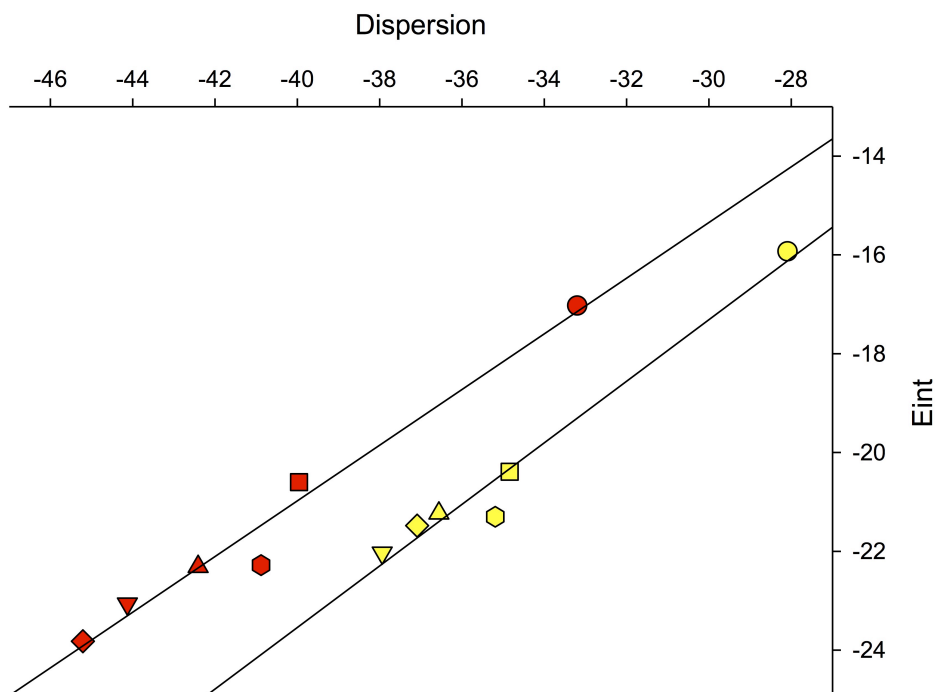




## A.2. Dispersion contribution vs. interaction energy

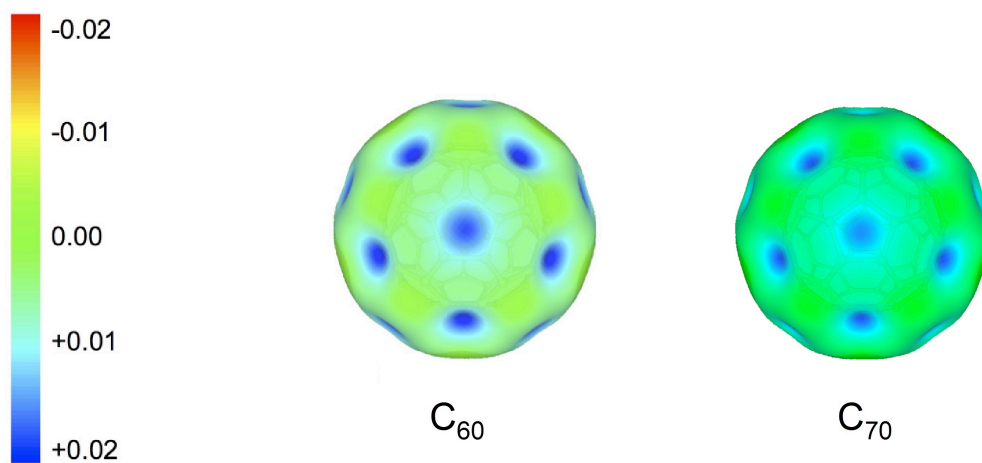


**Figure A.2:** Dispersion contribution vs. interaction energy (in kcal/mol). Corannulenes with  $C_{60}$  (Cora face). Corannulene: circle. Corannulene-5Br: triangle down. Corannulene-5Cl: square. Corannulene-5CH<sub>3</sub>: diamond. Corannulene-5C<sub>2</sub>H: triangle up. Corannulene-5CN: hexagon. B97-D2/TZVP: red.  $E_{\text{int}} = 0.5633 \times \text{Disp} + 1.558$ ,  $R^2 = 0.97$ . B3LYP-D3(BJ)/TZVP//B97-D2/TZVP: yellow.  $E_{\text{int}} = 0.6231 \times \text{Disp} + 1.383$ ,  $R^2 = 0.97$ .

	B97	D2	B3LYP	D3(BJ)
Corannulene...C <sub>60</sub>	16.17	-33.20	12.16	-28.09
Corannulene-5Br...C <sub>60</sub>	21.07	-44.13	15.91	-37.94
Corannulene-5Cl...C <sub>60</sub>	19.36	-39.96	14.45	-34.84
Corannulene-5CH <sub>3</sub> ...C <sub>60</sub>	21.39	-45.21	15.61	-37.09
Corannulene-5C <sub>2</sub> H...C <sub>60</sub>	20.10	-42.41	15.33	-36.56
Corannulene-5CN...C <sub>60</sub>	18.60	-40.88	13.89	-35.19

According to this figure it is clear that what was written for B97-D2 is also valid for B3LYP-D3(BJ): the good correlation between the dispersive contribution and the interaction energy, and the slight deviation for the bucky bowl with CN (the hexagons) remain.

### A.3. MEP of $C_{60}$ and $C_{70}$



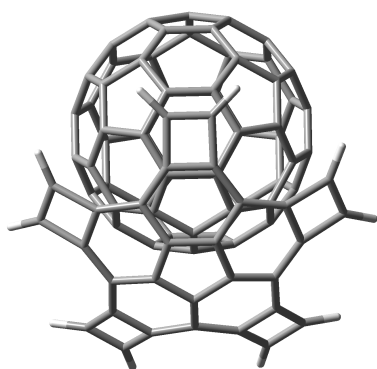
**Figure A.3:** Molecular electrostatic potential, MEP, onto an electron density isosurface of 0.001 a.u. Showing the *cora face* of  $C_{60}$  and  $C_{70}$ .



