ELECTRONIC SUPPLEMENTARY INFORMATION

Singlet 2-Adamantylidene – An Ambiphilic Foiled Carbene Stabilized by Hyperconjugation

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Figure S7: Plots of important NOCV pair of orbitals Ψ_{-n}/Ψ_n with their eigen values in the parenthesis, the associated deformation densities $\Delta\rho_n$ and the orbital stabilization energies ΔE for the complex **5** at the BP86/TZ2P level of theory.

Scheme S1: Schematic representation of the bending angle, θ_b, and the pyramidalization angle, θ_p, at the C2-atom.

Table S1: Computational Methodology

All geometries were optimized at the DFT level of theory using the exchange functional of Becke in conjunction with the correlation functional of Perdew (BP86).[1] The basis sets used is def2-TZVPP.[2] The calculations were carried out with the Gaussian 09 program package.[3] Single point calculations on the BP86/def2-TZVPP optimized geometries have also been carried out using meta-GGA exchange correlation functional M06 with def2-TZVPP basis set.[4] Natural bond order (NBO) calculations were computed at the same level of theory.[5] The energies at M06/def2-TZVPP level were corrected by adding the zero point energies from the BP86/def2-TZVPP level of theory.

Energy Decomposition Analysis (EDA)[6] were performed for the all the structures using ADF 2012.01[7] program package at the BP86 level with a triple ζ basis set with two sets of polarization functions (TZ2P) with a frozen-core approximation for the core electrons.[8] For performing the EDA calculations we have used the optimized geometries from the Gaussian 09 calculations at the BP86/def2-TZVPP level of theory.

The EDA analysis is a quantitative method for describing the chemical bonds in the molecule. We have used the Natural Orbital Chemical Valence (NOCV) approach to understand more about the nature of the donor acceptor interaction in our systems. In the EDA analysis the instantaneous interaction energy ΔE_{int} of the bond is calculated as the difference in energy between the molecule and its respective fragments in the frozen geometry states of the compound. The instantaneous interaction energy ΔE_{int} between the two fragments A and B is divided into sum of the three components (Equation (1)). First term, ΔE_{elstat}, includes the quasiclassical electrostatic interaction term, Second term, ΔE_{pauli}, incorporates the repulsive interaction between electrons of the fragments having the identical spin and the final term, ΔE_{orb}, is the energy term which involves stabilization of molecular orbitals to form the original molecule.

$$\Delta E_{int} = \Delta E_{elstat} + \Delta E_{pauli} + \Delta E_{orb} \qquad (1)$$

The bond dissociation energy D_e (Equation (2)) is calculated as the sum of the preparatory energy ΔE_{prep} and ΔE_{int}. The preparatory energy is the energy required to promote the fragments from their ground state to the electronic and geometric state in the molecule.

$$- D_e = (\Delta E_{int} + \Delta E_{prep}) \qquad (2)$$

Mitoraj and Michalak had extended the EDA analysis which decomposes the ΔE_{orb} term into the contributions from different natural orbitals of chemical valence (NOCV).[9] The EDA-NOCV schemes combines the charge rearrangement (NOCV) and the energy partitioning (EDA) analysis to decompose the deformation density, $\Delta\rho$, which is incorporated with bond formation into different components of the chemical bond. The EDA-NOCV calculations provide pair-wise energy contributions from the NOCV pairs (ψ_{-n}/ψ_n) to the total bond energy. NOCV are defined as the eigenvectors of the chemical valence operator, $\hat{P}$ (Equation (3)).

$$\hat{P}\psi_i = p_i\psi_i \qquad (3)$$

The deformation density $\Delta\rho$ (Equation (4)) can be expressed as the sum of pairs of complementary eigenfunctions (ψ_{-n},ψ_n) corresponding to the eigen values p_{-n} and p_n, respectively.

$$\Delta\rho = \sum \Delta\rho = \sum p_n \left[-\psi^2_{-n} + \psi^2_{-n}\right] \qquad (4)$$

In the EDA-NOCV analysis the orbital interaction, ΔE_{orb} is expressed in terms of NOCV as shown in the Equation 5.

$$\Delta E_{orb} = \sum_{n=1}^{N/2} \Delta E_n^{orb} = \sum_{n=1}^{N/2} p_n \left[-F^{TS}_{-n\,n} + F^{TS}_{-n\,n}\right] \qquad (5)$$

F^{TS}_{-n} and F^{TS}_{n} are diagonal transition-state Kohn-Sham matrix elements corresponding to the NOCV pairs with eigen values p_{-n} and p_n, respectively.

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Table S2: Optimized Cartesian coordinates and total energies including zero point energy correction E_1 (in a.u.) of all the calculated molecules at the BP86/def2-TZVPP level of theory and E_2 total energy at the M06/def2-TZVPP level of theory including zero point energy correction from the BP86/def2-TZVPP level of theory using G09 program package. Symmetry of the structures is mentioned in the parenthesis. The number of imaginary frequencies are abbreviated as Nimag.

1(T_d)
E_1 = -390.61151a.u.
E_2 = -390.31765 a.u.
Nimag = nil

6	-0.892476000	0.892476000	0.892476000
1	-1.528761000	1.528761000	1.528761000
6	0.000000000	1.781034000	0.000000000
1	-0.626748000	2.437208000	-0.626748000
1	0.626748000	2.437208000	0.626748000
6	0.000000000	0.000000000	1.781034000
1	0.626748000	0.626748000	2.437208000
1	-0.626748000	-0.626748000	2.437208000
6	0.892476000	-0.892476000	0.892476000
1	1.528761000	-1.528761000	1.528761000
6	0.892476000	0.892476000	-0.892476000
1	1.528761000	1.528761000	-1.528761000
6	-1.781034000	0.000000000	0.000000000
1	-2.437208000	-0.626748000	0.626748000
1	-2.437208000	0.626748000	-0.626748000
6	-0.892476000	-0.892476000	-0.892476000
1	-1.528761000	-1.528761000	-1.528761000
6	0.000000000	-1.781034000	0.000000000
1	-0.626748000	-2.437208000	0.626748000
1	0.626748000	-2.437208000	-0.626748000
6	0.000000000	0.000000000	-1.781034000
1	-0.626748000	0.626748000	-2.437208000
1	0.626748000	-0.626748000	-2.437208000
6	1.781034000	0.000000000	0.000000000
1	2.437208000	0.626748000	0.626748000
1	2.437208000	-0.626748000	-0.626748000

