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Decomposition of the Electronic Activity in Competing [5,6] and [6,6] Cycloaddition Reactions Between C₆₀ and Cyclopentadiene[†]

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Fullerenes, in particular C₆₀, are important molecular entities in many areas, ranging from material science to medicinal chemistry. However, chemical transformations have to be done in order to transform C₆₀ in added-value compounds with increased applicability. The most common procedure corresponds to the classical Diels-Alder cycloaddition reaction. In this research, a comprehensive study of the electronic activity that takes place in the cycloaddition between C₆₀ and cyclopentadiene toward the [5,6] and [6,6] reaction pathways is presented. These are competitive reaction mechanisms dominated by σ and π fluctuating activity. To better understand the electronic activity at each stage of the mechanism, the reaction force (RF) and the symmetry-adapted reaction electronic flux (SA-REF, $J_{T_i}(\xi)$) have been used to elucidate whether π or σ bonding changes drive the reaction. Since the studied cycloaddition reaction proceeds through a C_S symmetry reaction path, two SA-REF emerge: $J_{A'}(\xi)$ and $J_{A''}(\xi)$. In particular, $J_{A'}(\xi)$ mainly accounts for bond transformations associated with π bonds, while $J_{A''}(\xi)$ is sensitive toward σ bonding changes. It was found that the [6,6] path is highly favored over the [5,6] with respect to activation energies. This difference is primarily due to the less intensive electronic reordering of the σ electrons in the [6,6] path, as a result of the pyramidalization of carbon atoms in C₆₀ ($sp^2 \rightarrow sp^3$ transition). Interestingly, no substantial differences in the π electronic activity from the reactant complex to the transition state structure were found when comparing the [5,6] and [6,6] paths. Partition of the kinetic energy into its symmetry contributions indicates that when a bond is being weakened/broken (formed/strengthened) non-spontaneous (spontaneous) changes in the electronic activity occur, thus prompting an increase (decrease) of the kinetic energy. Therefore, contraction (expansion) of the electronic density in the vicinity of the bonding change is expected to take place.

1 Introduction

Fullerenes with potential applications in many fields that range from materials science to medicinal chemistry are important molecular entities in nanochemistry^{1–3}. The most prominent representative of the fullerene family is C₆₀. This molecule behaves as a polyolefin poor in electrons (with strong electron-withdrawing character). As a result, fullerenes undergo a va-

riety of chemical organic reactions, the most important being nucleophilic additions^{4–6}. Moreover, C₆₀ reacts through many metal-catalysed processes like Pauson-Khand^{7–9}, Suzuki-Miyaura reactions^{10–13}, or [2 + 2 + 2] cycloadditions reactions^{14–16}. However, one of the most frequently employed reactions for functionalization of fullerenes and their derivatives is the Diels-Alder (DA) cycloaddition^{17–22}. The electron-withdrawing nature of C₆₀ makes this molecule an ideal dienophile for DA reactions²³. The functionalization of C₆₀ through the DA reaction can yield many different products as a result of monoaddition, bisaddition and so on, up to six consecutive additions^{24,25}. In some cases, formed adducts are thermally unstable and can undergo cycloreversion²⁶.

C₆₀ has two different types of C-C bonds (see Figure 1). Corannulenic [5,6] bonds are located between a hexagon and a pentagon, whereas the pyracylene [6,6] bonds are found in the

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[†] Electronic Supplementary Information (ESI) available: Cartesian coordinates for relevant structures.

hexagon-hexagon ring junctions²⁷. The Diels-Alder reaction in empty fullerenes show an almost exclusive preference for the [6,6] versus the [5,6] bonds^{5,6,28,29}. The [5,6] becomes favored

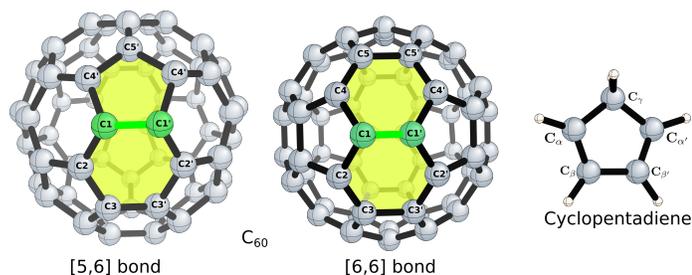


Fig. 1 Two types of bond in fullerene (C_{60}) schematized along with cyclopentadiene. Labeling of the relevant atoms is shown.

or at least competitive in some endohedral metallofullerenes (EMFs)³⁰. For chemists working on reactivity of fullerenes, it would be fascinating to have full control on the regioselectivity of the DA reactions. Interestingly, the [5,6] attack has been computationally predicted to be favored in strongly reduced C_{60} cages³¹ and in high spin states³². The accumulation of negative charge or spin density takes place in the 5-membered rings (5-MRs) of C_{60} . Consequently, the aromaticity of the 5-MRs increases and the [5,6] attack becomes preferred because it breaks the aromaticity of only an aromatic 5-MR³³, whereas the [6,6] attack destroys the aromaticity of two aromatic 5-MRs.

In general, functionalization of fullerenes and EMFs occurs regioselectively in a unique or a few addition sites³⁴. It would be desirable to have full control of the regioselectivity of additions to fullerenes and EMFs in such a way that chemists could fully determine the addition pattern in a given functionalization process. To move forward to this objective, it is necessary to have a deep understanding of the reasons for the high regioselectivity of fullerenes toward [6,6] bonds. The main aim of the present work is to provide insight into the question of why the DA cycloaddition to C_{60} occurs exclusively at the [6,6] bonds, using computational tools derived from the conceptual Density Functional Theory (CDFT).

