Supporting Information

When is Bell-Evans-Polanyi principle fulfilled in Diels-alder reactions on fullerenes?

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1 Computational details and functional benchmarking

DFT calculations of reactants, products and transition states (TSs) were optimized using M06-2X/6-31G(d,p)[1] level of theory with the Gaussian 09 program package.[2] The QST2 algorithm, in which the geometry of the products and reactants is given, was used to search and optimize TSs. Frequency and IRC calculations have been done to ensure that the TSs found were first order saddle points (one imaginary frequency) and that the located TSs were connected to the corresponding products. Also they were used to obtain energies for the reactant complexes on selected adducts. NICS and TDDFT calculations have been performed at the same M06-2X/6-31G(d,p) level of theory with Gaussian 09 program package. Maximum bonding fragment orbital (MBFO) analysis[3] was conducted to reveal the frontier orbital interactions between the diene and the fullerene fragments in the whole system at the geometry of the TS. Nomenclature of fullerene isomers follows the Fowler-Manolopoulos ring spiral algorithm.[4]

Fullerenes C\textsubscript{70} (1) and C\textsubscript{80} (6) were chosen as a test case to ensure that the trends obtained in this study do not vary with the functional chosen. Figure S1 shows the correlation between reaction energy and energy barriers of C\textsubscript{70} (1) and C\textsubscript{80} (6) using functionals M06-2X, B3LYP and BP86 with 6-31G(d,p) basis set. The same trends are observed independently of the functional, but the M06-2X was chosen due to the incorporation of at least, some dispersion. This functional has been used in previous studies of the DA reaction in fullerenes.[5] TS of adduct 4 of C\textsubscript{80} (6) using BP86 was not possible to optimize due to the tiny HOMO-LUMO gap.[6]

Figure S1: Benchmark of functionals M06-2X, B3LYP and BP86 for fullerenes C\textsubscript{70} (1) and C\textsubscript{80} (6).
2 Geometrical parameters of transition states of C_{68} (6290) and C_{76} (1)

Table S1 and S2 show the distances of the C–C bonds that are being formed during the DA reaction in the optimized geometry of the TS for C_{76} (1) and C_{68} (6290), respectively. The mean of the two distances is also presented in the last column.

**Table S1:** C–C distances of the two bonds that are formed during the DA reaction for adducts of C_{76} (1) in the optimized geometry of the TS.

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C$_6$(6290) in the optimized geometry of the TS.

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3 Correlation between reaction energies and reaction enthalpies and reaction Gibbs free energies

Figure S2 shows that the trends in the results obtained for reaction energies are also maintained when studying reaction enthalpies and reaction Gibbs free energies.

![Figure S2: Correlation between reaction energy and reaction enthalpy of a) C\textsubscript{76} (1) and c) C\textsubscript{80} (2) and between reaction energy and reaction Gibbs free energy of b) C\textsubscript{76} (1) and d) C\textsubscript{80} (2).](image)

4 Correlation between HOMO–LUMO gap and $R^2$

Figure S3 shows the correlation between HOMO–LUMO gap and $R^2$ for all fullerenes considered in this article (data of Table 1).

![Figure S3: Correlation between HOMO–LUMO gap and correlation coefficient $R^2$ of all fullerenes considered.](image)
5 Correlations for other fullerenes

Figure S4 shows the correlation between the reaction energy and energy barrier for the other fullerenes discussed in the main article.

(a) C₆₈ (6140) non-IPR

(b) C₇₀ (1)

(c) C₇₀ (7854) non-IPR

(d) C₇₈ (3)

(e) C₇₈ (5)

(f) C₈₀ (1)

(g) C₈₄ (23)

Figure S4: Correlations between reaction energies and energy barriers for all possible regioisomers of fullerenes a) C₆₈ (6140), b) C₇₀ (1), c) C₇₀ (7854), d) C₇₈ (3), e) C₇₈ (5), f) C₈₀ (1) and g) C₈₄ (23).
6 Correlation of C$_{70}$ (7854)

Figure S5 shows correlation of C$_{70}$ (7854) including all possible adducts found (left) and only showing the [4+2] adducts confirmed by the IRC (Intrinsic Reaction Coordinate) calculation (right).