2(C_s)
E_1 = -389.29457 a.u.
E_2 =-389.00486 a.u.
Nimag = nil

6	1.423528000	-0.568725000	0.000000000
1	2.464316000	-0.932000000	0.000000000
6	0.686713000	-1.088991000	1.244308000

1	0.705378000	-2.190452000	1.268021000
1	1.179255000	-0.744147000	2.170260000
6	1.417564000	0.972564000	0.000000000
1	1.952487000	1.353903000	0.885871000
1	1.952487000	1.353903000	-0.885871000
6	-0.034138000	1.495296000	0.000000000
1	-0.032007000	2.598522000	0.000000000
6	-0.784125000	-0.596215000	1.224171000
1	-1.319700000	-0.930801000	2.127923000
6	0.686713000	-1.088991000	-1.244308000
1	1.179255000	-0.744147000	-2.170260000
1	0.705378000	-2.190452000	-1.268021000
6	-0.784125000	-0.596215000	-1.224171000
1	-1.319700000	-0.930801000	-2.127923000
6	-0.784125000	0.990689000	-1.240031000
1	-0.296780000	1.298560000	-2.179168000
1	-1.815694000	1.371354000	-1.255159000
6	-1.584248000	-0.840661000	0.000000000
6	-0.784125000	0.990689000	1.240031000
1	-0.296780000	1.298560000	2.179168000
1	-1.815694000	1.371354000	1.255159000

2'(C_{2v})
E_1 = -389.29340 a.u.
E_2 = -389.00407 a.u.
Nimag = 1 (302.8i)

6	1.261017000	0.000000000	-0.837714000
1	2.161409000	0.000000000	-1.475229000
6	1.270941000	1.240736000	0.064141000
1	2.178817000	1.257150000	0.687261000
1	1.263100000	2.175541000	-0.521301000
6	0.000000000	0.000000000	-1.723837000
1	0.000000000	0.885901000	-2.380718000
1	0.000000000	-0.885901000	-2.380718000
6	-1.261017000	0.000000000	-0.837714000
1	-2.161409000	0.000000000	-1.475229000
6	0.000000000	1.226233000	0.979528000
1	0.000000000	2.135631000	1.603386000
6	1.270941000	-1.240736000	0.064141000
1	1.263100000	-2.175541000	-0.521301000
1	2.178817000	-1.257150000	0.687261000
6	0.000000000	-1.226233000	0.979528000
1	0.000000000	-2.135631000	1.603386000
6	-1.270941000	-1.240736000	0.064141000
1	-1.263100000	-2.175541000	-0.521301000

1	-2.178817000	-1.257150000	0.687261000
6	0.000000000	0.000000000	1.823857000
6	-1.270941000	1.240736000	0.064141000
1	-1.263100000	2.175541000	-0.521301000
1	-2.178817000	1.257150000	0.687261000

3(C_{2v})
E_1 = -389.29037 a.u.
E_2 =-388.99994 a.u.
Nimag = nil

6	1.263478000	0.000000000	-0.811983000
1	2.161228000	0.000000000	-1.452101000
6	1.271040000	1.268865000	0.068636000
1	2.173802000	1.297934000	0.697860000
1	1.277734000	2.172632000	-0.565518000
6	0.000000000	0.000000000	-1.698315000
1	0.000000000	0.886087000	-2.355466000
1	0.000000000	-0.886087000	-2.355466000
6	-1.263478000	0.000000000	-0.811983000
1	-2.161228000	0.000000000	-1.452101000
6	0.000000000	1.271517000	0.976850000
1	0.000000000	2.158445000	1.629726000
6	1.271040000	-1.268865000	0.068636000
1	1.277734000	-2.172632000	-0.565518000
1	2.173802000	-1.297934000	0.697860000
6	0.000000000	-1.271517000	0.976850000
1	0.000000000	-2.158445000	1.629726000
6	-1.271040000	-1.268865000	0.068636000
1	-1.277734000	-2.172632000	-0.565518000
1	-2.173802000	-1.297934000	0.697860000
6	0.000000000	0.000000000	1.731755000
6	-1.271040000	1.268865000	0.068636000
1	-1.277734000	2.172632000	-0.565518000
1	-2.173802000	1.297934000	0.697860000

4(C_s)
E_1 = -389.71855a.u.
E_2 =-389.42170 a.u.
Nimag = nil

6	1.437799000	-0.574286000	0.000000000
1	2.471764000	-0.949436000	0.000000000
6	0.711913000	-1.084090000	1.256870000
1	0.728131000	-2.182644000	1.309854000
1	1.197618000	-0.713247000	2.170995000
6	1.453788000	0.967350000	0.000000000
1	1.990090000	1.345014000	0.883325000

1	1.990090000	1.345014000	-0.883325000
6	0.006122000	1.501185000	0.000000000
1	0.016979000	2.606824000	0.000000000
6	-0.757855000	-0.608849000	1.244989000
1	-1.343546000	-0.914319000	2.121408000
6	0.711913000	-1.084090000	-1.256870000
1	1.197618000	-0.713247000	-2.170995000
1	0.728131000	-2.182644000	-1.309854000
6	-0.757855000	-0.608849000	-1.244989000
1	-1.343546000	-0.914319000	-2.121408000
6	-0.757855000	1.041321000	-1.235813000
1	-0.273327000	1.294406000	-2.190355000
1	-1.786968000	1.424152000	-1.260452000
6	-1.451414000	-0.803565000	0.000000000
6	-0.757855000	1.041321000	1.235813000
1	-0.273327000	1.294406000	2.190355000
1	-1.786968000	1.424152000	1.260452000
1	-2.544942000	-0.888807000	0.000000000

4'(C$_{2v}$)
E$_1$ = -389.71619a.u.
E$_2$ = -389.41741 a.u.
Nimag = 1 (297.2i)

