, the Total Charge on this C_{60} Core, the HOMO and LUMO Orbital Energies, and the Hardness Parameter[a]

species	$\Delta H_f°$	av pyr	$q_{C_{60}}$	ϵ_{HOMO}	ϵ_{LUMO}	η
1,3-butadiene	30.7			−9.36	0.47	4.92
C_{60}	973.3	11.64	0.000	−9.64	−2.95	3.35
1	953.2	11.63	-0.161	−9.22	−2.79	3.22
11′	933.6	11.62	-0.313	−8.95	−2.64	3.15
12	933.2	11.62	-0.307	−9.00	−2.54	3.23
11′2	913.6	11.61	-0.443	−8.73	−2.24	3.25
11′3	913.7	11.61	-0.443	−8.79	−2.39	3.20
123	913.1	11.61	-0.437	−9.07	−2.17	3.45
11′22′	894.4	11.60	-0.564	−8.52	−2.12	3.20
11′23	893.7	11.60	-0.558	−8.87	−1.99	3.44
11′22′3	874.3	11.59	-0.665	−8.68	−1.74	3.47
11′22′33′	854.8	11.58	-0.759	−8.70	−1.16	3.77
11′22′33′4	863.6	11.57	-0.776	−8.48	−1.07	3.71

[a] All enthalpy values are given in kcal/mol, charges in au, pyramidalization angles in degrees, and orbital energies and hardness in eV.

Table 2. Calculated Standard Enthalpy of Formation ($\Delta H_f°$) of Transition States at 25 °C for the Different Reactions Considered, Together with Reaction Enthalpies (ΔH_r), Enthalpy Barriers for the Diels−Alder ($\Delta H_{da}^{\ddagger}$) and Retro-Diels−Alder ($\Delta H_{rda}^{\ddagger}$) Processes, and the Imaginary Frequency of each Transition State ($\nu_i^{\ddagger}$)[a]

reaction[b]	$\Delta H_f°$	ΔH_r	$\Delta H_{da}^{\ddagger}$	$\Delta H_{rda}^{\ddagger}$	$\nu_i^{\ddagger}$	pyr[c]
TS(C_{60}→**1**)	1020.3	−50.8	16.2	67.1	687i	11.64
TS(**1**→**11′**)	1000.6	−50.3	16.7	67.0	714i	11.71
TS(**1**→**12**)	1000.4	−50.7	16.6	67.3	698i	11.54
TS(**12**→**123**)	980.8	−50.7	16.9	67.6	709i	11.59
TS(**123**→**11′23**)	961.1	−50.2	17.3	67.5	726i	11.60
TS(**11′23**→**11′22′3**)	942.0	−50.1	17.7	67.8	727i	9.89
TS(**11′22′3**→**11′22′33′**)	922.8	−50.1	17.8	67.9	731i	7.82
TS(**11′22′33′**→**11′22′33′4**)	921.0	−21.9	35.5	57.4	877i	7.84

[a] For the fullerene being attacked by 1,3-butadiene, there are also included in degrees the values of the pyramidalization angles of the carbons being attacked. [b] TS(**a**→**b**) refers to the transition state of the reaction **a** + 1,3-butadiene → **b**. [c] Average value of the pyramidalization angles of the two carbons in reactant **a** being attacked.

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namic analysis of the eight possible bisadducts at the AM1 level, showing that the **12** bisadduct (the so-called *e* in their work) is the most stable, in agreement with the experimental yield being the largest for this isomer. The fact that additions occur predominantly at the equatorial double bond has been confirmed by a number of investigations.[12,24,40] Hirsch *et al.*[16] in the same cyclopropanation addition reaction have found that the rest of the isomeric adducts have enthalpies of formation which differ by less than 2 kcal/mol from the most stable isomer, except the so-called *cis-1* isomer which is 17.7 kcal/mol destabilized with respect to the **12** isomer, in accordance with the fact that this is the only isomer that was not observed experimentally. This *cis-1* isomer corresponds to the addition at the 6−6 bond closest to the bond which has already been attacked, and therefore steric repulsions account for its important destabilization. In fact, for nonsterically demanding substituents the *cis-1* position has been found to be quite activated to addition.[41]

