Supporting Information

Simple Bond Patterns Predict the Stability of Diels–Alder Adducts of Empty Fullerenes

Paula Pla,^a Yang Wang,^{*abc} and Manuel Alcamí^{*abd}

^aDepartamento de Química, Módulo 13, Universidad Autónoma de Madrid, 28049 Madrid, Spain. ^bInstitute for Advanced Research in Chemical Sciences (IAdChem), Universidad Autónoma de Madrid, 28049 Madrid, Spain.

^cSchool of Chemistry and Chemical Engineering, Yangzhou University, Yangzhou, Jiangsu 225002, China. ^dInstituto Madrileño de Estudios Avanzados en Nanociencia (IMDEA-Nanociencia), Cantoblanco, 28049 Madrid, Spain.

Table of Contents

1. Correlation between reaction energies and energy barriers	2	
2. Computational details	2	
 Comparison between fullerene reactivity with dienes 1,3-butadiene and cyclopentadiene		
		7
		8 9
	9. Correlation between X^{j} and the \sum MCI descriptor for other fullerenes	
	References	21

1. Correlation between reaction energies and energy barriers.

Correlation between reaction energies and energy barriers for $C_{60}(1)^1$, $C_{70}(1)^1$, $C_{76}(1)$, $C_{84}(23)$, $C_{78}(5)^2$ and $C_{68}(6140)^3$, with BD. Reaction energies and energy barriers for fullerenes $C_{70}(1)$, $C_{78}(5)$ and $C_{68}(6140)$ have been taken from references 1-3. Values for $C_{76}(1)$ and $C_{84}(23)$ were calculated at M062X/6-31G(d,p)⁴ DFT level of theory.



Figure S1. Correlation between DFT reaction energies ΔE_R and DFT energy barriers ΔE^{\ddagger} for the most stable neutral cages of fullerenes a) $C_{60}(1)$, b) $C_{70}(1)$, c) $C_{76}(1)$ and d) $C_{84}(23)$ with BD. Correlation coefficient R^2 is indicated.

2. Computational details

Structure optimizations of regioadducts obtained from the Diels-Alder (DA) reaction of $C_{76}(1)$ and $C_{84}(23)$ with 1,3-butadiene (BD) and cyclopentadiene (Cp) to all non-equivalent bonds were performed. The computations were carried out in gas phase at the M062X/6-31G(d,p)⁴ DFT level of theory, by using the Gaussian 09 package.⁵ M062X functional was designed to treat non-covalent interactions and therefore it includes at least, partially dispersion. Nevertheless, although dispersion is important for DA reaction on fullerenes as it changes the absolute values of reaction energies and energy barriers, the relative energies do not vary with the inclusion of dispersion corrections.⁶ Results for C₆₀ and C₇₀ with BD were obtained at the same level of theory from the literature.¹

All possible candidates of the most stable isomers of bare IPR fullerenes were taken from previous works⁷, where geometries were fully optimized at the B3LYP/6-31G(d) level. These possible candidates were chosen as follows: for fullerenes from C_{60} to C_{88} , we included all possible IPR isomers; for fullerenes from C_{90} to C_{120} and from C_{122} to C_{180} , we chose, respectively the 10-12 and 5 lowest energy isomers.

The bond orders and free valences are calculated following the Coulson scheme.⁸ Within the framework of HMO theory, the π bond order between atoms *a* and *b*, B_{ab} , is calculated as:

$$B_{ab} = \sum_{i=1}^{n} c_{ai} c_{bi} \tag{S1}$$

where c_{ai} and c_{bi} are coefficients of the *i*-th Hückel molecular orbital (MO) corresponding to atoms *a* and *b*, respectively. The sum is over all *n* occupied MOs for a neutral fullerene C_{2n}. The π free valence of atom *a*, F_a , is calculated as:

$$F_a = \sqrt{3} - \sum_b B_{ab} \tag{S2}$$

where $\sqrt{3}$ is the maximum π bonding power for a carbon atom as in trimethylenemethane, and the sum is over all the neighboring atoms {*b*} that are bonded to atom *a*.

The multicenter index (MCI)⁹ of a given λ -membered ring R is calculated using the following formula¹⁰:

$$MCI(R) = \sum_{P(R)} I_{ring}(R)$$
(S3)

where string $R = \{ab, bc, ..., \lambda a\}$ contains λ elements that are ordered according to the connectivity of the atoms in the ring; P(R) is permutation operator that generates N! permutations of the elements in string R; $I_{\text{ring}}(R)$ is the multicenter bond index proposed by Giambiagi et al.¹¹, which can be calculated using the HMO theory, as follows:

$$I_{\rm ring}(R) = 2^{\lambda} B_{ab} B_{bc} \dots B_{\lambda a}$$
(S4)

Note that here in the HMO theory each atom has only one atomic basis that is orthogonal to others.

3. Comparison between fullerene reactivity with dienes 1,3-butadiene and cyclopentadiene

We wanted to analyze the influence of the diene in the relative DA reaction energies obtained for the different regioadducts. For that, we selected empty fullerenes $C_{76}(1)$ and $C_{84}(23)$, which are added to two different dienes, namely, BD and Cp. Figures S2 and S3 show that the relative reaction energies for both dienes are very similar, which highlights that the diene has a minor influence on the relative energies of the regioadducts.



Figure S2. Correlation between DFT reaction energies ΔE_R and π stabilization index X^j for fullerene C₇₆(1) with dienes (a) BD and (b) Cp. The color and symbol codes are the same as in Figure 2 of the manuscript and the correlation coefficient R^2 is indicated.



Figure S3. Idem Figure S2 for fullerene C₈₄(23).