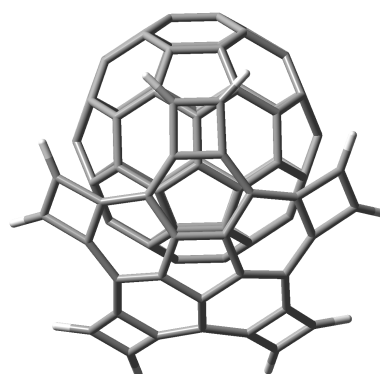
## Appendix B

### Supporting Information for Chapter 7

#### *B.1. Why 4...C<sub>60</sub> is more stable in the staggered conformation?*



**eclipsed conformation**

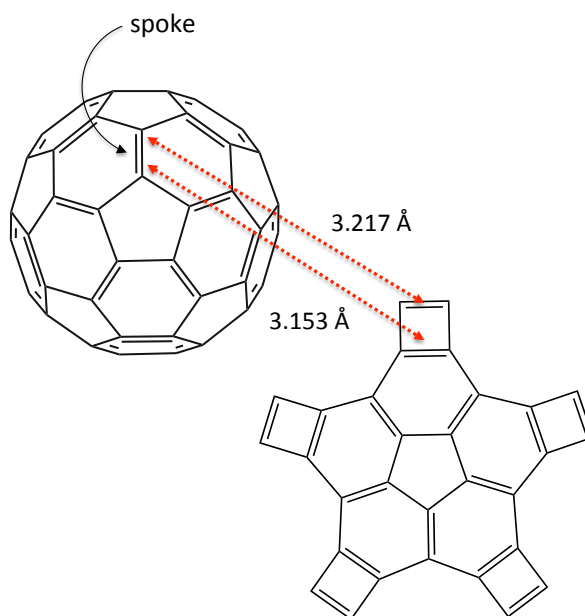


**staggered conformation**

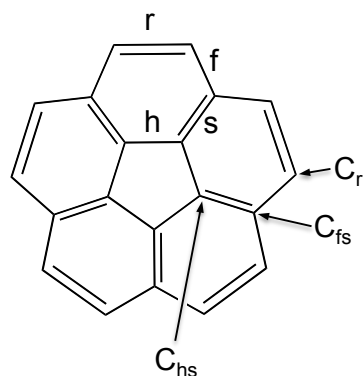
In the staggered conformation of complex 4...X both  $\pi$  bonds of the cyclobutadiene (which owns an extremely localized  $\pi$  clouds) are directly facing the *spoke* bond of fullerene, which is precisely the bond with the largest  $\pi$  character of fullerene (the largest bond order, the shortest bond length, the largest double-bond character). Thus, this additional  $\pi\cdots\pi$  interaction, that takes place in the staggered conformation in a more appropriate way, not only offsets the advantage of the general trend favouring the eclipsed conformation, but it also overcomes it.

To support the above explanation, QTAIM calculations and NCI plots were performed. Both methodologies make clear the interaction between the  $\pi$  bonds of the

cyclobutadiene and the *spoke* bonds of fullerene that takes place in the staggered conformation of the complex.



**staggered conformation**



**bonds:**

h = hub  
s = spoke  
f = flank  
r = rim

**C atom types:**

hs = hub-spoke  
fs = flank-spoke  
r = rim

**QTAIM:** BCP=Bond Critical Point, BP=Bond Path

**Eclipsed conformation:** there are two types of BP between corannulene 4 and fullerene.

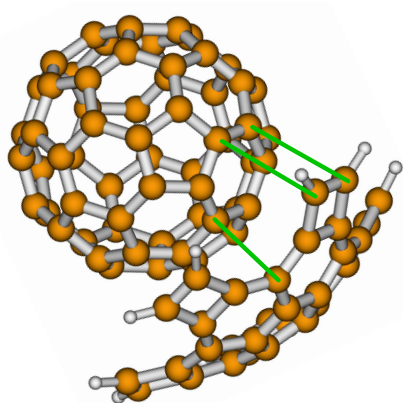
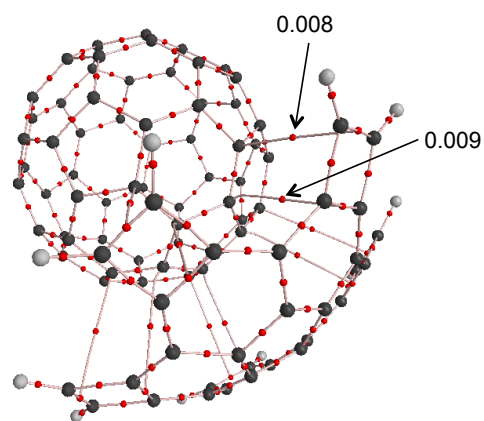
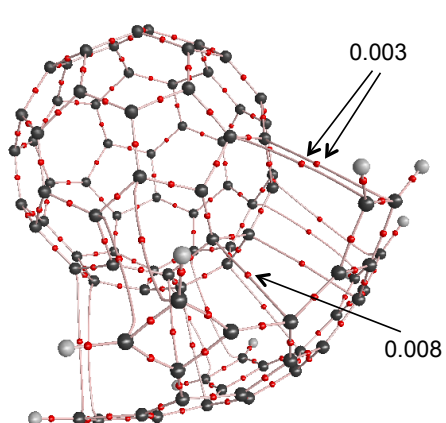
1) From each of the external carbons of cyclobutadiene to a  $C_r$  of fullerene (density of the BCP, 0.003). A total of 10 BPs.

2) From the  $C_{fs}$  of corannulene to a  $C_{hs}$  of fullerene (0.008). A total of 5 BPs.

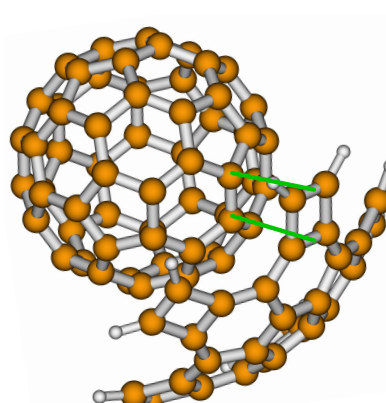
**Staggered conformation:** there are two types of BP between corannulene 4 and fullerene.

1) From the BCP between the external carbons of cyclobutadiene to a  $C_{fs}$  of fullerene (0.008): A total of 5 BPs.

2) From the BCP between the internal carbons of cyclobutadiene to a  $C_{hs}$  of fullerene (0.009): A total of 5 BPs.