Table 1 contains the values of the standard enthalpy of formation of isomers **11′** and **12**. The other bisadducts were also optimized for the sake of completeness. Our results also furnish the **12** bisadduct as the most stable bisadduct. Moreover, the four possible additions to the 6−6 bonds located at the hemisphere of the fullerene core not containing the first butadiene group yield bisadducts with enthalpies of formation which differ by less than 0.5 kcal/mol from the enthalpy of formation of **12**. However, additions to the hemisphere containing the first butadiene group are less favored, especially the attack leading to the *cis-1* isomer (in the nomenclature by Hirsch *et al.*[16]) which is destabilized by 16.1 kcal/mol. Thus, as already pointed out,[11] binding at one of the 6−6 bonds sterically protects four of the surrounding 6−6 ring fusions. Similar conclusions were reached by Chikama *et al.*[27] at the *ab initio* STO-3G level. Thus, despite at least five bisadducts having similar enthalpies of formation, we have kinetically analyzed only the **11′** and **12** cycloadditions, because these are the only processes that lead regioselectively to the hexakisadduct formation. As one can see from Table 2, and as found from a thermodynamic point of view, the **12** addition is slightly favored over the **11′** attack. However, the difference in enthalpy barrier between the TS(**1**→**11′**) and the TS(**1**→**12**) is quite small, and therefore both attacks should be experimentally observed.

Interestingly, and as a consequence of the deformation of the fullerene core after the first addition, the pyramidalization of the carbon atoms forming the target 6−6 bonds for the formation of the **11′** and **12** bisadducts is slightly larger on the pole than on the equator (11.71 *vs* 11.54). It has been shown that certain reactions[42] take place regioselectively at the sites of greater pyramidalization. A large pyramidalization stabilizes the LUMO orbital of the dienophile[43] and favors the overlap between the molecular orbitals of the carbon atoms forming the new C−C bonds. However, in this case, pyramidalization cannot be called upon to explain the most favorable **12** attack. As pointed out by Hirsch *et al.*,[17,24] this fact can only be rationalized by taking into account the coefficients of the LUMO orbital (−2.94 eV) of complex **1**, which are larger in the equator (position **2**) of the fullerene core than in the poles (position **1′**). As a consequence, the overlap between the HOMO of butadiene and the LUMO of C_{60} is larger in position **2** despite having a somewhat smaller pyramidalization angle. In fact, one has to consider the LUMO + 2 orbital (−2.54 eV) to have large coefficients in position **1′**.

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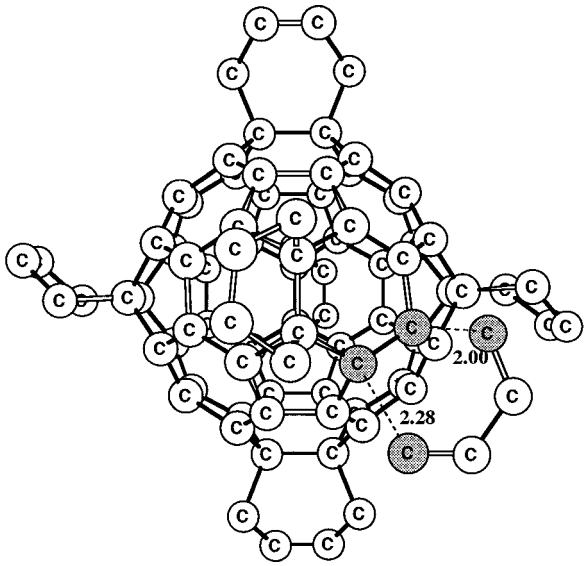

Figure 1. AM1 transition state corresponding to the addition of a 1,3-butadiene to the hexakisadduct. Hydrogen atoms have been omitted for clarity.

