

Physical Chemistry Chemical Physics

Electronic supplementary information

Unveiling the role of intra and interatomic interactions in the energetics of reaction schemes: a quantum chemical topology analysis

Jesús Jara-Cortés, Bruno Landeros-Rivera, Jesús Hernández-Trujillo

Departamento de Física y Química Teórica.
Facultad de Química, UNAM. México City, 04510 México.

Convergence of the energy contributions with the basis set

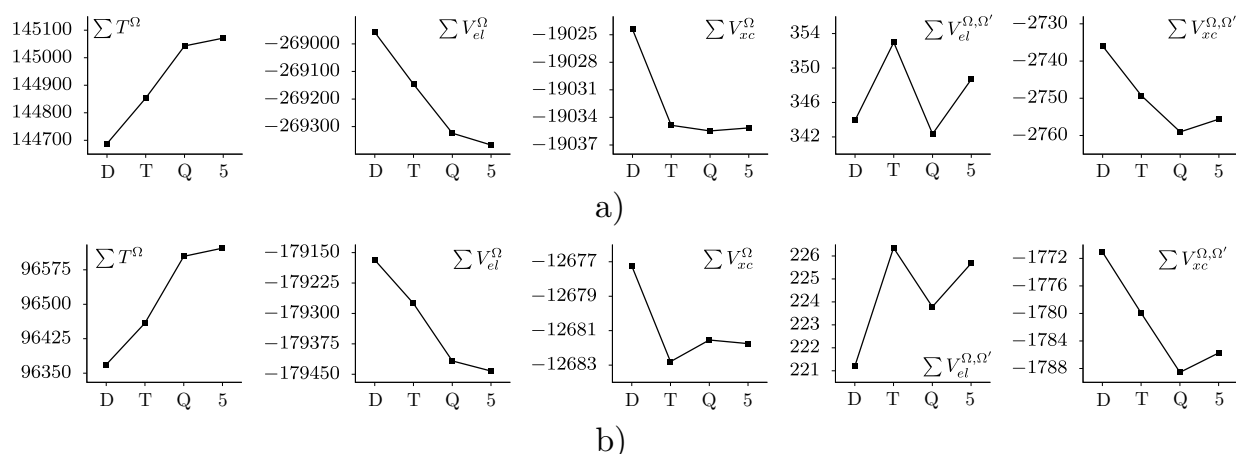


Figure S1. Total sum of the IQA energy components in terms of the basis size for a) benzene and b) cyclobutadiene. The basis sets correspond to cc-pVXZ, where X = (D,T,Q,5); the energies are given in kcal/mol.

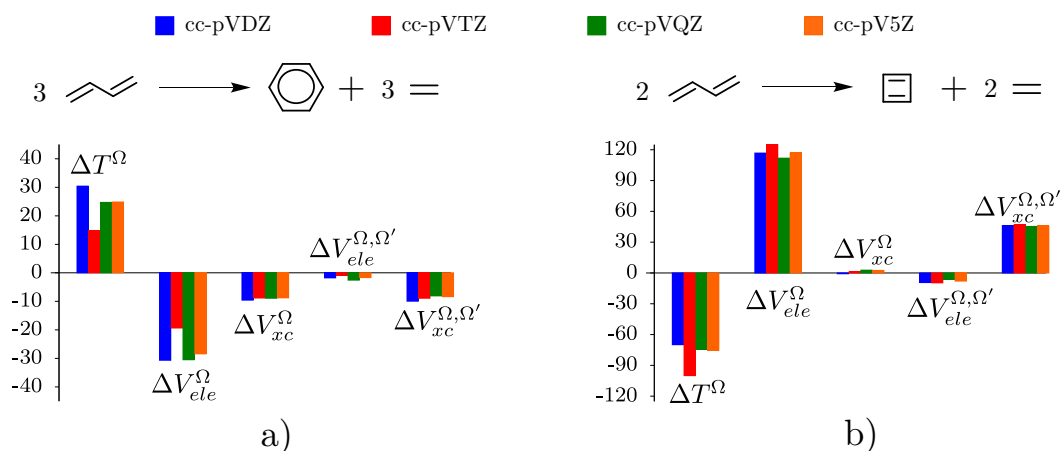


Figure S2. Total changes in the IQA energy components in terms of the basis size for the formation of a) benzene, and b) cyclobutadiene from t-1,3-cyclobutadiene and ethylene; the energies are given in kcal/mol.