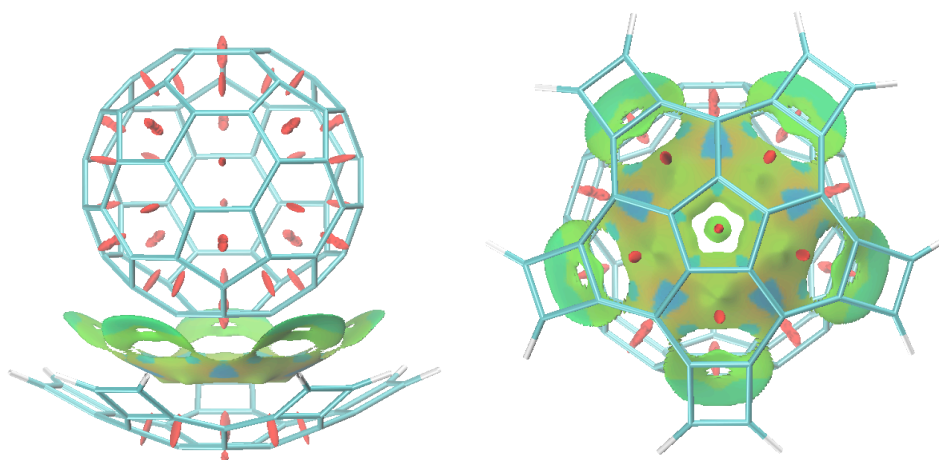
**eclipsed**



**staggered**

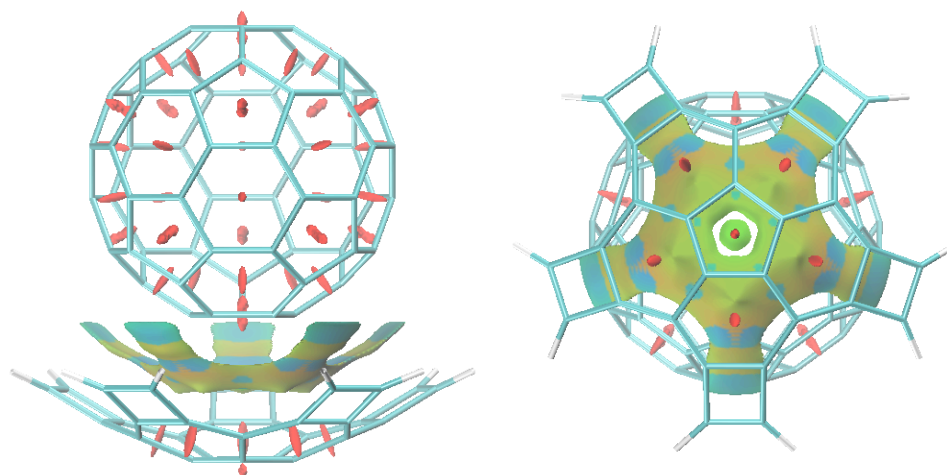
Thus, in the staggered conformation the density of the BCPs is significantly larger than in the eclipsed conformation (0.085 *vs.* 0.070).

***NCIPLOT, eclipsed conformation:***



The largest interaction (blue) takes place between the *spoke* of corannulene and the *spoke* of fullerene (which is clearly related to BP type 2, above commented).

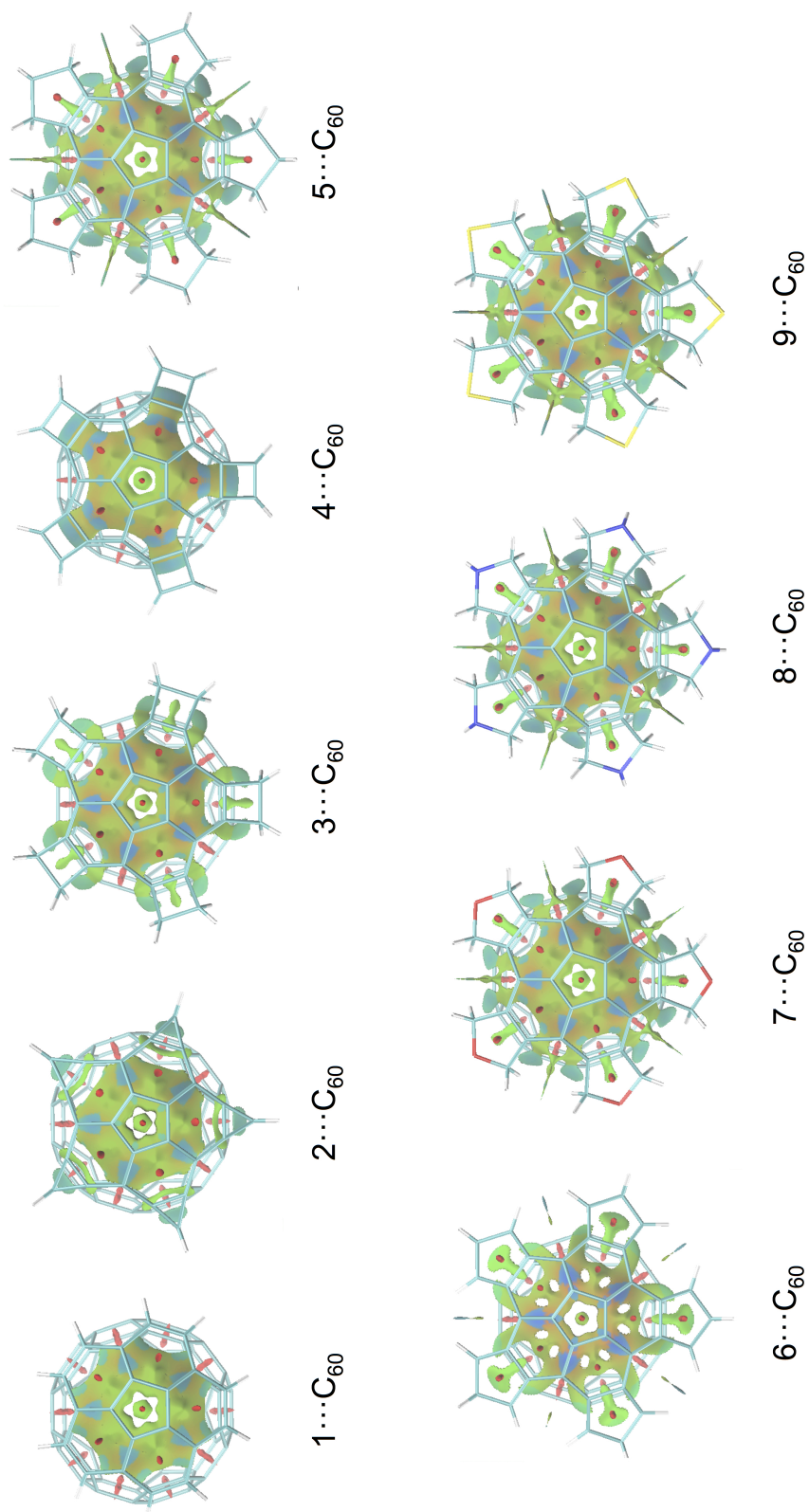
***NCIPLOT, staggered conformation:***



An important portion of *spoke-spoke* interaction is lost. However, this is not only offset, but it also overcome by the emergence of two new strong  $\pi\cdots\pi$  interactions which correspond to those that takes place between the two double bonds of cyclobutadiene (external and internal) and the *spoke* of fullerene (which are clearly related to BP types 1 and 2, respectively, above commented).

**Isosurface: 0.40**

**Colour scale: from -0.15 to 0.15**

**B.2. NCI PLOTSs**

### B.3. NBO Calculations

Second order perturbation analysis as the energies of delocalization of electrons from filled NBOs into empty NBOs-so that they do not finish up quite filled or quite empty.