![Figure S5: Correlation between reaction energies and energy barriers for C$_{70}$ (7854) including all possible adducts found (left) and only showing [4+2] adducts (right).](image)

7 Schlegel diagrams

Figure S6 shows Schlegel diagrams of selected fullerenes. Regioisomers that have been mentioned are highlighted in each case.

![Figure S6: Schlegel diagrams of fullerenes a) C$_{78}$ (3), b) C$_{78}$ (5), c) C$_{80}$ (2), d) C$_{80}$ (6) and e) C$_{80}$ (7).](image)
8 Difference of NICS between adduct and empty cage at 1 Å above the center of each ring for $C_{80}$ (2)

Figure S7 shows the difference of NICS at 1 Å above the center of each ring for selected adducts of $C_{80}$ (2). Note that the difference of NICS for adducts 3, 10 and 22 is smaller than for adducts 16, 19 and 30 that are the ones that deviate from the correlation.

**Figure S7:** Difference of NICS at 1 Å above the center of each ring for selected adducts of $C_{80}$ (2). The two carbon atoms where the addition is taking place are marked with green circles. The four rings that surround the bond where the addition is taking place are set to zero.
9 Correlation, NICS and molecular orbitals of $C_{78}$ (3)

Figure S8 shows correlation, NICS and molecular orbitals of $C_{78}$ (3). The same conclusions of Figure 4 of the main article can be drawn.

**Figure S8:** a) Correlation between reaction energies and energy barriers for all possible regioadducts formed by DA addition of 1,3-butadiene with fullerene $C_{78}$ (3). b) Evolution of the NICS value in the center of the cage during DA reaction of 1,3-butadiene with fullerene $C_{78}$ (3) for some adducts. c) HOMO and LUMO orbitals for selected adducts (10 and 12) and for the empty cage.
10 Correlation, NICS and molecular orbitals of C\textsubscript{78} (5)

Figure S9 shows correlation, NICS and molecular orbitals of C\textsubscript{78} (5). In this case, molecular orbitals are more mixed than in other cases and the correlation coefficient between reaction energies and energy barriers is not that good. For instance, HOMO of adduct b is HOMO-1 of the empty cage. Note that adduct c which has the HOMO and the LUMO orbitals exchanged, is the adduct which is more deviated from the correlation line.

\[
\begin{align*}
R^2 & = 0.67 \\
\Delta E^\ddagger / \text{kcal/mol} & = 0 \\
\Delta E_R / \text{kcal/mol} & = -50, -25, 0, 25 \\
\end{align*}
\]

\begin{figure}[h]
\centering
\includegraphics[width=\textwidth]{figure_s9.png}
\caption{a) Correlation between reaction energies and energy barriers for all possible regioadducts formed by DA addition of 1,3-butadiene with fullerene C\textsubscript{78} (5). b) Evolution of the NICS value in the center of the cage during DA reaction of 1,3-butadiene with fullerene C\textsubscript{78} (5) for some adducts. c) HOMO-1, HOMO, LUMO and LUMO+1 orbitals for selected adducts (1, 5, b and c) and for the empty cage.}
\end{figure}
Complete analysis of reaction energies and energy barriers of C\textsubscript{80} (2) considering reactant complexes

Table S3: Energy of formation of the reactant complex (\(\Delta E_{RC}\)), energy barrier from reactants (\(\Delta E_1\)) and reactant complex (\(\Delta E_2\)) and reaction energy (\(\Delta E_R\)) for all possible adducts of DA addition on C\textsubscript{80} (2) fullerene.

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Figure S10: Energy diagrams for the DA reaction on C<sub>80</sub> (2) of a) normal behavior adduct (3), b) one with high energy reactant complex (30) and c) one with high energy barrier (16).
References