Ring strain

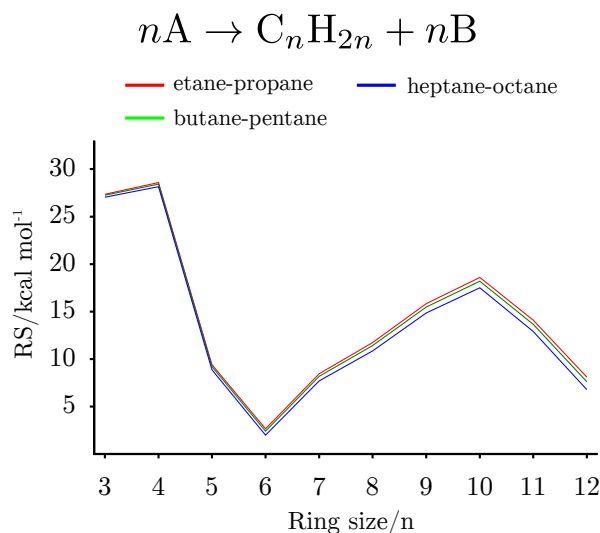


Figure S3. Ring strain values of the cycloalkanes obtained by reactions schemes in function of the ring size; the A-B pair refers to the reference molecules

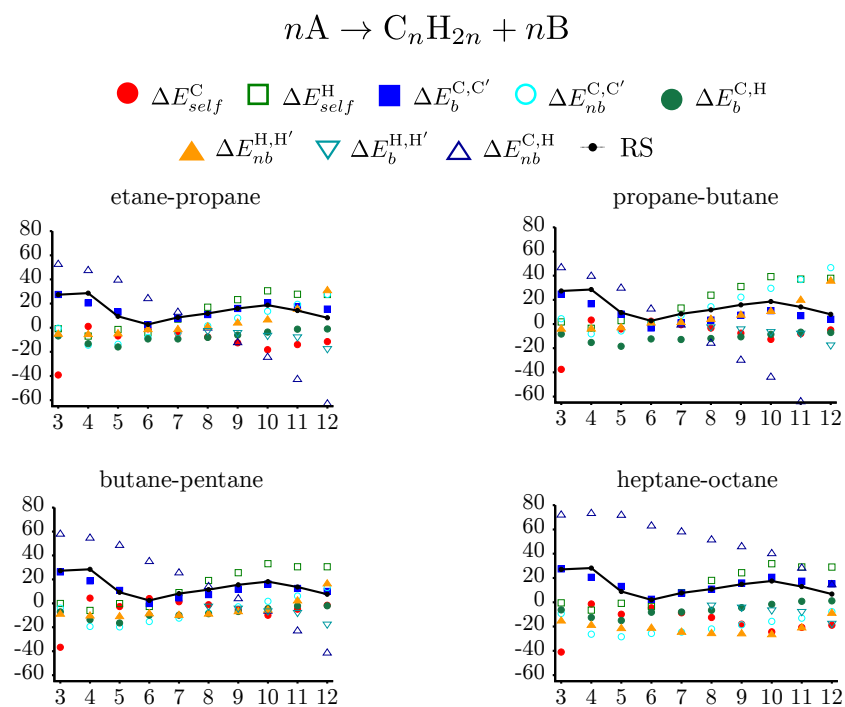


Figure S4. Total changes of the atomic and interaction contributions to ring strain (kcal/mol) in terms of the rings size (carbon number); the A-B pair refers to the reference molecules.