Stabilization energies (kcal/mol), E(2):

Donor	Acceptor	1...C <sub>60</sub>	2...C <sub>60</sub>	3...C <sub>60</sub>	4...C <sub>60</sub>	5...C <sub>60</sub>	6...C <sub>60</sub>	7...C <sub>60</sub>	8...C <sub>60</sub>	9...C <sub>60</sub>
$\pi$ (spoke) corannulene	$\pi^*$ (spoke) C <sub>60</sub>	0.86	1.05	1.46	-	1.28	1.71	1.07	1.18	1.32
$\sigma$ (spoke) corannulene	Ry*(C <sub>hs</sub> ) C <sub>60</sub>	0.45	0.55	0.62	-	0.51	0.77	0.48	0.48	0.55
$\pi$ (external <sup>a</sup> ) corannulene	$\pi^*$ (spoke) C <sub>60</sub>	-	-	-	1.05	-	-	-	-	-
$\sigma$ (external <sup>a</sup> ) corannulene	Ry*(C <sub>fs</sub> ) C <sub>60</sub>	-	-	-	0.52	-	-	-	-	-

<sup>a</sup>external bond of cyclobutadiene.

Only values larger than 0.45 are shown.

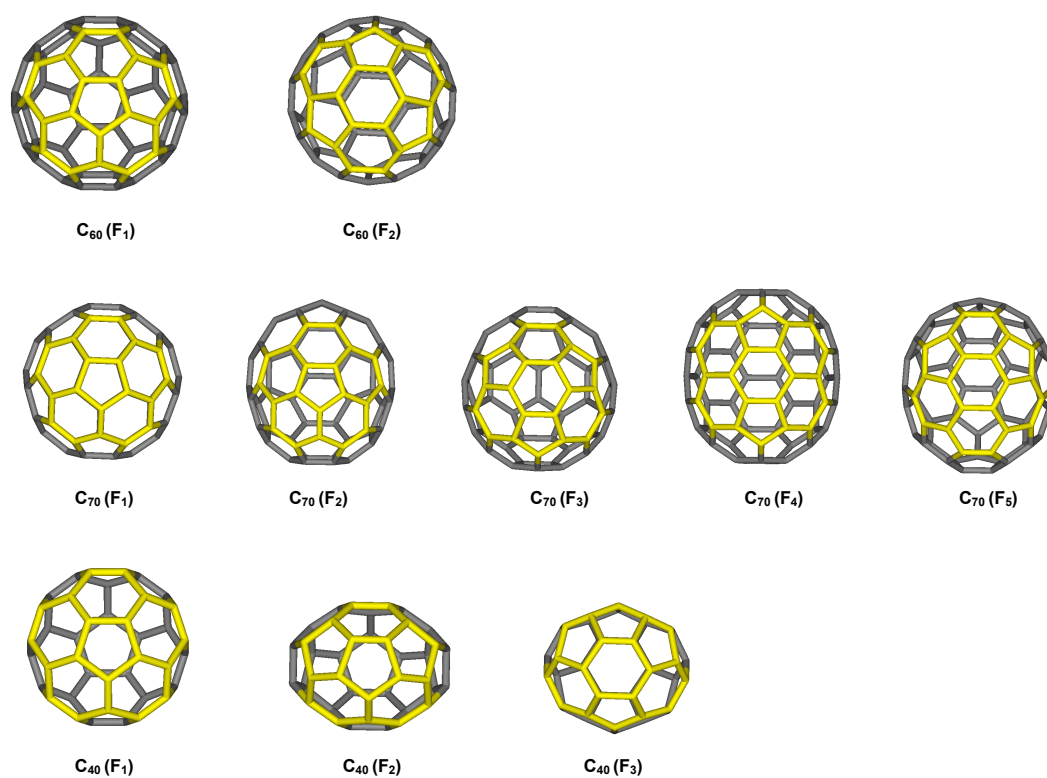
Eclipsed disposition, except for complex 4...C<sub>60</sub>, which is staggered.

- Except for 4...C<sub>60</sub>: the main contribution comes from the interaction between the  $\pi$  orbital of the *spokes* of both monomers. The second most important contribution is that which takes place between the  $\sigma$  orbital of the *spokes* of corannulene and the Rydberg orbital of the C<sub>hs</sub> of C<sub>60</sub>.
- Only for 4...C<sub>60</sub>: the main contribution comes from the interaction between the  $\pi$  orbital of the external bond of cyclobutadienes of 4 and the  $\pi$  orbital of the *spokes* of C<sub>60</sub>. The second most important contribution is that which takes place between the  $\sigma$  orbital of the external bond of cyclobutadienes of 4 and the Rydberg orbital of the C<sub>fs</sub> of C<sub>60</sub>.

## Appendix C

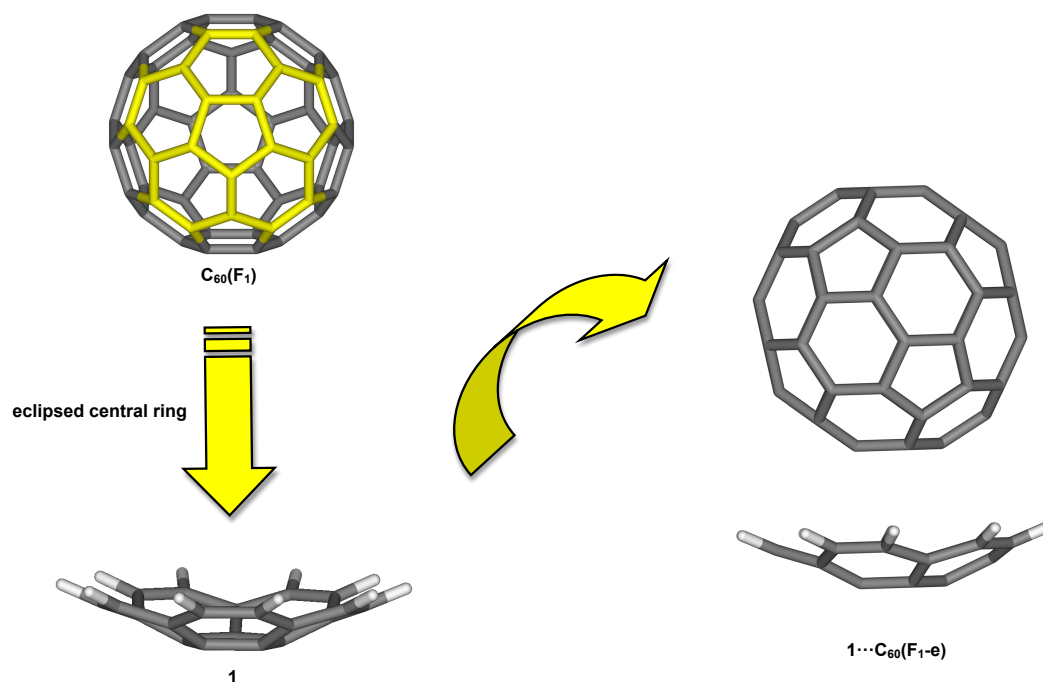
### Supporting information for Chapter 8

#### *C1. Fullerene faces*



**Figure C.1:** Faces of fullerenes used in the stacking interactions.

## C.2. Scheme for "building" the complexes



**Figure C.2:** Scheme for explaining the "building" of the complexes evaluated. Complex  $1 \cdots C_{60}(F_1-e)$  has been built eclipsing the central ring of face  $F_1$  of  $C_{60}$  (given in yellow, which is a corannulene type face) with the central ring of buckybowl 1 (this buckybowl is precisely the corannulene). The complex with staggered conformation is named as  $1 \cdots C_{60}(F_1-s_{36})$ ; with one of monomers rotated  $36^\circ$  around the axis defined by the centre of both five-membered rings.