2 Theory

2.1 Reaction Force

The reaction force (RF) is obtained as the derivative of the energy with respect to the reaction coordinate (ξ)^{35,36}:

$$F(\xi) = -\frac{dE(\xi)}{d\xi} \quad (1)$$

Computation of $F(\xi)$ is possible by obtaining an energy profile through the intrinsic reaction coordinate procedure (IRC \equiv ξ)³⁷⁻³⁹, which allows one to get the minimum energy path for the transformation of reactants into products passing by a transition state. The RF formalism permits the partition of the reaction coordinate into different regions where different reaction events might be taking place⁴⁰⁻⁴². The boundaries of reaction regions are obtained from the critical points on the $F(\xi)$ profile, a minimum at ξ_1 before the transition state and a maximum at ξ_2 there-

after⁴³. Figure 2 displays generic energy (a) and reaction force (b) profiles along with the partition of the reaction coordinate. For a reaction with a single transition state, three reaction regions are defined: reactant region **RR** ($\xi_R \leq \xi < \xi_1$), transition state region **TSR** ($\xi_1 \leq \xi \leq \xi_2$) and product region **PR** ($\xi_2 < \xi \leq \xi_P$)^{42,44}. For reactions taking place via more than one elementary step, more reaction regions have to be considered⁴⁵. In the **RR** deformations and geometrical changes that prepare reactants take place, leading to the formation of activated reactants at ξ_1 . The **TSR** is particularly dominated by electronic reordering; within this region most bonding changes take place. In this region a number of transient structures coalesce, and intensive electronic activity stressing bond breaking and formation processes takes place^{46,47}. After the **TSR**, structural relaxations take over, and the reaction force decreases until reaching a value of zero at the product's position, ξ_P . Therefore, the **PR** is characterized by structural relaxations that lead to the final reaction products. It is worth mentioning that the sign and slope of the RF allows rationalizing the driving forces in a chemical reaction^{44,48}. In addition, a reaction work (W_i) can be defined within each reaction region through numerical integration of the reaction force^{42,48,49}:

$$W_1 = -\int_{\xi_R}^{\xi_1} F(\xi) d\xi > 0 \quad W_2 = -\int_{\xi_1}^{\xi_{TS}} F(\xi) d\xi > 0 \quad (2)$$

$$W_3 = -\int_{\xi_{TS}}^{\xi_2} F(\xi) d\xi < 0 \quad W_4 = -\int_{\xi_2}^{\xi_P} F(\xi) d\xi < 0. \quad (3)$$

Since W_1 and W_4 are defined in the **RR** and **PR**, respectively, they primarily account for structural rearrangements, whereas W_2 and W_3 defined within the **TSR** measure energetics due to electronic reordering^{41,43,49}. In this context, a phenomenological decomposition of activation and reaction energies emerges^{41,49}

$$\Delta E^\ddagger = \int_{\xi_R}^{\xi_{TS}} F(\xi) d\xi = W_1 + W_2, \quad (4)$$

$$\Delta E^\circ = \int_{\xi_R}^{\xi_P} F(\xi) d\xi = W_1 + W_2 + W_3 + W_4. \quad (5)$$

2.2 Symmetry Adapted Reaction Electronic Flux

The reaction electronic flux (REF) has been introduced with the aim of understanding the electronic activity that takes place along a reaction coordinate^{50,51}. It is based on the changes of the electronic chemical potential (CP, μ) in a chemical reaction and defined as:

$$J(\xi) = -\frac{d\mu(\xi)}{d\xi} = -\left(\frac{d\left(\frac{\partial E(\xi)}{\partial N}\right)_{v(\mathbf{r})}}{d\xi}\right) \approx -\frac{1}{2} \underbrace{\left(-\frac{dIP(\xi)}{d\xi} - \frac{dEA(\xi)}{d\xi}\right)}_{\text{FDA}} \approx -\frac{1}{2} \underbrace{\left(\frac{d\epsilon_H(\xi)}{d\xi} + \frac{d\epsilon_L(\xi)}{d\xi}\right)}_{\text{KJT}} \quad (6)$$

In density functional theory (DFT)⁵², the CP is obtained after differentiation of the energy with respect to N , the total number of

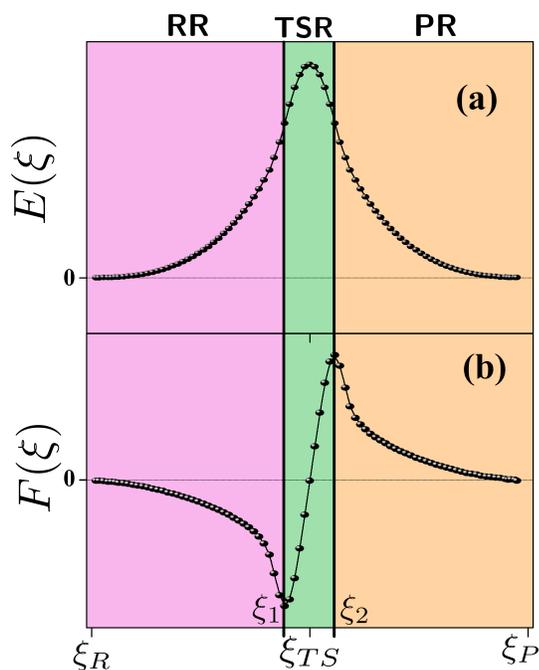


Fig. 2 Generic energy (a) and reaction force (b) profile. Reaction regions are represented in color-code. The quantities ξ_R , ξ_1 , ξ_{TS} , ξ_2 and ξ_P represent the positions of reactant, activated reactant (force minimum), transition state, activated product (force maximum) and product.

electrons of the system, at constant external potential $v(\mathbf{r})$ ^{52–55}. Since the energy is not a continuous function of N , differentiation is performed using the finite difference approximation (FDA)⁵² that allows to obtain numerical values of μ in terms of the first ionization potential (IP) and the electron affinity (EA), as in Eq (6). In analogy with the RF scheme, the $-\frac{dIP(\xi)}{d\xi}$ and $-\frac{dEA(\xi)}{d\xi}$ terms in Eq (6) can be thought as the cation and anion forces, respectively. A further approximation based on the Koopmans' and Janak's theorems (KJT)⁵⁶, links IP and EA with the energy of frontier molecular orbitals, HOMO (ϵ_H) and LUMO (ϵ_L)^{52,53,55}, via the last expression in Eq (6).