Resonance energy

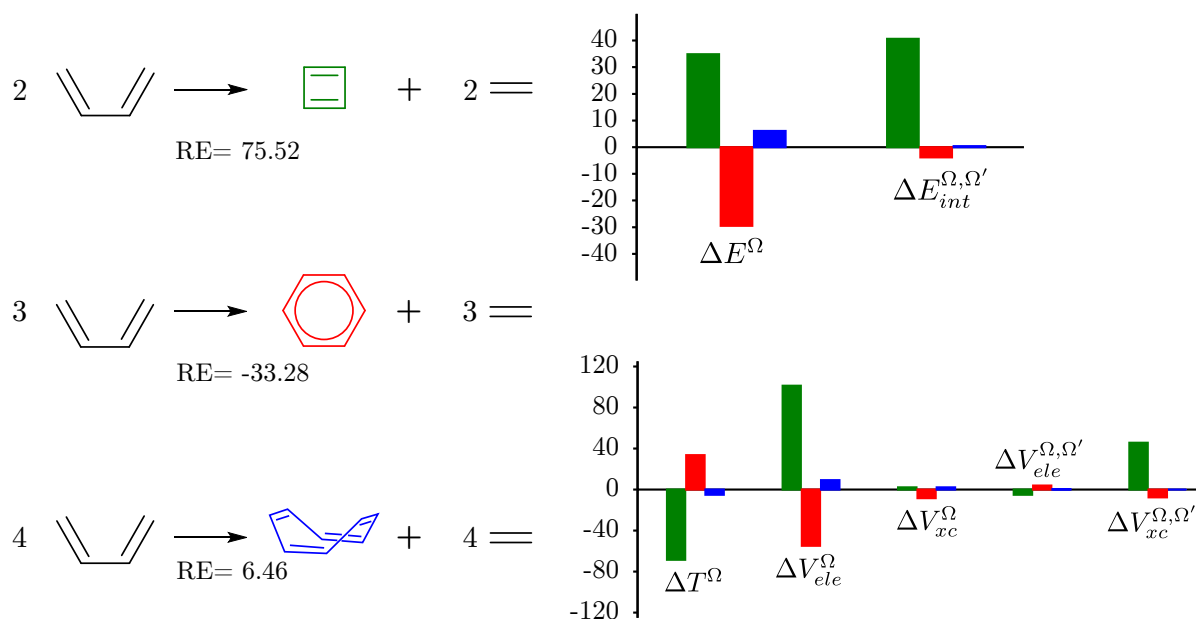


Figure S5. Total changes of the IQA energy components for the formation of cyclobutadiene, benzene and 1,3,5,7-cyclooctatetraene from c-1,3-butadiene and ethylene. The values are given in kcal/mol.

	C ₄ H ₄	C ₆ H ₆	C ₈ H ₈
ΔE_{self}^C	38.41	-14.96	7.92
ΔE_{self}^H	-3.54	-8.29	-1.84
$\Delta E_b^{C,C'}$	20.77	-4.29	-5.13
$\Delta E_{nb}^{C,C'}$	-0.37	-5.42	-0.21
$\Delta E_b^{C,H}$	1.18	-15.25	-7.38
$\Delta E_{nb}^{C,H}$	17.03	15.91	11.48
$\Delta E_{nb}^{H,H'}$	2.04	1.27	1.61
<i>RE</i>	75.52	-31.04	6.46

Table S1: Resonance energies (RE), and the sum of the atomic and interaction contributions to RE for the formation of cyclobutadiene, benzene and 1,3,5,7-cyclooctatetraene from c-1,3-butadiene and ethylene. The *b* (*nb*) subscript refers to interaction terms of atoms pairs linked (not linked) by a bond path; the data are in kcal/mol.