6	-1.251769000	0.000000000	0.860803000
1	-2.155940000	0.000000000	1.495327000
6	-1.281474000	1.248739000	-0.018644000
1	-2.187382000	1.294448000	-0.638355000
1	-1.226815000	2.178652000	0.565670000
6	0.000000000	0.000000000	1.757946000
1	0.000000000	0.884054000	2.412732000
1	0.000000000	-0.884054000	2.412732000
6	1.251769000	0.000000000	0.860803000
1	2.155940000	0.000000000	1.495327000
6	0.000000000	1.244430000	-0.972750000
1	0.000000000	2.121122000	-1.631258000
6	-1.281474000	-1.248739000	-0.018644000
1	-1.226815000	-2.178652000	0.565670000
1	-2.187382000	-1.294448000	-0.638355000
6	0.000000000	-1.244430000	-0.972750000
1	0.000000000	-2.121122000	-1.631258000
6	1.281474000	-1.248739000	-0.018644000
1	1.226815000	-2.178652000	0.565670000
1	2.187382000	-1.294448000	-0.638355000
6	0.000000000	0.000000000	-1.703229000
6	1.281474000	1.248739000	-0.018644000
1	1.226815000	2.178652000	0.565670000

1	2.187382000	1.294448000	-0.638355000
1	0.000000000	0.000000000	-2.800358000

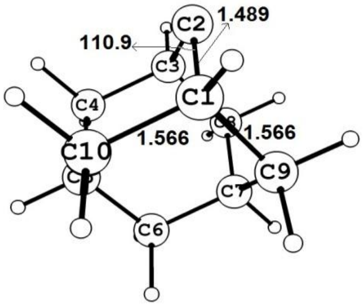
5(C_s)
E_1 = -389.96040a.u.
E_2 =-389.66083a.u.
Nimag = nil

6	0.058962000	1.529549000	0.000000000
1	0.072723000	2.637384000	0.000000000
6	0.766705000	0.997131000	1.266339000
1	1.812489000	1.345788000	1.288053000
1	0.246156000	1.392037000	2.163716000
6	-1.406624000	1.041883000	0.000000000
1	-1.936048000	1.432404000	0.890178000
1	-1.936048000	1.432404000	-0.890178000
6	-1.442556000	-0.501741000	0.000000000
1	-2.497111000	-0.837129000	0.000000000
6	0.766705000	-0.550415000	1.238761000
1	1.260457000	-0.917234000	2.160884000
6	0.766705000	0.997131000	-1.266339000
1	0.246156000	1.392037000	-2.163716000
1	1.812489000	1.345788000	-1.288053000
6	0.766705000	-0.550415000	-1.238761000
1	1.260457000	-0.917234000	-2.160884000
6	-0.725190000	-1.017490000	-1.268928000
1	-1.275587000	-0.653756000	-2.170619000
1	-0.753451000	-2.120974000	-1.294781000
6	1.532618000	-1.030168000	0.000000000
6	-0.725190000	-1.017490000	1.268928000
1	-1.275587000	-0.653756000	2.170619000
1	-0.753451000	-2.120974000	1.294781000
1	1.563315000	-2.144647000	0.000000000

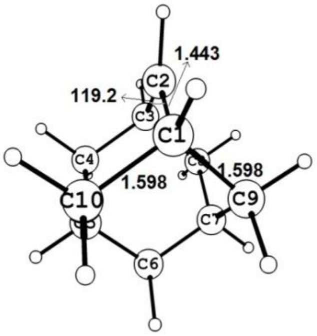
Table S3: Selected charge, occupancy and second order interaction energies given by the natural population analysis for **1**, **2**, **2'**, **3**, **4**, **4'** and **5** at the M06/def2-TZVPP//BP86/def2-TZVPP level of theory.

Structure	**NBO Charge**		**Occupancy**				**Second Order Interaction**		
	C2	**C2–X**[a]	**σ(C2)**[b]	**p_x(C2)**[b]	**C1-C9**	**C1-C10**	**Donor**	**Acceptor**	**Energy (kcal/mol)**
1	-0.39	-	-	-	1.98	1.98	σ(C2–H)	σ∗(C1–C10)	3.2
2	0.20	-	1.89	0.20	1.97	1.92	σ(C1–C10) σ(C2)	p_x(C2) σ∗(C1–C9)	15.4 8.5
2′	0.24	-	1.90	0.16	1.95	1.95	σ(C1–C10) σ(C2)	p_x(C2) σ∗(C1–C9)	5.8 3.5
3	0.23	-	0.96	0.93	1.96	1.96	σ(C1–C9) σ(C1–C9) σ(C2) p_x(C2)	σ(C2) p_x(C2) σ∗(C1–C9) σ∗(C1–C9)	4.1 2.8 1.6 4.9
4	0.32	0.55	-	0.47	1.97	1.82	σ(C1–C10)	p_x(C2)	30.1
4′	0.37	0.60	-	0.42	1.90	1.90	σ(C1–C10)	p_x(C2)	10.6
5	-0.70	-0.57	1.82	-	1.98	1.98	σ(C2)	σ∗(C1–C9)	12.3

[a] X represents the substituent on the C2 atom , where X = H_2, H^+, H^+ and H^- in **1**, **4, 4'** and **5**, respectively. [b] **σ(C2)** formally represents the lone-pair orbital on C2 atom in **2**, **2'** and **5** whereas half filled orbital in **3** and **p_x(C2)** represents the vacant p-orbital on C2 atom in **2**, **2'**, **4** and **4'**and half filled orbital in **3**.