Regarding the REF, when it is zero no electronic activity beside that of the equilibrium state is deduced. Positive values of the REF indicate spontaneous changes in the electronic density that are driven by bond forming or bond strengthening processes. On the other hand, negative values of $J(\xi)$ are evidence of non-spontaneous electronic activity, driven by bond weakening or breaking processes^{42,45,48,50,51,57–60}.

For reactions in which symmetry is conserved, degeneracies in orbital energies may appear, causing nondifferentiable points along the μ profile^{61,62}. To overcome the problem of computing μ , a newly proposed symmetry adapted extension of the REF has been introduced^{61,62}. For reactions in which a given punctual group (\mathcal{G}) is conserved along the reaction path, a symmetry-adapted extension of the CP has been introduced (SA-CP). The SA-CP is obtained in such a way that to every irreducible representation $\Gamma_s \in \mathcal{G}$ there corresponds a SA-CP, which is computed as shown in Eq. (7) (the reader is referred to ref⁶¹ for derivation

of the equations):

$$\mu_s = \frac{1}{2n}(\epsilon_s^{occ} + \epsilon_s^{virt}) \quad (7)$$

where ϵ_s^{occ} and ϵ_s^{virt} stand for the highest occupied and lowest unoccupied molecular orbital energies of symmetry s , respectively; n is the number of irreducible representations of \mathcal{G} . The total CP $\mu(\xi)$ is obtained as the sum of the symmetrized CP values:

$$\mu(\xi) = \sum_s^{\mathcal{G}} \mu_s(\xi) \quad (8)$$

Once the SA-CPs are obtained, the SA-REFs are computed by evaluating the negative derivative with respect to the reaction coordinate,

$$J(\xi) = -\left(\frac{d\mu(\xi)}{d\xi}\right) = -\sum_s^{\mathcal{G}} \left(\frac{d\mu_s(\xi)}{d\xi}\right) = \sum_s^{\mathcal{G}} J_s(\xi) \quad (9)$$

According to Eq. (9) the total REF is composed as a sum of individual REF with a given irreducible representation. SA-REF has been successfully applied to a classical proton transfer in methanethionic O-acid ($\text{HO}(\text{C}=\text{S})\text{H}$)⁶¹ and two parent Diels Alder reactions: the cycloaddition between butadiene and ethylene, together with the cycloaddition between diacetylene and acetylene⁶². It was possible to track the electronic activity and distinguish whether π or σ electronic flux is driving the reaction along ξ ^{61,62}.

3 Computational Details

The cycloaddition reaction between C_{60} and cyclopentadiene was studied with a well-tested DFT method. The M06-2X exchange-correlation functional was used for all atoms. The 6-31G(d) basis set was used in conjunction with Truhlar's selected exchange correlation functional. The Beryny Synchronous Transit-Guided Quasi-Newton (STQN) algorithm^{63,64} was used in searching for the TS geometries^{65,66}, which were confirmed through vibrational frequency computations. Then, reactions leading toward the [5,6] and [6,6] reaction pathways were followed through the intrinsic reaction coordinate (ξ , IRC) by means of the IRC procedure as implemented in *Gaussian09*^{37–39,67}. All along the reaction coordinate the interaction between C_{60} (I_h) and cyclopentadiene (C_{2v}) takes place under a C_s symmetry pathway. The cutoffs used to ensure the C_s point group in the IRC computations were set to be loose (threshold of 0.1 Å). Single point calculations on the gas-phase M06-2X geometries were carried out using the domain-based local pair-natural orbital coupled cluster (DLPNO-CCSD(T)) scheme^{68–72} in conjunction with the cc-pVTZ basis set⁷³. Density fitting was used to compute two electron integrals⁷⁴. The Orca 4.0.1 Software package was used for the DLPNO-CCSD(T)/cc-pVTZ computations⁷⁵.

For comparative purposes the profiles are presented in a reduced reaction coordinate (RRC, ξ_i^*) in which reactants and products at ξ_R^* and ξ_P^* are 0 and 1, respectively. Each point on the RRC (ξ_i^*) is computed as follows

$$\xi_i^* = \frac{\xi_i - \xi_R}{\xi_P - \xi_R} \quad (10)$$

were ξ_i corresponds to point i on the IRC. For a given property A defined in both coordinates, it follows that

$$\frac{d^n A(\xi)}{d\xi^n} = \Omega_n \frac{d^n A(\xi^*)}{d\xi^{*n}}, \quad \Omega_n = \frac{1}{(\xi_P - \xi_R)^n} \quad (11)$$

4 Results and Discussion

The cycloaddition reaction between C_{60} and cyclopentadiene was computed along the reaction coordinate, energy profiles for the [5,6] and [6,6] pathways are displayed in Figure 3(a). Activation energies computed at the M06-2X/6-31G(d) level were found to be 22.7 and 6.5 kcal mol⁻¹ for the [5,6] and [6,6] reaction pathways, while the predicted exothermicities are -4.9 and -27.1 kcal mol⁻¹ (both activation and reaction energies reported above were computed using the energies of the isolated reactants). * As previously reported^{29,76}, the occurrence of the [6,6] cycloaddition is favored both kinetically and thermodynamically due to its relatively small activation energy and more exoenergetic character compared to that of the [5,6] reaction. By inspection of the energy profiles shown in Figure 3(a) it can be seen that both reaction pathways can be classified as anti-Hammond, with a late transition state closer to the product ($\xi^* > 0.5$)⁷⁷. However, the TS in the [5,6] is found to be much closer to the product than that on the [6,6] path.