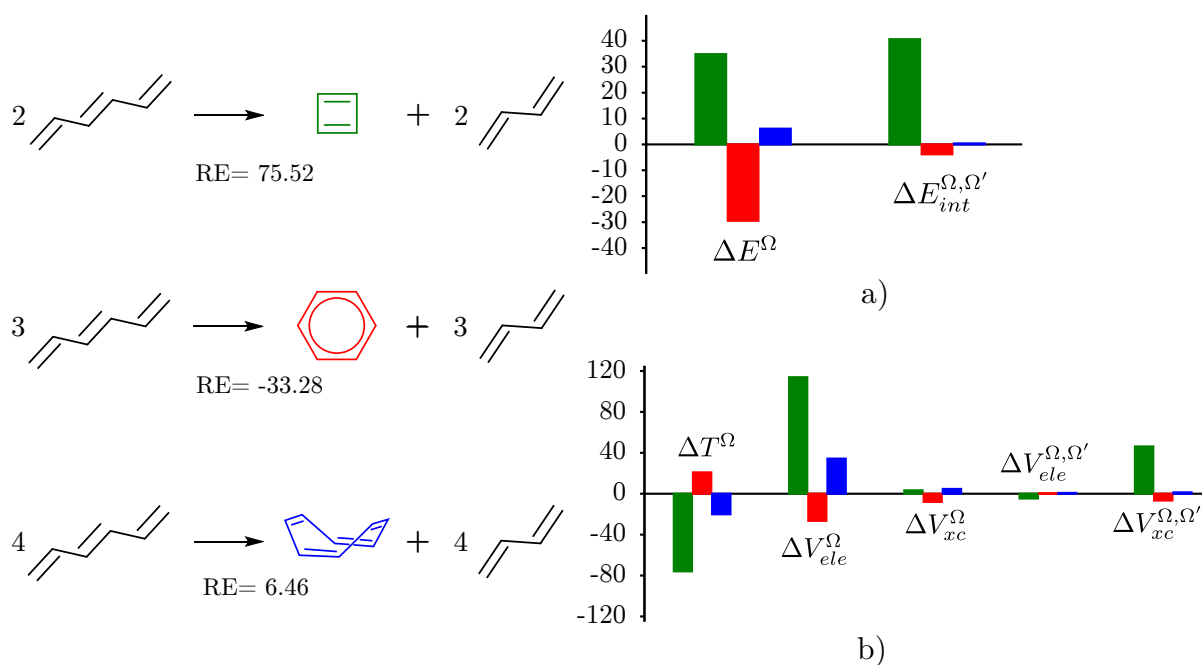


Figure S6. Total changes of the IQA energy components for the formation of cyclobutadiene, benzene and 1,3,5,7-cyclooctatetraene from (E)-1,3,5-hexatriene and t-1,3-butadiene. The values are given in kcal/mol.

	C ₄ H ₄	C ₆ H ₆	C ₈ H ₈
ΔE_{self}^C	40.57	-11.71	12.25
ΔE_{self}^H	0.73	-1.89	6.69
$\Delta E_b^{C,C'}$	23.03	-0.89	-0.60
$\Delta E_{nb}^{C,C'}$	0.04	-4.81	0.61
$\Delta E_b^{C,H}$	1.17	-15.27	-7.40
$\Delta E_{nb}^{C,H}$	12.47	9.06	2.36
$\Delta E_{nb}^{H,H'}$	4.81	5.43	7.16
<i>RE</i>	82.83	-20.08	21.07

Table S2: Resonance energies (RE), and the sum of the atomic and interaction contributions to RE for the formation of cyclobutadiene, benzene and 1,3,5,7-cyclooctatetraene from (E)-1,3,5-hexatriene and t-1,3-butadiene. The *b* (*nb*) subscript refers to interaction terms of atoms pairs linked (not linked) by a bond path; the data are in kcal/mol.

		C ₄ H ₄	C ₆ H ₆
	$2 \text{ } \square \longrightarrow \square + \square$		
	$3 \text{ } \text{C}_6\text{H}_6 + \text{C}_6\text{H}_6 \longrightarrow \text{C}_6\text{H}_6 + 3 \text{ } \text{C}_6\text{H}_6$		
		ΔE_{self}^C	19.31 -18.46
		ΔE_{self}^H	5.23 -0.44
		$\Delta E_b^{C,C}$	23.11 -6.55
		$\Delta E_{nb}^{C,C}$	2.48 -3.64
		$\Delta E_b^{C,H}$	-10.68 -7.72
		$\Delta E_{nb}^{C,H}$	-5.36 4.06
		$\Delta E_{nb}^{H,H}$	1.27 -1.91
		RE	35.37 -34.65

Figure S7. Total changes of the IQA energy components for the formation of benzene and cyclobutadiene. The values are given in kcal/mol.