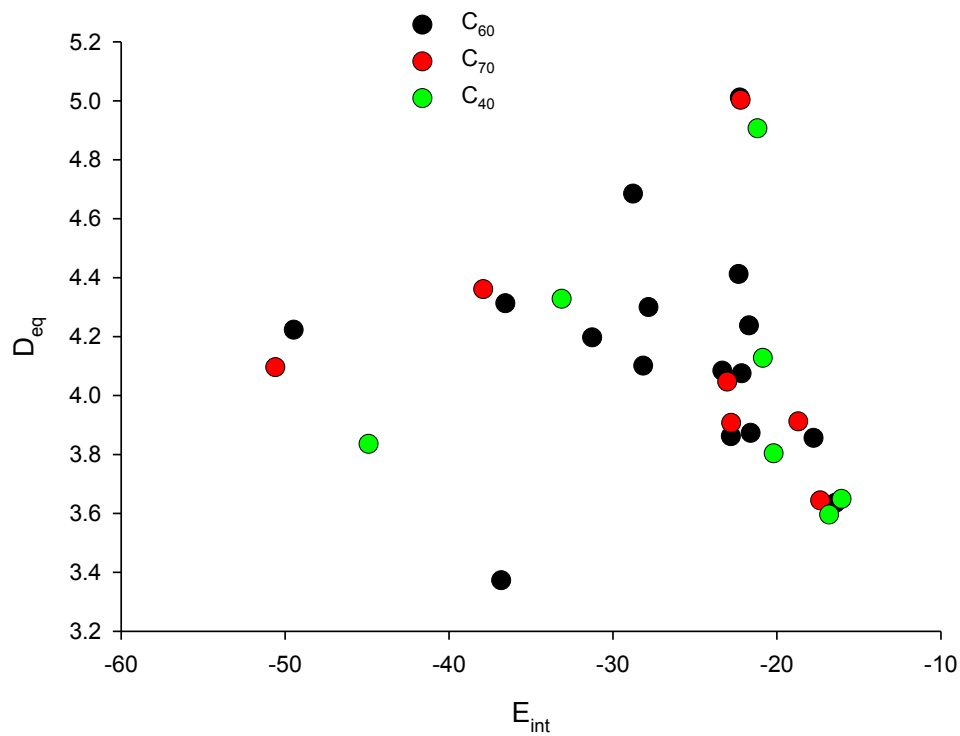
When there is no any correspondence between the central core of the buckybowl and the face of fullerene, the used name is consecutively  $F_x-1$ ,  $F_x-2$ , ... For example for the complex  $5 \cdots C_{70}$  with the face  $F_5$ , three different optimizations were performed with three different starting points. However, since compound 5 is sumanene, and face  $F_3$  is a sumanene type face, then in this case three defined options are possible: one eclipsed ( $F_3-e$ ), and two staggered ( $F_3-s_{30}$  and  $F_3-s_{60}$ ).



6...C <sub>70</sub> (F <sub>4-1</sub> )	-21.78
6...C <sub>70</sub> (F <sub>4-2</sub> )	-21.67
6...C <sub>70</sub> (F <sub>4-3</sub> )	-21.79
6...C <sub>70</sub> (F <sub>5-1</sub> )	-22.51
6...C <sub>70</sub> (F <sub>5-2</sub> )	-22.00
6...C <sub>70</sub> (F <sub>5-3</sub> )	<b>-23.03</b>
8...C <sub>70</sub> (F <sub>1</sub> )	-20.48
8...C <sub>70</sub> (F <sub>2</sub> )	-20.22
8...C <sub>70</sub> (F <sub>3-e</sub> )	-19.88
8...C <sub>70</sub> (F <sub>3-S30</sub> )	<b>-22.21</b>
8...C <sub>70</sub> (F <sub>3-S60</sub> )	-19.65
8...C <sub>70</sub> (F <sub>4-1</sub> )	-19.61
8...C <sub>70</sub> (F <sub>4-2</sub> )	-21.95
8...C <sub>70</sub> (F <sub>5-1</sub> )	-19.02
8...C <sub>70</sub> (F <sub>5-2</sub> )	-22.11
8...C <sub>70</sub> (F <sub>5-3</sub> )	-19.33
10...C <sub>70</sub> (F <sub>1-1</sub> )	-20.99
10...C <sub>70</sub> (F <sub>1-2</sub> )	-20.98
10...C <sub>70</sub> (F <sub>2-1</sub> )	-22.15
10...C <sub>70</sub> (F <sub>2-2</sub> )	-22.11
10...C <sub>70</sub> (F <sub>3-1</sub> )	-21.86
10...C <sub>70</sub> (F <sub>3-2</sub> )	-21.63
10...C <sub>70</sub> (F <sub>4-1</sub> )	-22.63
10...C <sub>70</sub> (F <sub>4-2</sub> )	<b>-22.79</b>
10...C <sub>70</sub> (F <sub>5-1</sub> )	-22.28
10...C <sub>70</sub> (F <sub>5-2</sub> )	-22.64
15...C <sub>70</sub> (F <sub>1</sub> )	-48.79
15...C <sub>70</sub> (F <sub>2</sub> )	-49.14
15...C <sub>70</sub> (F <sub>3-1</sub> )	-48.78
15...C <sub>70</sub> (F <sub>3-2</sub> )	-47.51
15...C <sub>70</sub> (F <sub>4-1</sub> )	-47.63
15...C <sub>70</sub> (F <sub>4-2</sub> )	-46.96
15...C <sub>70</sub> (F <sub>5-1</sub> )	<b>-50.60</b>
15...C <sub>70</sub> (F <sub>5-2</sub> )	-47.53
<b>Complexes with C<sub>40</sub></b>	
1...C <sub>40</sub> (F <sub>1-e</sub> )	<b>-16.05</b>
1...C <sub>40</sub> (F <sub>1-S36</sub> )	-13.42