Experimentally, it has been found that the reaction product of the [4 + 2] cycloaddition reaction between C_{60} and cyclopentadiene only gives the [6,6] adduct, without manifestation of subsequent ring openings^{28,78,79}. Reactions of C_{60} with cyclopentadiene and other dienophiles have been experimentally reported, in which the cycloadducts formed are sometimes unstable and prone to revert to the formation of the initial reactants with elevation of temperature^{26,80,81}. The available experimental data shows that the activation energy for the cycloaddition between C_{60} and cyclopentadiene is 6.9 kcal mol⁻¹ as reported by Pang and Wilson⁸⁰ which agrees very well with our findings. Furthermore, Giovanne *et al.* reported an activation energy of 26.7 ± 2.2 kcal mol⁻¹ for the corresponding retro Diels Alder reaction⁸¹. From the suitable subtraction of these two numbers, the experimental reaction energy can be estimated to be -19.8 ± 2.2 kcal mol⁻¹⁷⁶. The activation enthalpy of reaction in terms of the reactant complex and the isolated reactants, ΔH^\ddagger and ΔH_{isol}^\ddagger , for the [6,6] path in toluene solution were 18.7 and 23.9 kcal mol⁻¹, respectively. Furthermore, the corresponding reaction enthalpy energies, ΔH° and ΔH_{isol}° , were found to be -22.3 and -19.9 kcal mol⁻¹. Clearly the obtained activation energies disagree with the activation barriers experimentally obtained. The M06-2X/6-31G(d) method has been used as a part of the two-layered ONIOM approach (ONIOM2), ONIOM2(M06-2X/6-31G(d):SVWN/STO-3G). Cyclopentadiene and the pyracenylic moiety in C_{60} were treated with the M06-2X/6-31G(d) level of theory while the rest of carbon atoms in C_{60} were treated with SVWN/STO-3G. With this composite method an activation energy of 8.2 kcal mol⁻¹ is obtained referenced to the reactant complex

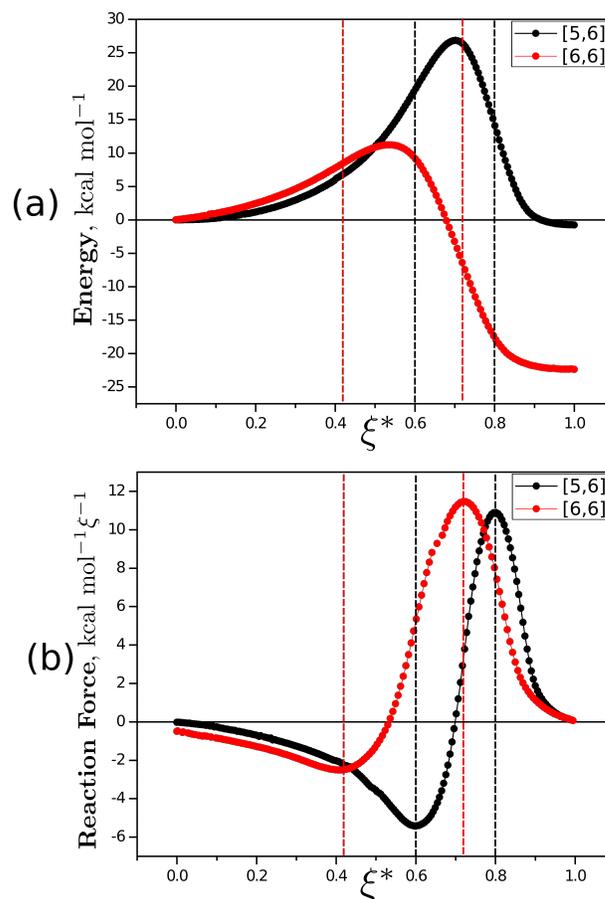


Fig. 3 Energy (a) and reaction force profiles (b) for the cycloaddition between C_{60} and cyclopentadiene computed in gas phase. The [5,6] and [6,6] reaction is represented in black and red, respectively. Energies computed at the M06-2X/6-31G(d) level of theory. Vertical dashed lines correspond to the minimum and maximum of the reaction force. These vertical lines divide the reaction coordinate into reactant, transition state and product regions, respectively. In the reduced reaction coordinate, $\xi^* = 0$ is the reactant complex and $\xi^* = 1$ is the product complex (both with C_s symmetry).

and 12.1 kcal mol⁻¹ relative to the isolated reactants, the latter very close to the experimental value⁷⁶. For a more detailed discussion of the activation energies with respect to the level of theory, the reader is referred to ref⁷⁶.

To gain insights into the reaction mechanism, the RF was obtained, and it is displayed in Figure 3(b). Within the RF formalism, the reaction coordinate can be divided into regions where different reaction mechanisms might be operating. The limits of the reaction regions are denoted by vertical dashed lines in black and red for the [5,6] and [6,6] reaction channels, respectively. For numerical results extracted from the RF formalism, refer to Table 1. On one hand, it is worth noting that when the two pathways are compared, the same percentage of structural and electronic expending is exhibited: 73% of the energy barrier is mainly used in structural reorganizations to reach the TS structure, whereas only a 27% of ΔE^\ddagger accounts of electronic expenditure. This result is consistent with the work of Fernández *et al.*, where the deformation energy obtained by the activation-strain model was

* These values are slightly different from those coming out from the energy profiles of Figure 3 which are not referenced to the isolated reactants.

Reaction	ΔE^\ddagger	ΔE°	$W_1(\% \Delta E^\ddagger)$	$W_2(\% \Delta E^\ddagger)$
[5,6] pathway	26.84	-0.75	19.63 (73)	7.21 (27)
[6,6] pathway	11.22	-22.38	8.18 (73)	3.04 (27)

Table 1 Activation and reaction energies extracted from energy profiles obtained through the IRC procedure in the gas phase at the M06-2X/6-31G(d) level of theory. The reaction works (W_i) computed from the reaction force analysis are also quoted. Energetic values reported in kcal mol⁻¹.