Aromaticity dilution

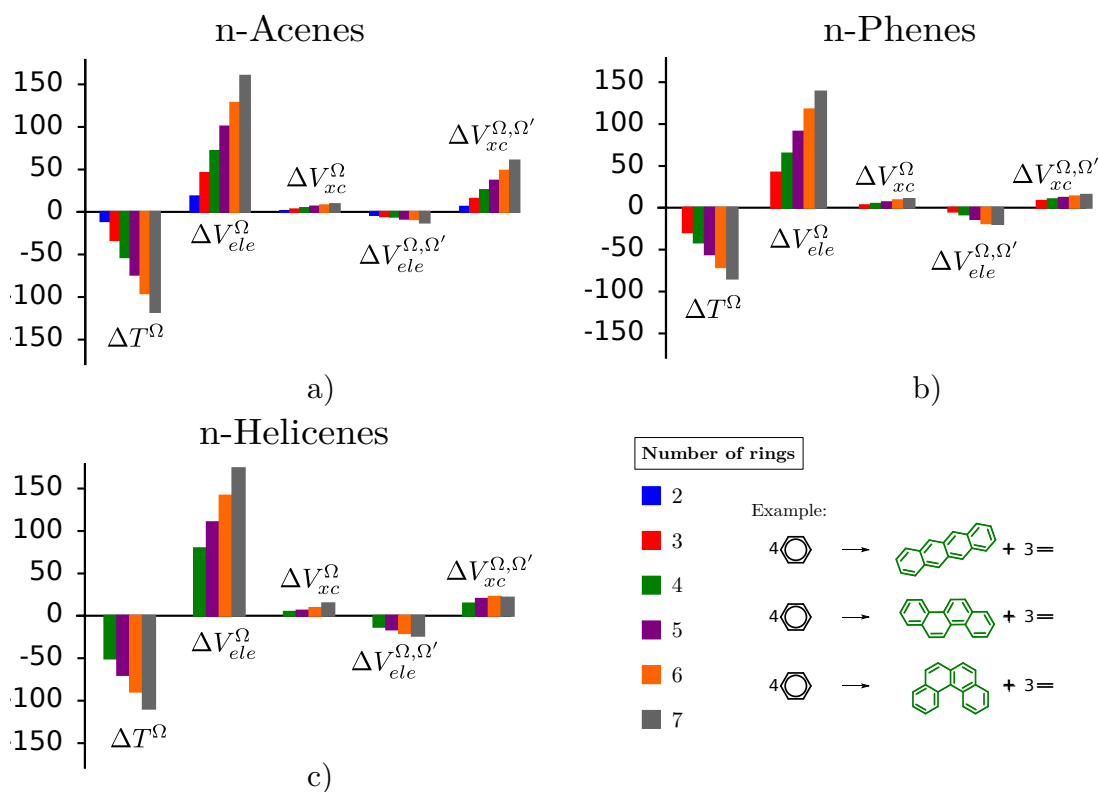


Figure S8. Total changes of the IQA energy components for the formation of the n-acenes, n-phenes and n-helicene series from ethylene and benzene; the data are given in kcal/mol.

Hydrogen bond

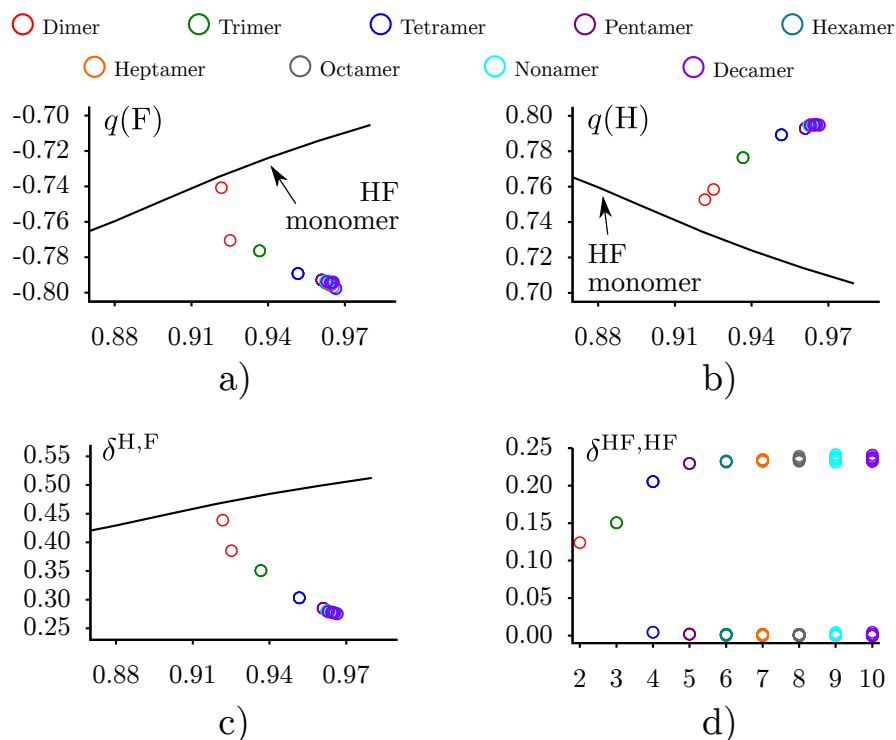


Figure S9. Fluoride and hydrogen atomic charges (a, b) and intratomic H-F delocalization indexes (c) in terms of the R_{HF} distance; d) HF-HF intermolecular delocalization indexes in terms of the cluster size (HF molecules). The charges and delocalizations are in a.u. and the distances in Å.