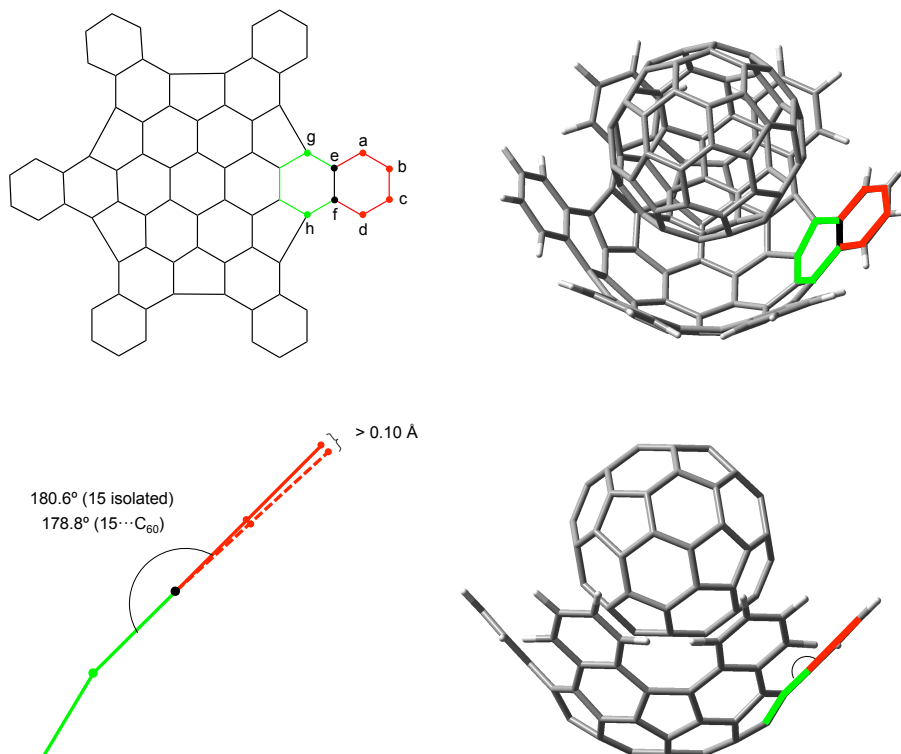
1...C <sub>40</sub> (F <sub>2-1</sub> )	-13.76
1...C <sub>40</sub> (F <sub>2-2</sub> )	-12.45
1...C <sub>40</sub> (F <sub>3</sub> )	-14.99
2...C <sub>40</sub> (F <sub>1-e</sub> )	-30.53
2...C <sub>40</sub> (F <sub>1-S36</sub> )	<b>-33.13</b>
2...C <sub>40</sub> (F <sub>2-1</sub> )	-33.12
2...C <sub>40</sub> (F <sub>2-2</sub> )	-31.48
2...C <sub>40</sub> (F <sub>3</sub> )	-31.46
5...C <sub>40</sub> (F <sub>1</sub> )	-16.45
5...C <sub>40</sub> (F <sub>2</sub> )	-15.30
5...C <sub>40</sub> (F <sub>3-1</sub> )	-16.40
5...C <sub>40</sub> (F <sub>3-2</sub> )	<b>-16.81</b>
5...C <sub>40</sub> (F <sub>3-3</sub> )	-16.41
6...C <sub>40</sub> (F <sub>1</sub> )	<b>-20.86</b>
6...C <sub>40</sub> (F <sub>2</sub> )	-20.79
6...C <sub>40</sub> (F <sub>3-1</sub> )	-19.85
6...C <sub>40</sub> (F <sub>3-2</sub> )	-20.40
6...C <sub>40</sub> (F <sub>3-3</sub> )	-20.81
8...C <sub>40</sub> (F <sub>1</sub> )	-18.61
8...C <sub>40</sub> (F <sub>2</sub> )	-18.10
8...C <sub>40</sub> (F <sub>3-1</sub> )	-19.00
8...C <sub>40</sub> (F <sub>3-2</sub> )	<b>-21.18</b>
8...C <sub>40</sub> (F <sub>3-3</sub> )	-18.91
10...C <sub>40</sub> (F <sub>1-1</sub> )	-20.19
10...C <sub>40</sub> (F <sub>1-2</sub> )	<b>-20.20</b>
10...C <sub>40</sub> (F <sub>2-1</sub> )	-18.16
10...C <sub>40</sub> (F <sub>2-2</sub> )	-17.87
10...C <sub>40</sub> (F <sub>3-1</sub> )	-19.67
10...C <sub>40</sub> (F <sub>3-2</sub> )	-19.51
15...C <sub>40</sub> (F <sub>1</sub> )	-41.71
15...C <sub>40</sub> (F <sub>2</sub> )	<b>-44.91</b>
15...C <sub>40</sub> (F <sub>3-1</sub> )	-42.25
15...C <sub>40</sub> (F <sub>3-2</sub> )	-43.86

### C.4. Interaction energy vs. equilibrium distance



### C.5. Flexibility of flaps

**Compound 15.** Angle between the planes (a-b-c-d-e-f) and (g-e-f-h): is a measure of the torsion of the bond e-f (the *hinge* between the planes).



Upon complexation, the closure of *flaps* is small (1.4, 1.8, and 2.5° with C<sub>70</sub>, C<sub>60</sub>, and C<sub>40</sub>, respectively<sup>1</sup>), but strong enough to get a significant increase of proximity of the atoms of the external rings to the fullerene. For example, with C<sub>60</sub>, the external C atoms (b, c) move more than 0.10 Å closer.

Moreover, as expected, as the fullerene becomes smaller, the angle becomes smaller and the external rings are closer to the fullerene.

Similar conclusions are obtained analysing the other two cases with flaps: compounds 2 and 7.

<sup>1</sup> These are average values, since for the three complexes different angles are obtained for the six external hexagonal rings (the most stable complex of each case is taken into account):

With C<sub>70</sub>: 180.4, 180.9, 178.0 (2), and 179.1° (2)

With C<sub>60</sub>: 178.60 (3), and 179.0° (3)

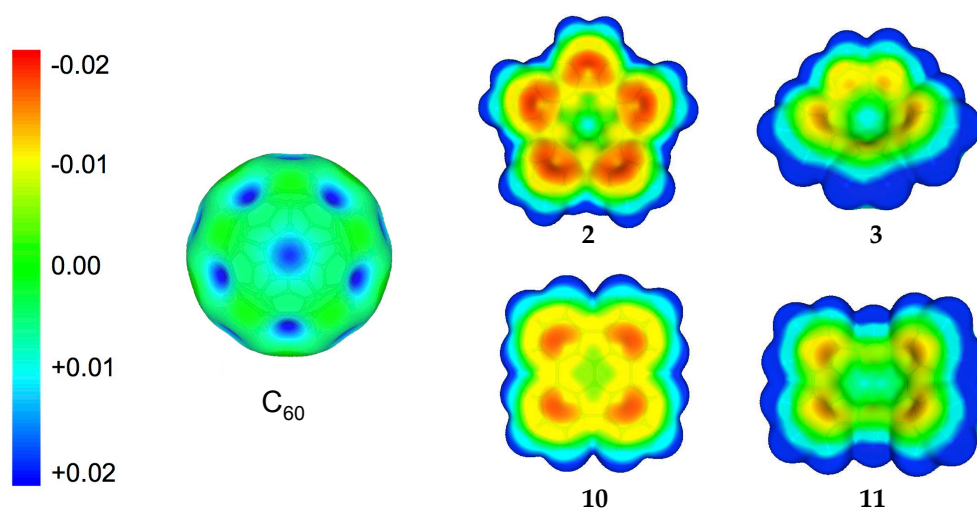
With C<sub>40</sub>: 182.4 (2), 175.7 (2), and 176.2° (2)