4. Correlation between DFT reaction energies and X^{j} for IPR fullerenes C₇₄(1), C₇₈(5), C₈₀(6) and C₈₀(7)

The correlation between DFT reaction energies and π stabilization index was also obtained for other empty IPR fullerenes. The results of C₇₄(1), C₇₈(5), C₈₀(6) and C₈₀(7), together with their Schlegel diagrams, are depicted in Figures S4-S7, respectively. As we can see, they follow the same trend as in the cases presented in Figure 2 of the manuscript. DFT reaction energies for these systems have been obtained from the literature^{2,12} except for C₇₄(1) that has been calculated at M062X/6-31G(d,p) level of theory.



Figure S4. Correlation between DFT reaction energies ΔE_R and π stabilization index X^j for fullerene C₇₄(1) with BD. Correlation coefficient is indicated. Non-equivalent bonds are highlighted in the Schlegel diagram. Pentagons are colored in yellow. DFT reaction energies have been calculated at M062X/6-31G(d,p) level of theory.



Figure S5. Idem Figure S4 for fullerene $C_{78}(5)$ with BD. DFT reaction energies have been obtained from reference 2.



Figure S6. Idem Figure S4 for fullerene $C_{80}(6)$ with BD. DFT reaction energies have been obtained from reference 12.



Figure S7. Idem Figure S4 for fullerene $C_{80}(7)$ with BD. DFT reaction energies have been obtained from reference 12.

5. Correlation between DFT reaction energies and XSI index for non-IPR fullerenes C₆₈(6140) and C₇₈(22010)

The correlation between DFT reaction energies and the XSI index¹³ was also obtained for some non-IPR fullerenes. In this case, the classification of bond types has been realized using the major bond types first proposed by Poblet and co-workers¹⁴ depicted in Figure S8. The results of C₆₈(6140) and C₇₈(22010) together with their Schlegel diagrams are depicted in Figures S9 and S10, respectively. DFT reaction energies for these systems have been obtained from the literature^{3,15}.



Figure S8. Illustrations of all major bond types found in IPR and non-IPR fullerenes without triple fused pentagons. Isolated pentagon rings are colored in yellow and fused pentagons in purple. Major bond types E and F are only found in non-IPR fullerenes.



Figure S9. Correlation between DFT reaction energies ΔE_R and the XSI index for non-IPR fullerene C₆₈(6140) with BD. Correlation coefficient is indicated. Non-equivalent bonds are highlighted in the Schlegel diagram colored according to major bond types of Figure S8. Isolated pentagons are colored in yellow and fused pentagons in purple. DFT reaction energies have been obtained from reference 3.



Figure S10. Idem Figure S9 for fullerene $C_{78}(22010)$ with BD. DFT reaction energies have been obtained from reference 15.

6. All possible bond patterns in IPR fullerenes

Figure S11 depicts explicitly all possible bond patterns of IPR fullerenes defined in Figure 1 of the manuscript.



Figure S11. Explicit illustrations of all bond patterns in Figure 1 of the manuscript. Different major types of bonds are denoted with a capital letter and grouped into different colors (A: blue, B: green, C: red, D: magenta). The following number counts the pentagon rings in the second layer. Pentagon rings in the first layer are colored in yellow whereas pentagons in the second layer are colored in light blue. Note that for C2 subtype there exist three different patterns, as we do not distinguish the locations of pentagon rings in the second layer.

7. General correlations

General correlations exist for all the cages studied in the main article. In particular, two correlations can be obtained for the values of the reaction energies (ΔE_R) and the X^j and CARI indexes:

 $\Delta E_R = 133.0 * X^j - 307.9 \text{ kcal/mol}$

 $\Delta E_R = -206.8 * CARI - 478.9 \text{ kcal/mol}$



Figure S12. General correlations including fullerenes $C_{60}(1)$, $C_{70}(1)$, $C_{76}(1)$ and $C_{84}(23)$ between reaction energies ΔE_R and (a) X^j index and (b) CARI index.



8. Correlation between X^j and the CARI descriptor for other fullerenes

Figure S13. Correlation between X^j and the CARI descriptor for all possible DA adducts of empty IPR fullerenes C₆₀ and C₇₀–C₇₈. For each cage size, the cage structure corresponds to the lowest-energy isomer.^{7,16} The color and symbol codes are the same as in Figure 2 in the manuscript. Correlation coefficients R^2 are indicated.



Figure S14. Idem Figure S13 for fullerenes C_{80} - C_{90} .



Figure S15. Idem Figure S13 for fullerenes C_{92} - C_{102} .



Figure S16. Idem Figure S13 for fullerenes C_{104} - C_{114} .



Figure S17. Idem Figure S13 for fullerenes C_{116} - C_{126} .



Figure S18. Idem Figure S13 for fullerenes C₁₂₈-C₁₃₈.



Figure S19. Idem Figure S13 for fullerenes C_{140} - C_{150} .



Figure S20. Idem Figure S13 for fullerenes C_{152} - C_{162} .



Figure S21. Idem Figure S13 for fullerenes C_{164} - C_{174} .



Figure S22. Idem Figure S13 for fullerenes C_{176} - C_{180} .

9. Correlation between X^{j} and the \sum MCI descriptor for other fullerenes



Figure S23. Correlation between X^{j} and the Σ MCI descriptor for all possible DA adducts of empty IPR fullerenes C₇₀, C₈₀, C₉₀, C₁₀₀, C₁₁₀ and C₁₂₀. For each cage size, the cage structure corresponds to the lowest-energy isomer.^{7,16} The color and symbol codes are the same as in Figure 2 in the manuscript. Correlation coefficients R^{2} are indicated.



Figure S24. Idem Figure S23 for fullerenes C_{130} , C_{140} , C_{150} , C_{160} , C_{170} and C_{180} .

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