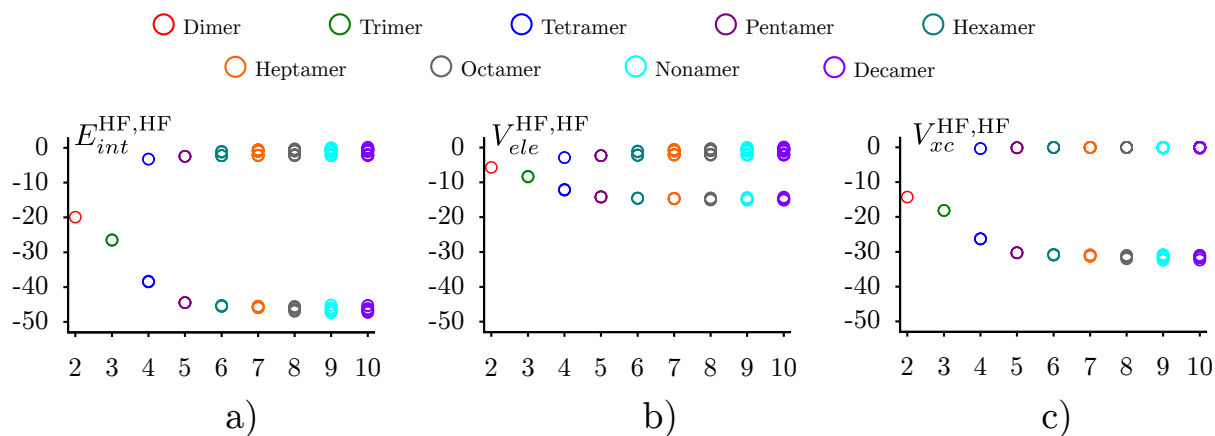


Figure S10. a) HF-HF intermolecular interaction energies along with its b) electrostatic and c) exchange-correlation contributions in terms of the cluster size (HF molecules). All energies are given in kcal/mol.

Binding energy of hydrated *d*-block metals

An initial arrangement with a T_h symmetry point group was used for the geometry optimization calculations of the $[M(H_2O)_6]^{+2}$ complexes. The optimized geometries, along with the final point groups and the non-equivalent M-O distances are depicted in Figure S11. Unless otherwise stated, all O-M-O angles correspond to 90° . Two imaginary frequencies were found for the Fe and Cu complexes. For the former, both frequencies were associated with rotations of water molecules on two perpendicular C_2 axis. For the latter, the two frequencies are associated with out-of-plane bending moments. Further exploration of the potential energy surface with the def2-TZVP basis set revealed that these configurations are only 0.25 and 0.08 kcal/mol above the corresponding equilibrium geometries, in which the D_{2h} symmetry is lost. This justifies the use of the highly symmetric complexes for the analysis, since the energy differences are negligible compared to BE_{hyd} .