Isolated: 180.6° (6)

## C.6. MEPs of compounds 2, 3, 10, and 11

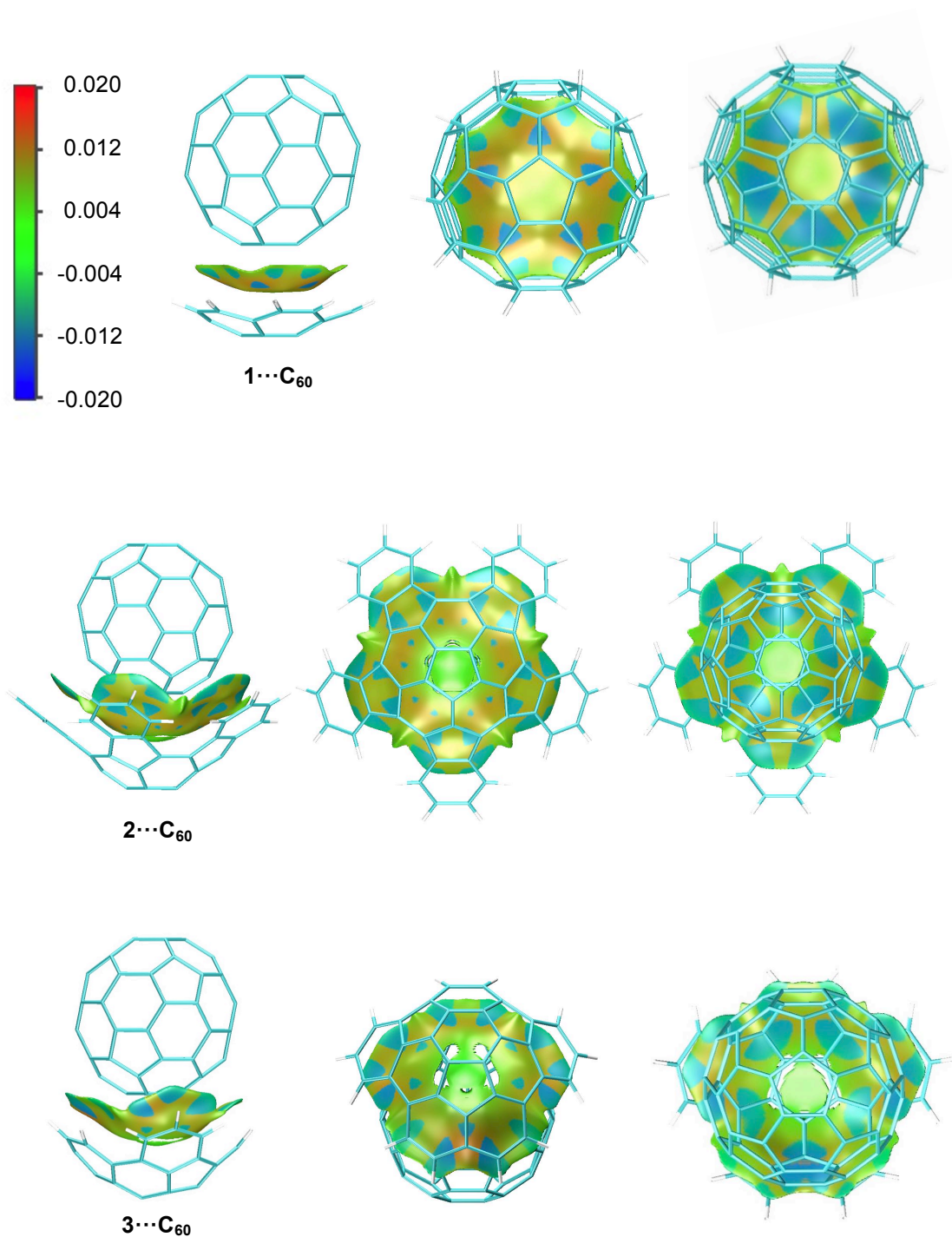
### Why do compounds 3, 10, and 11 deviate slightly of the linear behaviour between the dispersive contribution and interaction energy?

As it was commented in a recent paper [Josa *et al.*, *RSC Adv.*, **2014**, 4, 29826], although electrostatics do not play an important role in the interaction (due to the very small multipole moments of fullerenes), however its contribution is able to alter to small extent the classification given by the more important contribution, dispersion. Figure C.4 shows maps of molecular electrostatic potential, MEP, of  $C_{60}$  and the concave side of compounds 2, 3, 10, and 11.  $C_{60}$  ( $C_{70}$  virtually has the same map) shows an almost neutral MEP, but slightly positive on top of the five-membered rings. In the complexes one of these five-membered rings faces the central region of the bowls. Consequently, a negative MEP above this region will favour a larger electrostatic interaction between the bowl and the fullerene. Examining Figure C.4 and taking as reference the MEP of the central region of compound 2 (compound perfectly aligned with the line in Figure 8.5), it can be observed that compound 10 shows a slightly more favourable MEP (less positive than that of 2) for interacting with  $C_{60}$ . This fact agrees with Figure 8.5, where this compound obtains larger interaction energy than that predicted by its dispersion contribution. On the contrary, compounds 3 and 11 show a less favourable MEP (more positive than that of 2) in the central region; so these two compounds are found over the straight line of Figure 8.5, that is to say, these compounds obtain smaller interaction energy than that predicted by its dispersion contribution. In summary, MEP maps can help to explain (in a rather qualitative way) the small deviations of Figure 8.5.



**Figure C.4:** Molecular electrostatic potential, MEP, onto an electron density isosurface of 0.001 a.u.

### C.7. NCIPLoTs



**Figure C.5:** Front, bottom, and top views of the NCIPLoT gradient isosurface (0.4 a.u.). The surfaces are coloured on a blue-green-red scale according to the strength and type (attractive or repulsive) of interaction. Blue indicates strong attractive interactions, green indicate weak VdW interactions, and red indicates strong nonbonded overlap.