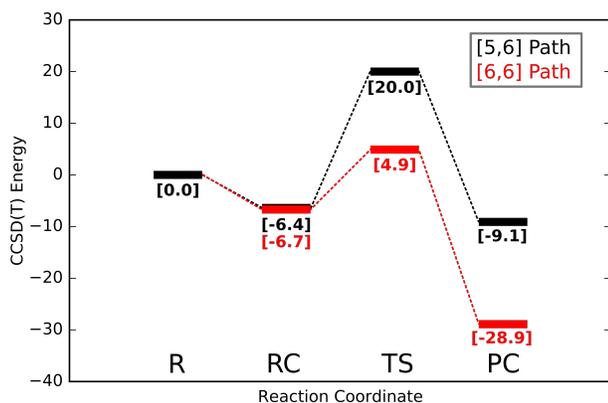


Fig. 4 DLPNO-CCSD(T)/cc-pVTZ energies for the [5,6] and [6,6] paths associated with the cycloaddition between C₆₀ and cyclopentadiene. Energetics are in kcal mol⁻¹.

quite similar for the [5,6] and [6,6] attack²⁹. On the other hand, solely in terms of energy, clearly the [5,6] pathway exhibits both structural and electronic energies larger than the [6,6] pathway, which explains the higher activation energy obtained for the [5,6] path.

To obtain more reliability regarding the activation and reaction energies and to validate the level of theory used in this study, we have computed coupled cluster energies with single, double and perturbative triple excitations (CCSD(T)) using the DLPNO scheme as implemented in the *Orca* software. Coupled cluster energies were computed over the M06-2X geometries previously optimized, and it was verified that they correspond to a minimum or a transition state (see Computational Details Section). In Figure 4, energies for both reaction pathways are presented. As may be seen from Figure 4, the formation of the reactant complex is exoenergetic and interestingly both reactant complexes lie roughly at the same energy. The latter result indicates that the energetic difference between both reaction paths arises after formation of the reactant complex, and therefore formation of it does not play a significant role in the obtention of the activation barriers. In this regard, activation energies were found to be 20.0 and 4.9 kcal mol⁻¹, while reaction energies amount to -9.1 and -28.9 kcal mol⁻¹ for the [5,6] and [6,6] paths. Interestingly, activation energies obtained with the M06-2X functional are very close to those predicted by DLPNO-CCSD(T). This not only confirms the reasonable choice of the methodology but also the reliability of the results here presented.

4.1 Symmetry-Adapted Reaction Electronic Flux

In this section the SA-REF profiles are discussed. The C_s symmetry pathway in which the cycloaddition between C₆₀ and cyclopentadiene takes place allows the definition of two SA-REFs: $J_{A'}(\xi^*)$ and $J_{A''}(\xi^*)$, following the irreducible representation of \mathcal{G} . The $J_{A'}(\xi^*)$ and $J_{A''}(\xi^*)$ fluxes are sensitive for π and σ bonding information, as previously reported⁶². The symmetrized orbital representation (A' and A'') along with the wavefunction of the reaction under consideration is depicted in Figure 5. The $J_{A'}(\xi^*)$ is obtained from the symmetric 109a' and 110a' orbitals whereas $J_{A''}(\xi^*)$ is computed from the antisymmetric 89a'' and 90a'' orbitals. The total REF is then obtained as $J(\xi) = J_{A'}(\xi^*) + J_{A''}(\xi^*)$. It is worth noting that the 90a'' molecular orbital for the [5,6] pathway corresponds to the LUMO+1 while for the [6,6] pathway the LUMO+2 is used.

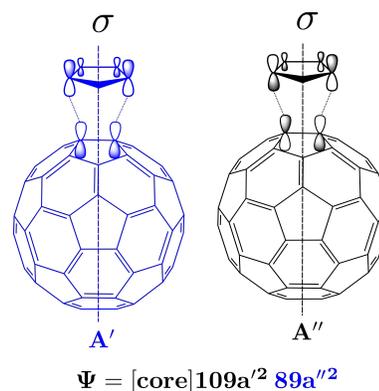


Fig. 5 A' and A'' orbital interactions for cycloaddition between fullerene and C₆₀. Only representative p orbitals are shown for C₆₀. The dotted lines represent the σ molecular plane. The system's electronic wave function is shown below the orbital representation.

In the present cycloaddition mechanisms (for both [5,6] and [6,6] paths), three π bonds are broken: one in C₆₀ (C1-C1') and two in cyclopentadiene (C α -C β and C α' -C β'). Moreover, one π (C β -C β') and two σ bonds (C1-C α and C1'-C α') are formed.

The total electronic activity and what accounts for π and σ reordering in the [5,6] and [6,6] reaction pathways are shown in Figure 6 (a) and 6(b), respectively. Starting with the [5,6] path, it can be seen in the $J(\xi^*)$ profile that a non-spontaneous electronic activity starts to drive the reaction from the very beginning until reaching a minimum at the end of the RR (force minimum). Therefore, in the RR, bond weakening/breaking dominates in this region of the mechanism. At the REF minimum, the electron flux experiences a step; it increases sharply to reach a maximum at the end of the TSR. This change is reflected by means of an increment of the electronic activity, an indicator that bond forming processes are predominant at this stage of the mechanism. Then, the total REF decreases until reaching the product complex structure with $J(\xi^*) = 0$. When the $J(\xi^*)$ are compared between the [5,6] and [6,6] mechanisms in Figures 6(a) and 6(b), respectively, it can be observed that the same electronic pattern is found for both reactions: the REF's minimum and maximum coincide with RF's minimum and maximum. However,