Of the 46 possible regioisomeric trisadducts,[23] only three of them (**11′2**, **11′3**, and **123**) lead to the formation of the hexakisadduct. As one can see from the values of Table 1, the **123** isomer is the most stable, which is also coincident with the fact that, experimentally, the **123** trisadduct is the isomer that predominates.[16,17,24,40] The enthalpy barrier for this addition is 16.9 kcal/mol.

As mentioned above, only two of all possible tetrakisadducts (**11′22′** and **11′23**) can intervene in the synthesis of the hexakisadduct. The AM1 results show that the **11′23** isomer is more stable than **11′22′** by 0.7 kcal/mol, in agreement with the experimental fact that among the tetrakisadducts **11′23** is the prevalent one.[17,40] The enthalpy barrier for this addition is 17.3 kcal/mol, while the enthalpy barriers for the next two additions are 17.7 and 17.8 kcal/mol, respectively.

Experimentally the formation of a heptakisadduct has not been observed so far. Our AM1 results explain this fact, showing that despite the formation of the **11′22′33′4** heptakisadduct being thermodynamically favored by −21.9 kcal/mol, it is kinetically not feasible with an enthalpy barrier of 35.5 kcal/mol. This demonstrates that the remarkable regiocontrol observed in multiple Diels−Alder reactions with C_{60}, which terminate invariably at the same hexakisadduct, arises from kinetic factors.

The TS for the addition of a 1,3-butadiene to the hexakisadduct is depicted in Figure 1. Up to this TS, among the TSs corresponding to previous additions, the forming C−C single bonds are remarkably constant, lying in the range of 2.15−2.17 Å, thus reflecting its concerted and synchronous nature. In contrast, the nature of the attack of 1,3-butadiene to the hexakisadduct is concerted but somewhat asynchronous: the bond to the C atom near a previously attacked carbon stretches while the bond to the carbon close to unsubstituted carbons contracts. It is worth noting that this attack is carried out to the very unfavorable *cis-1* positions. Thus, it is not at all surprising to find a large kinetic barrier for this cycloaddition.

C. A Global Discussion on the Whole Process. The AM1 energy profile for the successive addition of seven 1,3-butadiene molecules to C_{60} following reaction path number *9* is depicted in Figure 2. From the analysis of this picture three issues worth considering emerge. First, as the cycloaddition proceeds, the enthalpy barrier of the Diels−Alder cycloaddition slightly increases and the reaction becomes somewhat less exothermic.

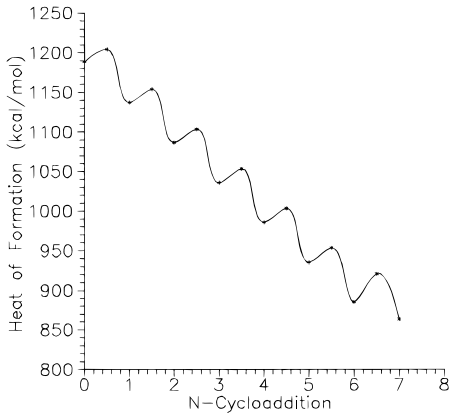

Figure 2. AM1 energy profile for the multiple additions of 1,3-butadiene to C_{60}. The heat of formation for $N = 0$ corresponds to the sum of heats of formation of C_{60} and seven free 1,3-butadiene molecules.

The increase in the enthalpy barrier together with the fact that the available bonds for the addition decrease as the cycloaddition proceeds prompts for the conclusion that the reactivity diminishes with an increasing degree of addition, as experimentally confirmed for a similar reaction.[17] Nevertheless, the change in the enthalpy barrier is quite small, showing that the influence of addition to a 6−6 bond on the other distinct 6−6 bonds is minimal, and supporting the local character of the interaction between 1,3-butadiene and the fullerene core.[15] Second, the enthalpy barrier for the retro-Diels−Alder reaction slightly increases, the cycloaddition being somewhat less reversible as the number of dienes added increases. Third, as mentioned above, it is found that the heptakisadduct is kinetically unreachable at the usual temperatures of reaction.