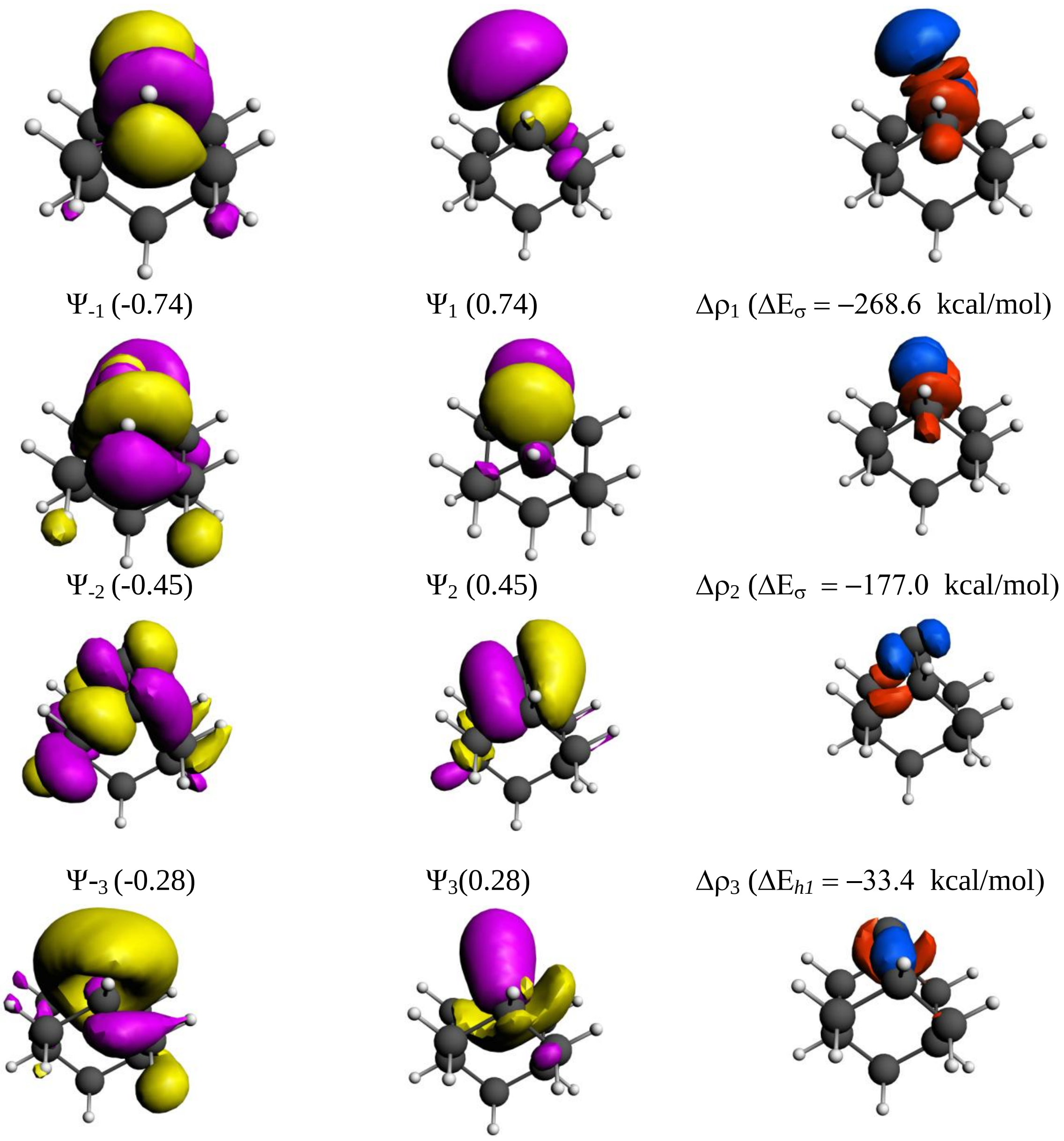


2'(C$_{2v}$)
Nimag = 1 (302.8i)



4'(C$_{2v}$)
Nimag = 1 (297.2i)

Figure S1: Optimized geometries (BP86/def2-TZVPP) of the transition states **2'**and **4'**. The point group symmetry and imaginary vibrational frequency are also given.



Ψ_{-1} (-0.74)

Ψ_{1} (0.74)

$\Delta\rho_1$ ($\Delta E_{\sigma} = -268.6$ kcal/mol)

Ψ_{-2} (-0.45)

Ψ_{2} (0.45)

$\Delta\rho_2$ ($\Delta E_{\sigma} = -177.0$ kcal/mol)

Ψ_{-3} (-0.28)

Ψ_{3}(0.28)

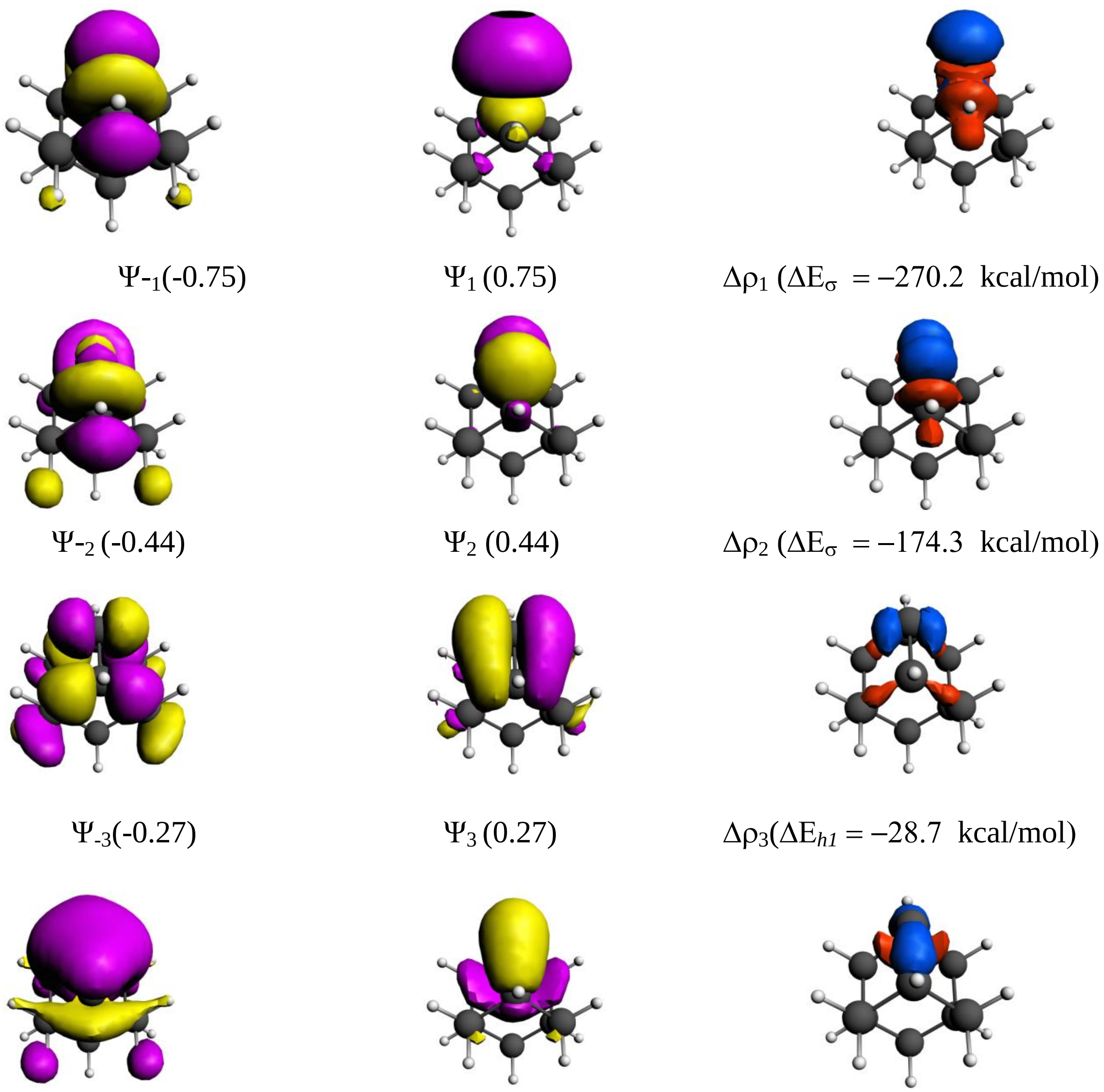
$\Delta\rho_3$ ($\Delta E_{h1} = -33.4$ kcal/mol)