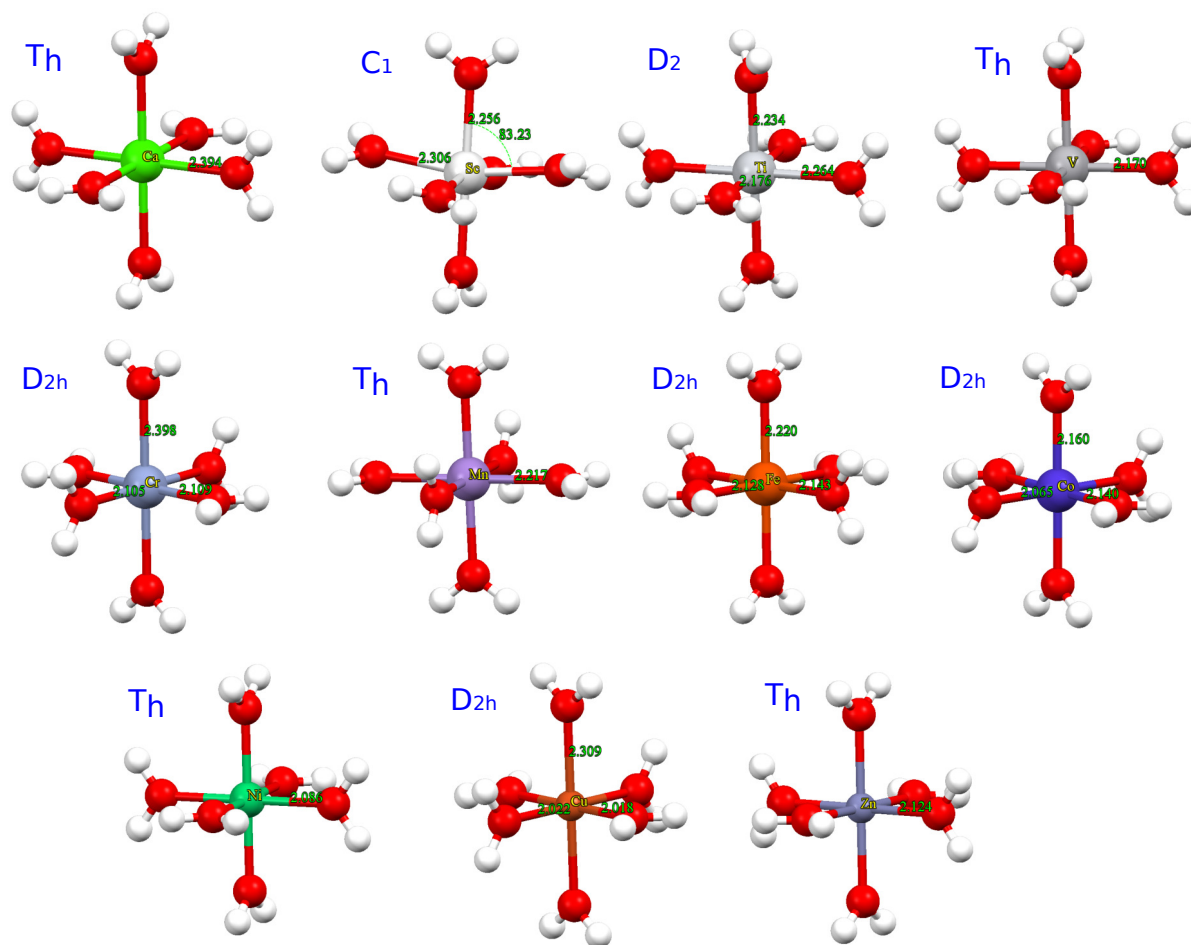


Figure S11. Optimized geometries of the $[M(H_2O)_6]^{+2}$. Non-equivalent M-O distances (Å) and final point groups in green and red colors, respectively.

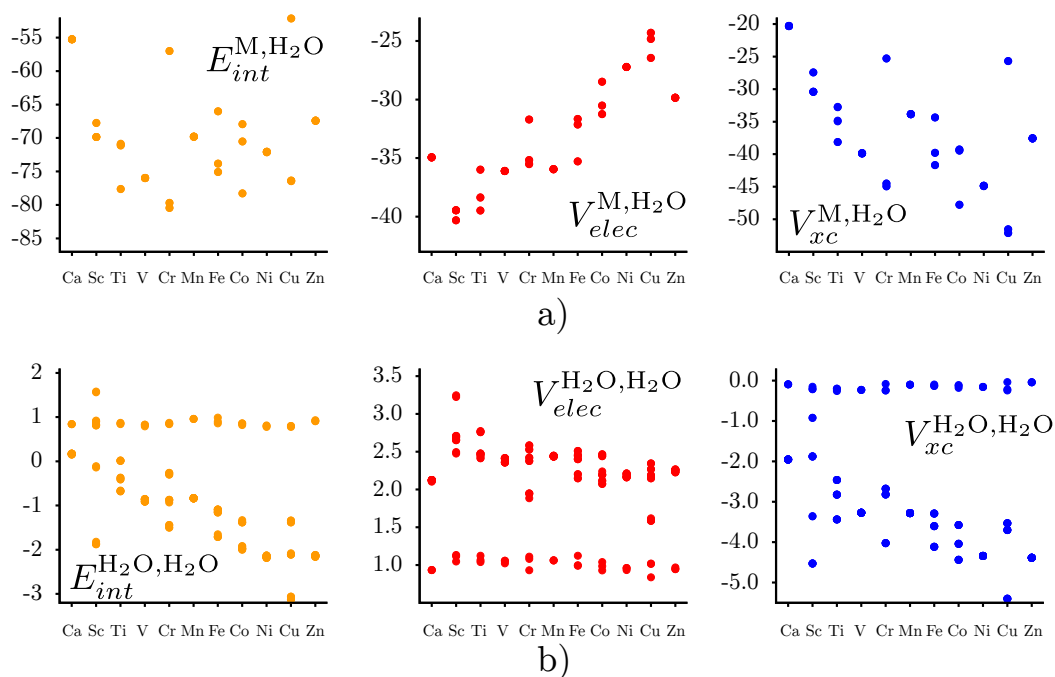


Figure S12. Water-metal (a) and water-water (b) intermolecular interaction energies along with its electrostatic and exchange-correlation contributions. All the data are given in kcal/mol.