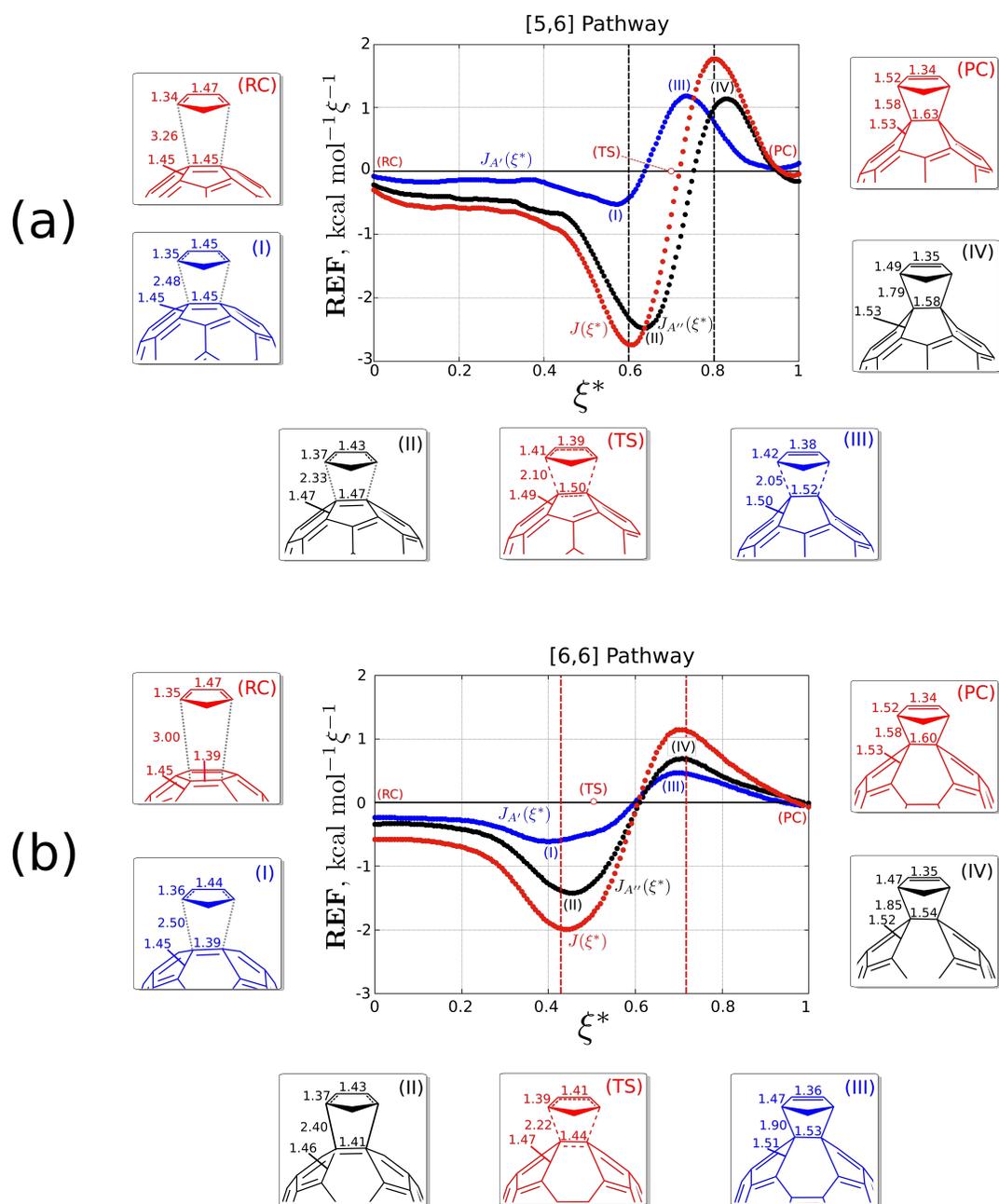


Fig. 6 Total, A' and A'' electron fluxes represented by $J(\xi^*)$, $J_{A'}(\xi^*)$ and $J_{A''}(\xi^*)$, respectively, for the [5,6] (a) and [6,6] pathway (b). Structures at key points (labeled as RC, I, II, TS, III, IV, and PC) along the reaction coordinate are shown. Distances are given in Angstroms. Vertical dashed lines correspond to the minimum and maximum of the reaction force. The vertical separators divide the reaction coordinate into reactant, transition state and product regions, respectively. In the reduced reaction coordinate, $\xi^* = 0$ is the reactant complex and $\xi^* = 1$ is the product complex (both with C_s symmetry).

the electron flux is more intense in the [5,6] path than that observed in the [6,6] path. This fact has a preponderant influence on the difference observed in the activation energies: the more intense is the electronic reordering in the activation process, the larger is the activation energy. This general pattern has been reported previously⁸².

To gain more information concerning the electronic activity that takes place along the reaction, the $J_{A'}(\xi^*)$ and $J_{A''}(\xi^*)$ fluxes are discussed hereafter. In general, it is observed that $J_{A''}(\xi^*)$ prevails over the $J_{A'}(\xi^*)$ for both cycloadditions along the entire reaction coordinate, although these differences are stressed at the flux minimum.

Regarding the $J_{A'}(\xi^*)$ profile for the [5,6] path (Figure 6(a)), it is negative all along the **RR**. The main event here is the weakening of the π bonds centered in the C1-C1' bond in fullerene and the C α -C β and C α' -C β' bonds in cyclopentadiene (see Figure 1 for labeling of atoms). The weakening and subsequent breaking of these bonds is prompted by an strong Pauli electrostatic repulsion as the reactants approach one another^{44,62}. At the $J_{A'}(\xi^*)$ minimum denoted by **(I)**, it is observed that the C α -C β and C α' -C β' bonds have changed by only 0.01 Å. The C1-C1' bond remains unchanged with respect to the **(RC)** structure, which supports the idea that up to this point weakening over breaking processes is found. Subsequent to **(I)** the π electronic activity, captured by $J_{A'}(\xi^*)$, is driven toward positive values passing through the **(TS)** structure and reaching a maximum at **(III)**. It is worth noting that at the TS structure the C α -C β and C β -C β' bond distances are very close with values of 1.41 and 1.39 Å, respectively, denoting a highly delocalized cyclopentadiene moiety. At **(III)**, the formation of the π C β -C β' bond is completed, according to the $J_{A'}(\xi^*)$ pattern. Afterwards, the π electronic activity decreases toward zero, where the π bonds both in fullerene and cyclopentadiene are formed.