Ψ_{-4}(-0.10)

Ψ_{4} (0.10)

$\Delta\rho_4$($\Delta E_{h2} = -13.0$ kcal/mol)

Figure S2: Plots of important NOCV pair of orbitals Ψ_{-n}/Ψ_n with their eigen values in the parenthesis, the associated deformation densities $\Delta\rho_n$ and the orbital stabilization energies ΔE for the complex **2** at the BP86/TZ2P level of theory. The direction of charge flow in the deformation densities is from red→ blue. The NOCV orbitals are plotted with a contour value 0.03. The deformation density, $\Delta\rho_n$ is plotted with a contour value 0.003 for n=1–3 and 0.001 for $\Delta\rho_4$.



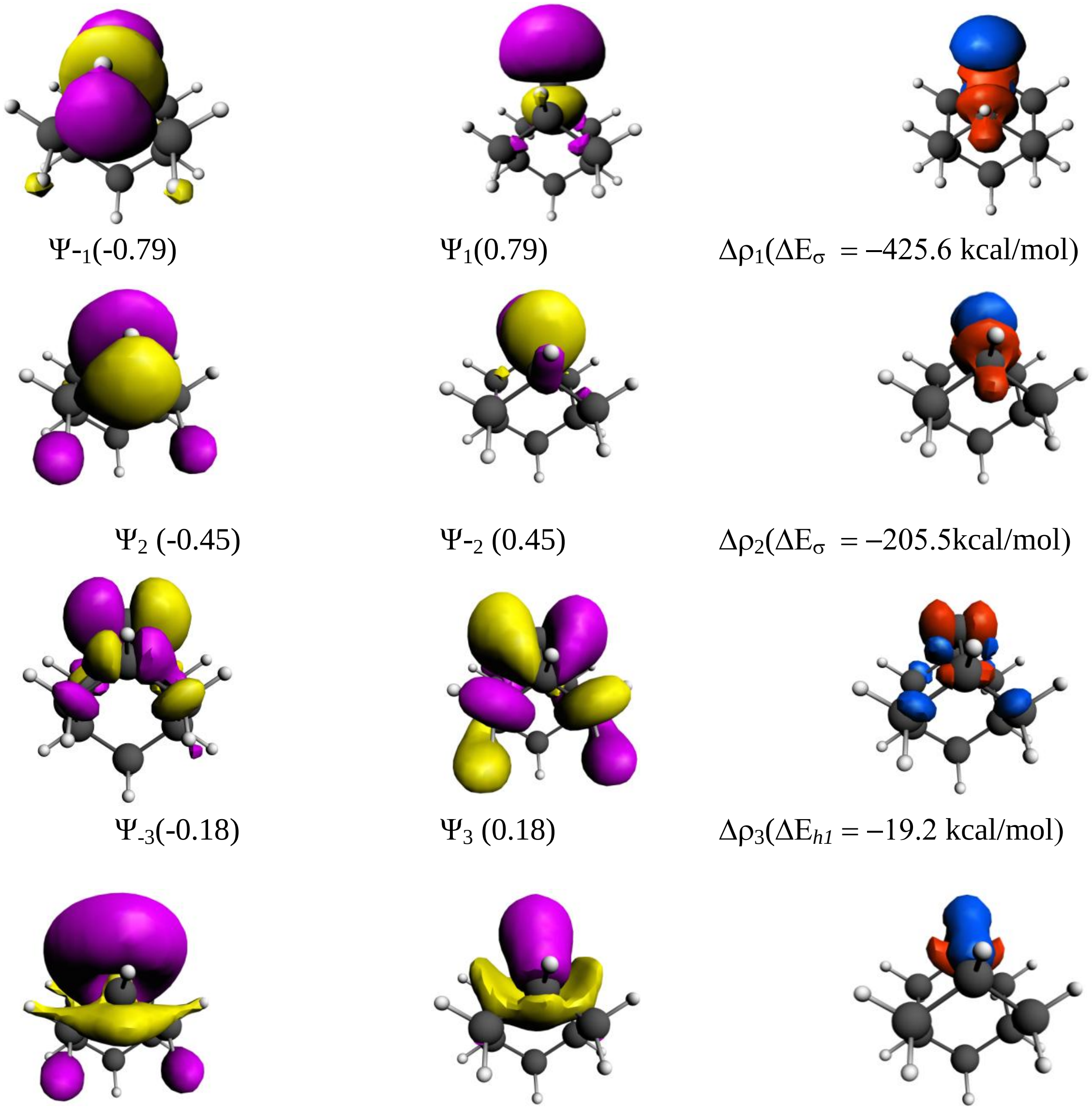
Ψ_{-1}(-0.75) Ψ_1 (0.75) $\Delta\rho_1$ ($\Delta E_\sigma = -270.2$ kcal/mol)