Energy decomposition analysis

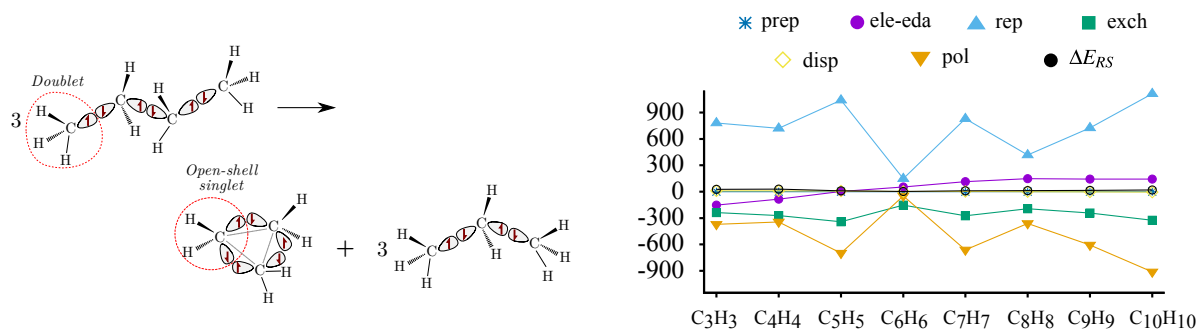


Figure S13. LMOEDA electrostatic, exchange, repulsion, polarization and dispersion energy changes for the cycloalkanes reaction schemes; the energy values are given in kcal/mol.

Scaling of the IQA contributions

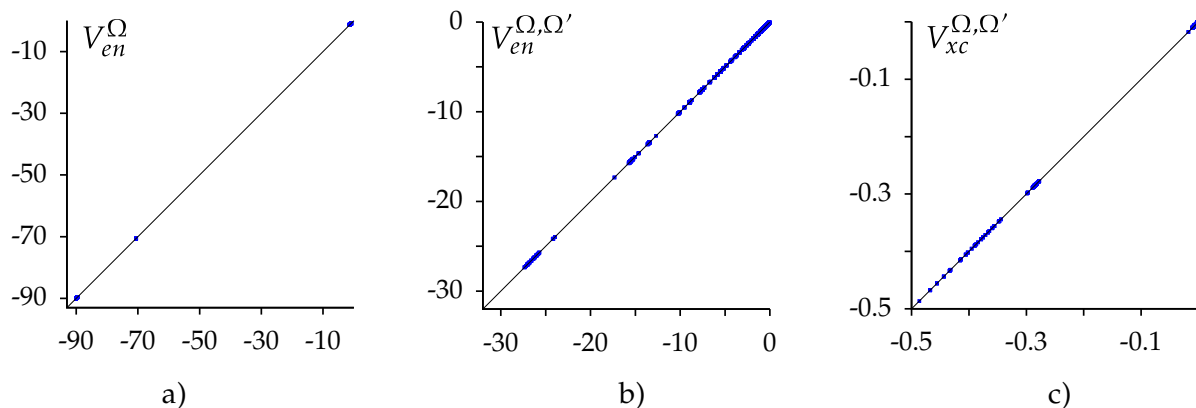


Figure S14. IQA energy components (u.a.) obtained by integration as a function of the values evaluated from the θ weighting factors and the total energetic terms. a) Atomic nucleus-electron potential energy, b) nucleus-electron interaction and c) exchange-correlation interaction. The data (DFT/cc-pVQZ) correspond to the equilibrium geometries of: cyclopropane, cyclobutane, octane, ethylene, 1,3,5-hexatriene, benzene, naphthalene, anthracene, phenanthrene and heptacene. The linear least-squares parameters $m = 1.0000$ and $b = 0.0000$, and a correlation coefficient of $R^2 = 1.0000$ are obtained in the three cases.