The $J_{A''}(\xi^*)$ profile for the [5,6] path shows the electronic reordering for σ electrons according with the SA-REF scheme (Figure 6(a)). In the $J_{A''}(\xi^*)$ profile the electronic activity also decreases from the onset of the reaction until reaching a minimum at **(II)** located within the **TSR**. This non-spontaneous electronic activity is observed due to the weakening of the σ bonds neighboring the C1 and C1' carbon atoms in fullerene, as a consequence of the pyramidalisation of the above-mentioned atoms in the transition $sp^2 \rightarrow sp^3$. This negative peak has not been observed before for similar DA reactions⁶². When the electronic activity reaches a minimum, it increases sharply until it encounters a maximum at **(IV)**. At this spontaneous reordering, the formation of the cycloadduct by means of the synchronous formation of the two σ bonds between C1-C α and C1'-C α' is evidenced. At the **(IV)** stage, the bond distance of the C1-C α and C1'-C α' is 1.79 Å, suggesting a loosely bonded complex. Afterwards the electronic activity decreases toward the equilibrium condition, reaching zero. At the **(PC)** structure the σ bonds formed at **(IV)** are strengthened and they acquire a distance of 1.58 Å. Moreover, it is worth mention that an adjacent bond to the C1-C1' has been tracked along the reaction

coordinate from **(RC)** to **(PC)**, and has been selected to account for the pyramidalization toward the formation of the new simple bonds. As may be seen, this bond changes in length from 1.45 to 1.53 Å. Similar distortions take place in the vicinal bonds to start the σ bond formation.

Regarding the [6,6] fluxes, similar tendencies and results are extracted from $J(\xi^*)$, $J_{A'}(\xi^*)$ and $J_{A''}(\xi^*)$ (Figure 6(b)). The minimum and maximum of the REF and SA-REFs have the same interpretation as those observed for the [5,6] reaction pathway. Furthermore, some differences along the two reaction paths will be discussed hereafter. Since some differences in terms of the total REF were discussed above, special attention will be devoted to the SA-REFs, with the aim of finding differences along the two competitive paths. When the $J_{A''}(\xi^*)$ is compared between both pathways (Figures 6(a) and 6(b)) it can be seen that both minima lie at the same magnitude ca. $-0.5 \text{ kcal mol}^{-1} \xi^{-1}$, whereas the maximum in these profiles differs slightly, being of larger magnitude for the [5,6] pathway than for the [6,6] one. As shown in ref.²⁹, this difference can be attributed to the weaker orbital interactions along the reaction coordinate for the [5,6] attack as compared to the [6,6] path. It is inferred that a larger π reorganization is needed for the [5,6] path, due to a stronger Pauli electrostatic repulsion takes place on this path²⁹.

A larger difference in both reaction mechanisms that has direct consequence in the observed activation barriers is the minimum observed by entering the **TSR** in the $J_{A''}(\xi^*)$ profile. As can be observed from the $J_{A''}(\xi^*)$ profiles in Figures 6(a) and 6(b), the $J_{A''}(\xi^*)$ reaches a minimum with magnitude $|J_{A''}(\xi^*)| = 2.5$ and $|J_{A''}(\xi^*)| = 1.5 \text{ kcal mol}^{-1} \xi^{-1}$ for the [5,6] and [6,6] paths, respectively. This difference is associated with the fact that a larger energy is needed to distort the corannulenic moiety with respect to the pyracenylic fragment in the [6,6] path, in the transition $sp^2 \rightarrow sp^3$ of the C1 and C1' carbon atoms. This argument is reinforced since the TS in the [5,6] path is more product-like than that in the [6,6] path, and therefore in this former path more energy is required to distort the reactants up to the transition state structure. This energy required for a larger reorganization of the σ electrons contributes to a higher energy barrier.

4.2 Symmetry-Adapted Kinetic Energy

The kinetic energy of the electrons comes from the application of a one-electron Hermitian operator whose eigenvalues do not vary through a symmetry operation. On this basis, the obtention of kinetic energy values belonging to a different irreducible irrerepresentations is possible given the molecular symmetry. In Figure 7, the kinetic energies associated with each irreducible representation of the C_S point group are shown for each reaction path. $T_{A'}(\xi^*)$ and $T_{A''}(\xi^*)$ represent the kinetic energies of the electrons that occupy the orbitals that transform as the A' and A'' irreducible representations, respectively. In Figure 7(a), the $T_{A'}(\xi^*)$ for both reactions are shown. In this plot two maxima are seen that account for the π electronic activity, and they are located at $\xi^* \approx 0.5$ and $\xi^* \approx 0.3$ (for the [5,6] and [6,6] reaction, respectively), which are almost at the same position of the respec-