Ψ_{-2} (-0.44) Ψ_2 (0.44) $\Delta\rho_2$ ($\Delta E_\sigma = -174.3$ kcal/mol)

Ψ_{-3}(-0.27) Ψ_3 (0.27) $\Delta\rho_3$($\Delta E_{h1} = -28.7$ kcal/mol)

Ψ_{-4}(-0.10) Ψ_4 (0.10) $\Delta\rho_4$ ($\Delta E_{h2} = -12.5$ kcal/mol)

Figure S3: Plots of important NOCV pair of orbitals Ψ_{-n}/Ψ_n with their eigen values in the parenthesis, the associated deformation densities $\Delta\rho_n$ and the orbital stabilization energies ΔE for the complex **2′** at the BP86/TZ2P level of theory. The direction of charge flow in the deformation densities is from red→ blue. The NOCV orbitals are plotted with a contour value 0.03. The deformation density, $\Delta\rho_n$ is plotted with a contour value 0.003 for n=1–3 and 0.001 for $\Delta\rho_4$.



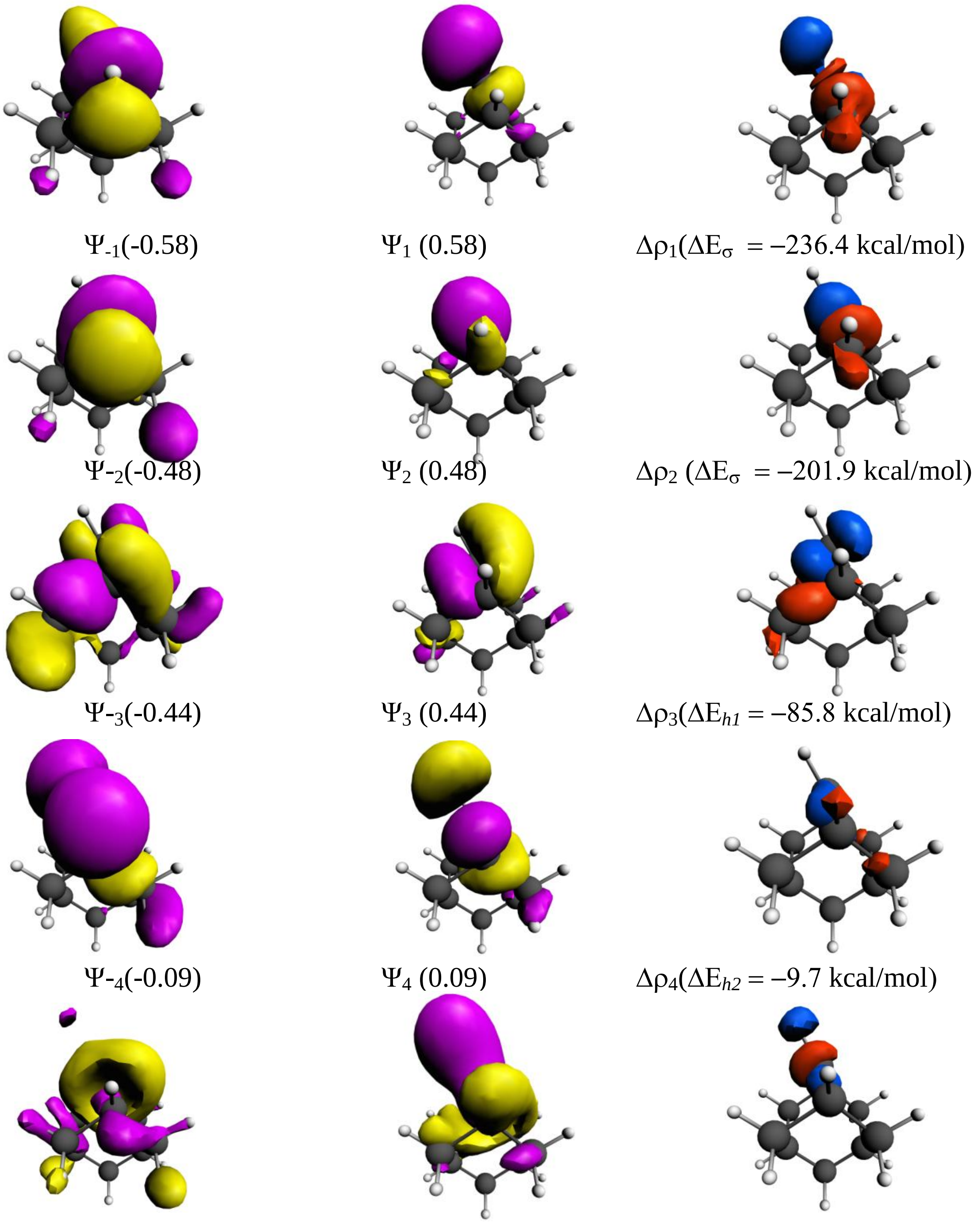
$\Psi_{-1}(-0.79)$ $\Psi_1(0.79)$ $\Delta\rho_1(\Delta E_\sigma = -425.6$ kcal/mol)

Ψ_2 (-0.45) Ψ_{-2} (0.45) $\Delta\rho_2(\Delta E_\sigma = -205.5$kcal/mol)

$\Psi_{-3}(-0.18)$ Ψ_3 (0.18) $\Delta\rho_3(\Delta E_{h1} = -19.2$ kcal/mol)

$\Psi_{-4}(-0.10)$ Ψ_4 (0.10) $\Delta\rho_4(\Delta E_{h2} = -12.3$ kcal/mol)

Figure S4: Plots of important NOCV pair of orbitals Ψ_{-n}/Ψ_n with their eigen values in the parenthesis, the associated deformation densities $\Delta\rho_n$ and the orbital stabilization energies ΔE for the complex **3** at the BP86/TZ2P level of theory. The direction of charge flow in the deformation densities is from red→ blue. The NOCV orbitals are plotted with a contour value 0.03. The deformation density, $\Delta\rho_n$ is plotted with a contour value 0.003 for n = 1,2 and 0.001 for n = 3,4.