Another aspect worth being analyzed is the change in hardness owing to successive additions. The hardness is a measure of the resistance of a chemical system species to changes in its electronic configuration, and it is thought to be an indicator of stability.[44] The larger the hardness, the more stable the compound. Hardness values[44,45] calculated by the following operational formula

$$\eta = (1/2)(\epsilon_{\mathrm{LUMO}} - \epsilon_{\mathrm{HOMO}}) \qquad (1)$$

together with HOMO and LUMO values for reactants and adducts have been collected in Table 1. The principle of maximum hardness (PMH)[45] states that systems with constant chemical potential, temperature, and external potential tend to a state of maximum hardness. Apart from temperature, no restriction imposed by the PMH is accomplished in our system, although Pearson has shown a number of cases[45] in which the PMH is more general and less restrictive. This turns out to be the present case. Although not monotonically, the hardness value tends to increase during the formation of higher adducts, being especially large for the hexakisadduct, which is at the same time the most stable and less reactive adduct. It is worth noting that reaction path number *9* always goes through the adducts which have the maximum hardness, as expected from the fact that they are also thermodynamically the most stable. On the other hand, both the HOMO and LUMO orbital energies become more positive as the cycloaddition proceeds, giving rise to less electrophilic and more stable adducts. Loss of conjugation as a result of the successive addition increases the HOMO−LUMO energy gap, hence making frontier orbital interactions less favorable. This trend is experimentally observed by the lightening of the color of the successive adducts.[17]

It must be mentioned also that the Diels−Alder cycloadditions studied here have a normal electronic demand;[46] *i.e.*, there is an electron transfer from the 1,3-butadiene to the fullerene core. This is not surprising given the high electron affinity of C_{60} as a result of having a very low-lying 3-fold degenerate LUMO orbital.[8] Table 1 collects the charge on the fullerene core for the successive adducts. As one can see, there is a monotonic increase in the electronic charge accumulated by the fullerene core as the multiple addition proceeds. Interestingly, the amount of charge transferred in each addition decreases but not dramatically[15] as a result of the electron affinity of the fullerene core being reduced with successive additions.

Finally, we consider how the pyramidalization angles evolve along the successive cycloadditions. As can be extracted from results in Table 1, the average value of the pyramidalization angle for the fullerene core remains almost constant with the increase in the degree of cycloaddition, confirming the statement made by Haddon[8] that hybridization and strain are approximately conserved in fullerenes during reactions. Further, it is found that the pyramidalization angle of the two carbon atoms being attacked decreases as the successive cycloaddition proceeds. This is easily understood by taking into account that this angle increases for the two carbons attacked in the last addition (they change from roughly sp^2 to sp^3 hybridization), and therefore since the average of the pyramidalization angles remains constant, the pyramidalization angle must decrease in most of the rest of the carbon atoms which have not yet undergone the addition.

4. Conclusions

In this work we have reported an AM1 theoretical study of the successive 1,3-butadiene Diels−Alder cycloadditions to C_{60}. Given (a) the small enthalpy differences between the different adducts and (b) the semiempirical methodology used in this study, it is not possible to unequivocally establish which is the most accessible pathway leading to the hexakisadduct. However, it is reasonable to state the following conclusions: first, most of the nine reaction pathways leading to the hexakisadduct will be active and, thus, competitive; second, the enthalpy barriers increase and the reaction enthalpies diminish as the multiaddition proceeds because the LUMO orbital becomes less stable and the pyramidalization of the carbons being attacked smaller; third, the cycloaddition becomes less reversible with the increasing degree of addition; and four, the heptakisadduct is not formed owing to kinetic reasons. We think that the main conclusions reached by this work should not be altered in a significant way by the use of a higher-level theoretical method, because the error due to the approximations should be similar for the different compounds studied here.

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