tive $J_{A'}(\xi^*)$ values shown in Figures 6(a) and 6(b). At the same time, a minimum for both pathways is observed (once leaving the respective TSR) that lies almost at the same position where the maximum of the $J_{A'}(\xi^*)$ is observed in Figures 6(a) and 6(b). This decrease of the kinetic energy for both irreducible representations in the vicinity of the transition state structure can be attributed to the increase in aromaticity of the transient species^{83–85} with delocalized electrons that have lower kinetic energy⁸⁶. The variation of the kinetic energy along the path indicates that when a bond is being weakened or broken (negative REF values) an increase in the kinetic energy is observed, which promotes a contraction of the electronic density. Conversely, when a bond is being formed or strengthened, a decrease of the kinetic energy is observed, promoting an expansion of the electronic density. Such a pattern has been reported previously by Doubleday and Houk for a series of Diels-Alder reactions⁸⁷. The authors obtained the mean kinetic energy from molecular dynamics and plotted it against the forming C–C bond distances. It was found that in the transition zone a dip in the mean kinetic energy is observed. As the C–C bond stretching dominates the transition vector for Diels-Alder reactions, the kinetic energy is a good proxy for the “flux”[†] along the reaction coordinate. This is in agreement with our results in which the minima/maxima observed in the REF profiles are in close agreement with the maxima/minima observed in the kinetic energy plots. The same conclusion can be drawn by inspection of the $T_{A''}(\xi^*)$ values with respect to the $J_{A''}(\xi^*)$ minima and maxima.

It is worth mention that in Figure 7(a) both kinetic energy profiles follow quite similar trends, although they appear shifted one with respect to the other along ξ^* . However, in Figure 7(b) a huge difference in the $T_{A''}(\xi^*)$ energy is found at the maximum for both reaction pathways. The above mentioned maxima lies almost at the same position where weakening of the σ bonds is carried out, which is observed as a negative peak in the $J_{A''}(\xi^*)$ profiles in Figures 6(a) and 6(b). Interestingly, the difference in magnitude of the negative peak observed in the $J_{A''}(\xi^*)$ profile for both reaction pathways can be understood by the positive peaks observed in $T_{A''}(\xi^*)$. Thus, the larger σ electronic activity observed in the [5,6] path caused by the weakening of the σ bonds neighboring the C1 and C1' carbon atoms (prompted by the $sp^2 \rightarrow sp^3$ transition) is fully consistent with a larger kinetic energy for those σ electrons.

5 Conclusions

We have analyzed the two reaction mechanisms of the cycloaddition reaction between C_{60} and cyclopentadiene corresponding to the [5,6] and [6,6] attacks. Partition of the total reaction electronic flux $J(\xi^*)$ into $J_{A'}(\xi^*)$ and $J_{A''}(\xi^*)$ contributions allowed us to understand whether π and/or σ bonding changes take place along the progress of the reaction. The $J_{A'}(\xi^*)$ facilitates understanding the π reordering, whereas $J_{A''}(\xi^*)$ accounts for σ bonding

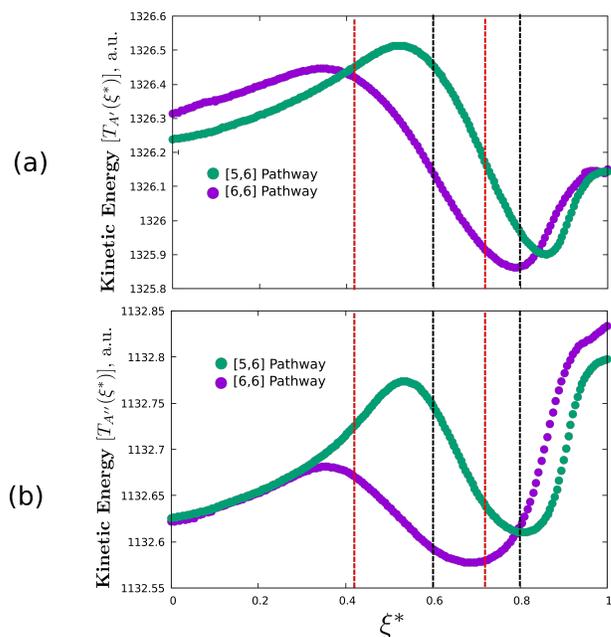


Fig. 7 Kinetic energies computed for each irreducible representation ($T_{\Gamma_i}(\xi^*)$) along the reaction coordinate. Reported are (a) A' kinetic energy $[T_{A'}(\xi^*)]$ and (b) A'' kinetic energy $[T_{A''}(\xi^*)]$ for the [5,6] and [6,6] reaction pathways. Vertical dashed lines correspond to the minimum and maximum of the reaction force; they are black and red for the [5,6] and [6,6] paths, respectively. These vertical lines divide the reaction coordinates into reactant, transition state and product regions, respectively. In the reduced reaction coordinate, $\xi^* = 0$ is the reactant complex and $\xi^* = 1$ is the product complex (both with C_s symmetry).

changes. It was found that the [6,6] path prevails over the [5,6] due to a lower activation energy and greater exothermicity. With the use of the SA-REF it was found that the dominating event that drives the appearance of the differences in activation energies between the [5,6] and [6,6] path is due to a non-spontaneous σ electronic activity, which appears as a result of the weakening of the C–C bonds due to pyramidalization of the C1, C1', C_α and $C_{\alpha'}$ carbon atoms. Inspection of the kinetic energy of both irreducible representations showed that when a bond is being weakened/broken (negative values of REF) an increase in the kinetic energy occurs which we associate with a contraction of the electronic density in the vicinity of the chemical event. Conversely, when a bond is being formed/strengthened (positive REF values) a decreasing of the kinetic energy is observed and therefore an expansion of the electronic density occurs. Moreover, the decrease of the kinetic energy of electrons suppose the increase in aromaticity in the vicinity of the transition state. The SA-REF is a useful tool derived from a global property that gives valuable information about local bonding changes taking place along a reaction pathway. From the detailed characterization and rationalization of the chemical events in the present contribution, modulation of reactivity could be achieved as desired, thus controlling the regioselectivity of this kind of reactions.

[†] The “flux” reported by Doubleday and Houk differs from the definition of the REF, which comes from the change of the electronic chemical potential. The “flux” is referred to the fingerprint of transition state theory, i.e., the TS is the minimum flux of forward-moving trajectories – the dynamical bottleneck.

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