$\Psi_{-1}(-0.58)$ $\Psi_1\ (0.58)$ $\Delta\rho_1(\Delta E_{\sigma} = -236.4$ kcal/mol)

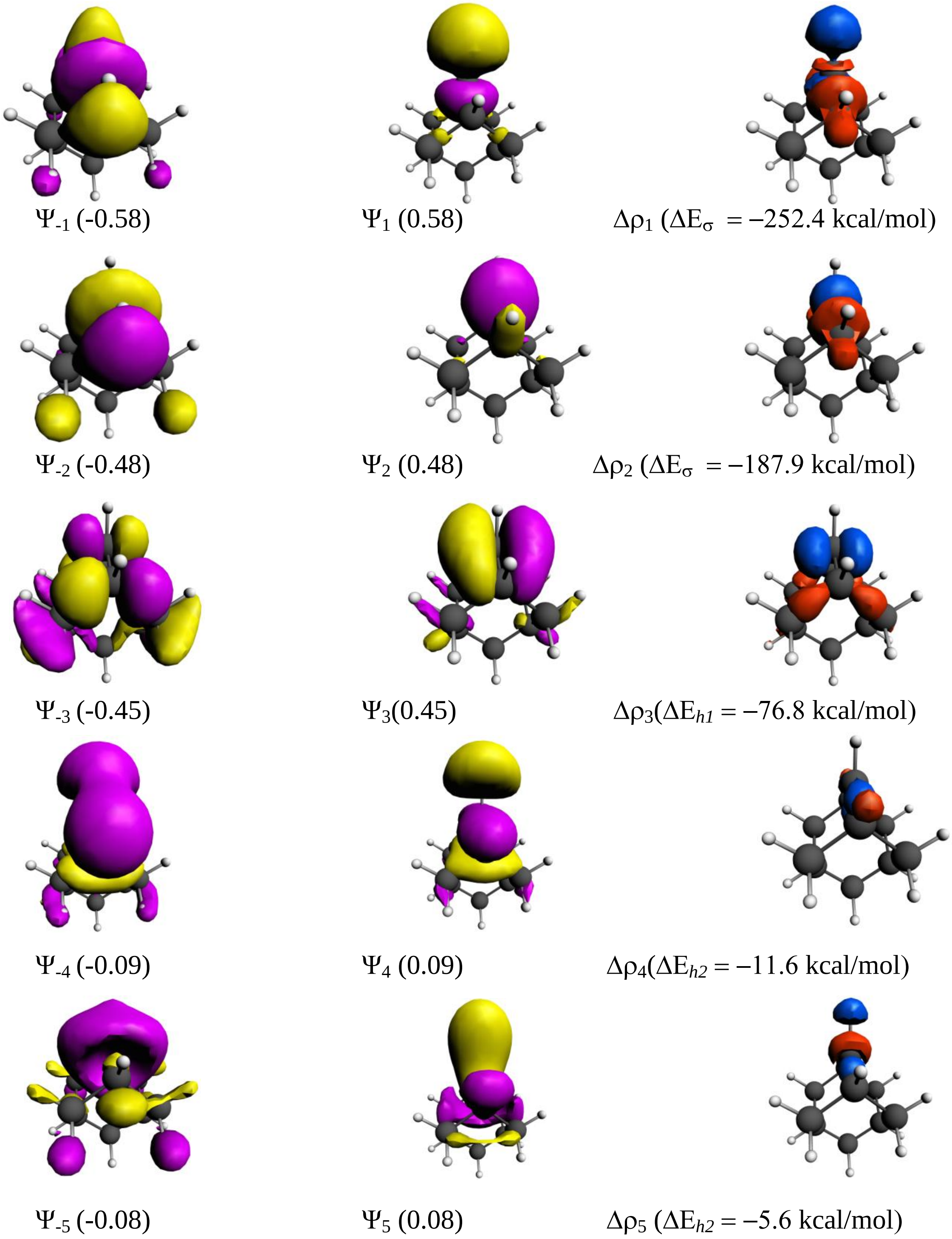
$\Psi_{-2}(-0.48)$ $\Psi_2\ (0.48)$ $\Delta\rho_2\ (\Delta E_{\sigma} = -201.9$ kcal/mol)

$\Psi_{-3}(-0.44)$ $\Psi_3\ (0.44)$ $\Delta\rho_3(\Delta E_{h1} = -85.8$ kcal/mol)

$\Psi_{-4}(-0.09)$ $\Psi_4\ (0.09)$ $\Delta\rho_4(\Delta E_{h2} = -9.7$ kcal/mol)

$\Psi_{-5}(-0.08)$ $\Psi_5\ (0.08)$ $\Delta\rho_5(\Delta E_{h2} = -7.5$ kcal/mol)

Figure S5: Plots of important NOCV pair of orbitals Ψ_{-n}/Ψ_n with their eigen values in the parenthesis, the associated deformation densities $\Delta\rho_n$ and the orbital stabilization energies ΔE for the complex **4** at the BP86/TZ2P level of theory. The direction of charge flow in the deformation densities is from red→ blue. The NOCV orbitals are plotted with a contour value 0.03. The deformation density, $\Delta\rho_n$ is plotted with a contour value 0.003 for n= 1–3;0.001 for n = 4, 5.



Ψ_{-1} (-0.58) Ψ_1 (0.58) $\Delta\rho_1$ (ΔE_σ = −252.4 kcal/mol)

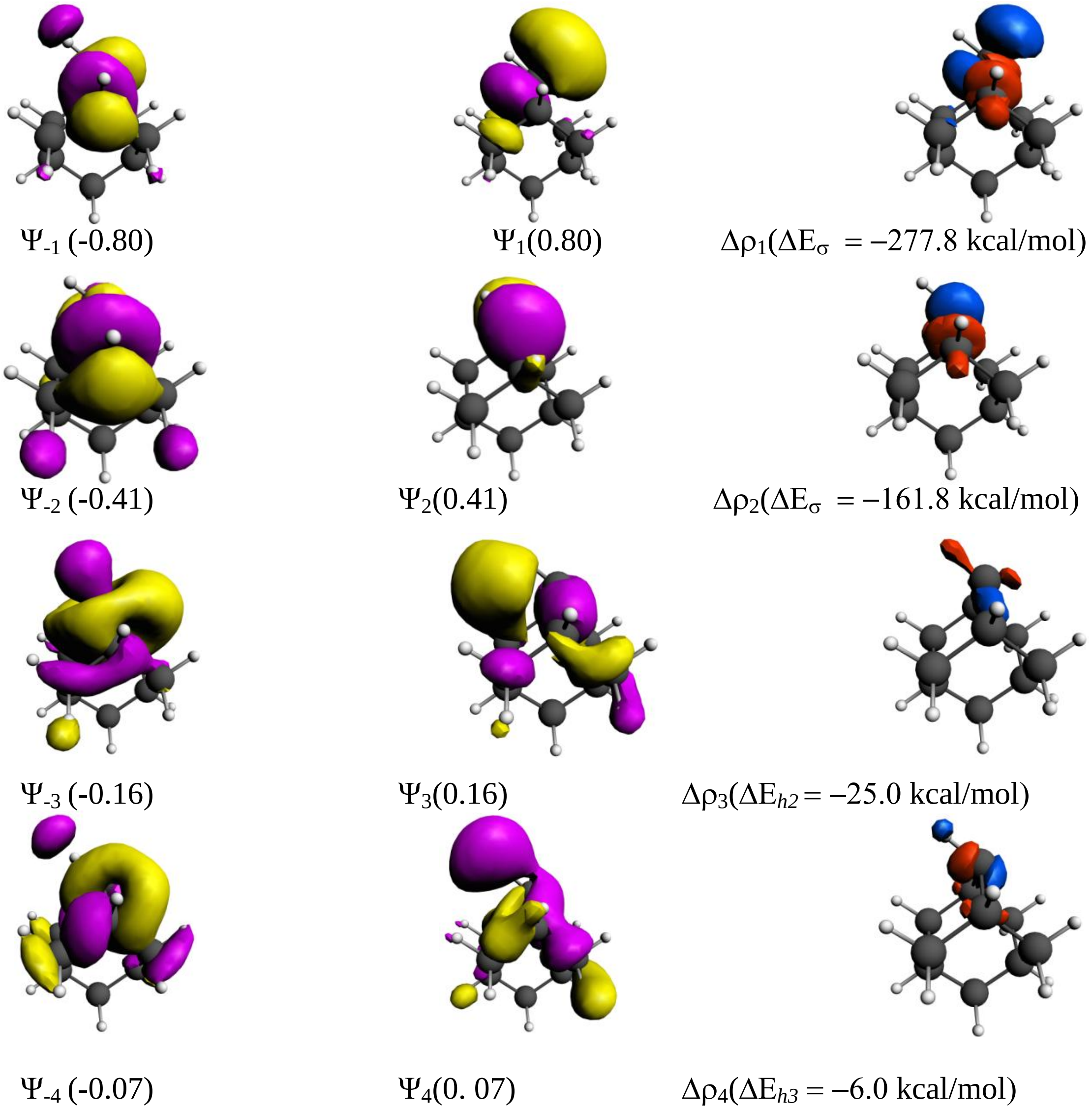
Ψ_{-2} (-0.48) Ψ_2 (0.48) $\Delta\rho_2$ (ΔE_σ = −187.9 kcal/mol)

Ψ_{-3} (-0.45) Ψ_3(0.45) $\Delta\rho_3$(ΔE_{h1} = −76.8 kcal/mol)

Ψ_{-4} (-0.09) Ψ_4 (0.09) $\Delta\rho_4$(ΔE_{h2} = −11.6 kcal/mol)

Ψ_{-5} (-0.08) Ψ_5 (0.08) $\Delta\rho_5$ (ΔE_{h2} = −5.6 kcal/mol)

Figure S6: Plots of important NOCV pair of orbitals Ψ_{-n}/Ψ_n with their eigen values in the parenthesis, the associated deformation densities $\Delta\rho_n$ and the orbital stabilization energies ΔE for the complex **4′** at the BP86/TZ2P level of theory. The direction of charge flow in the deformation densities is from red→ blue. The NOCV orbitals are plotted with a contour value 0.03. The deformation density, $\Delta\rho_n$ is plotted with a contour value 0.003 for n= 1–3;0.001 for n = 4, 5.



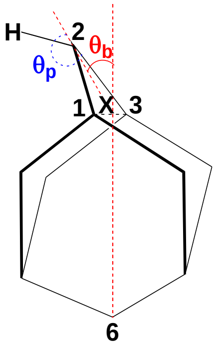
Ψ_{-1} (-0.80) Ψ_1(0.80) $\Delta\rho_1$(ΔE_σ = –277.8 kcal/mol)

Ψ_{-2} (-0.41) Ψ_2(0.41) $\Delta\rho_2$(ΔE_σ = –161.8 kcal/mol)

Ψ_{-3} (-0.16) Ψ_3(0.16) $\Delta\rho_3$(ΔE_{h2} = –25.0 kcal/mol)

Ψ_{-4} (-0.07) Ψ_4(0. 07) $\Delta\rho_4$(ΔE_{h3} = –6.0 kcal/mol)

Figure S7: Plots of important NOCV pair of orbitals Ψ_{-n}/Ψ_n with their eigen values in the parenthesis, the associated deformation densities $\Delta\rho_n$ and the orbital stabilization energies ΔE for the complex **5** at the BP86/TZ2P level of theory. The direction of charge flow in the deformation densities is from red→ blue. The NOCV orbitals are plotted with a contour value 0.03. The deformation density, $\Delta\rho_n$ is plotted with a contour value 0.003 for n= 1–3;0.001 for n = 4.



Scheme S1: Schematic representation of the bending angle, θ_b, and the pyramidalization angle, θ_p, at the C2-atom.Thebending angle, θ_b, is calculated as 180°– bond angle (C6–X–C2), where X is the centre of the C1 and C3 atoms. The pyramidalization angle, θ_p, around the C2-atom is calculated as 360º–bond angles (C1–C2–H + C1–C2–C3 + H–C2–C3).