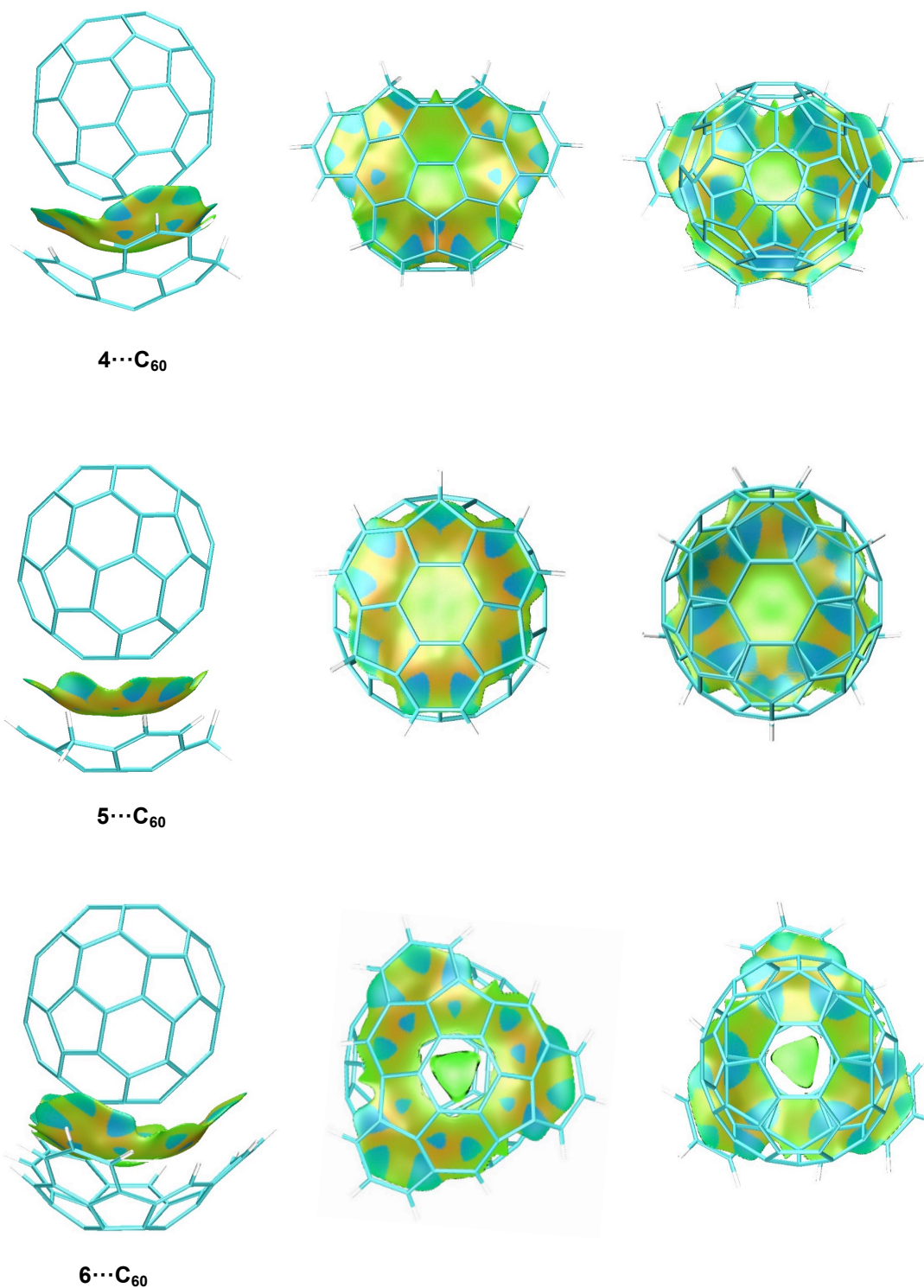


Figure C.5: (cont.)

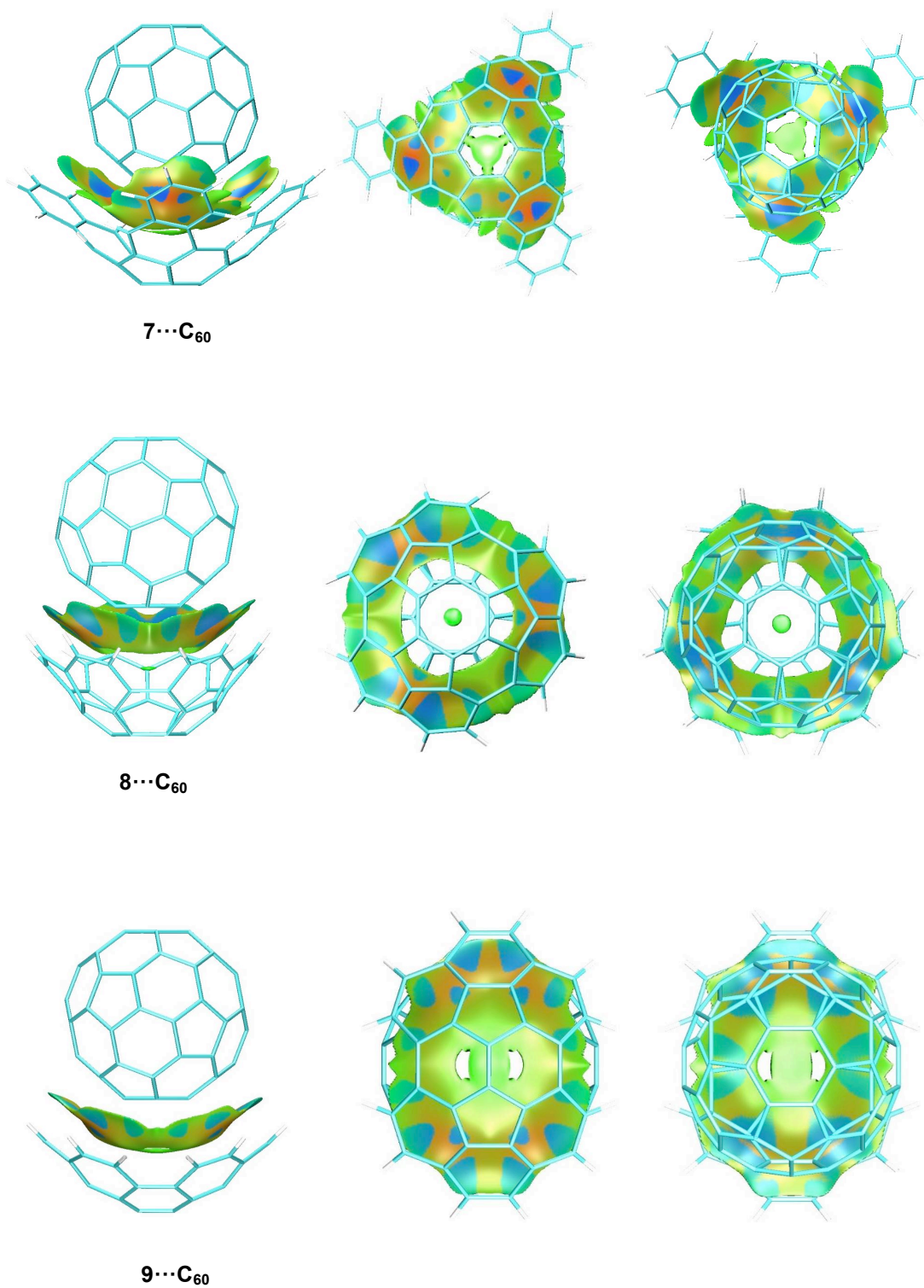


Figure C.5: (cont.)

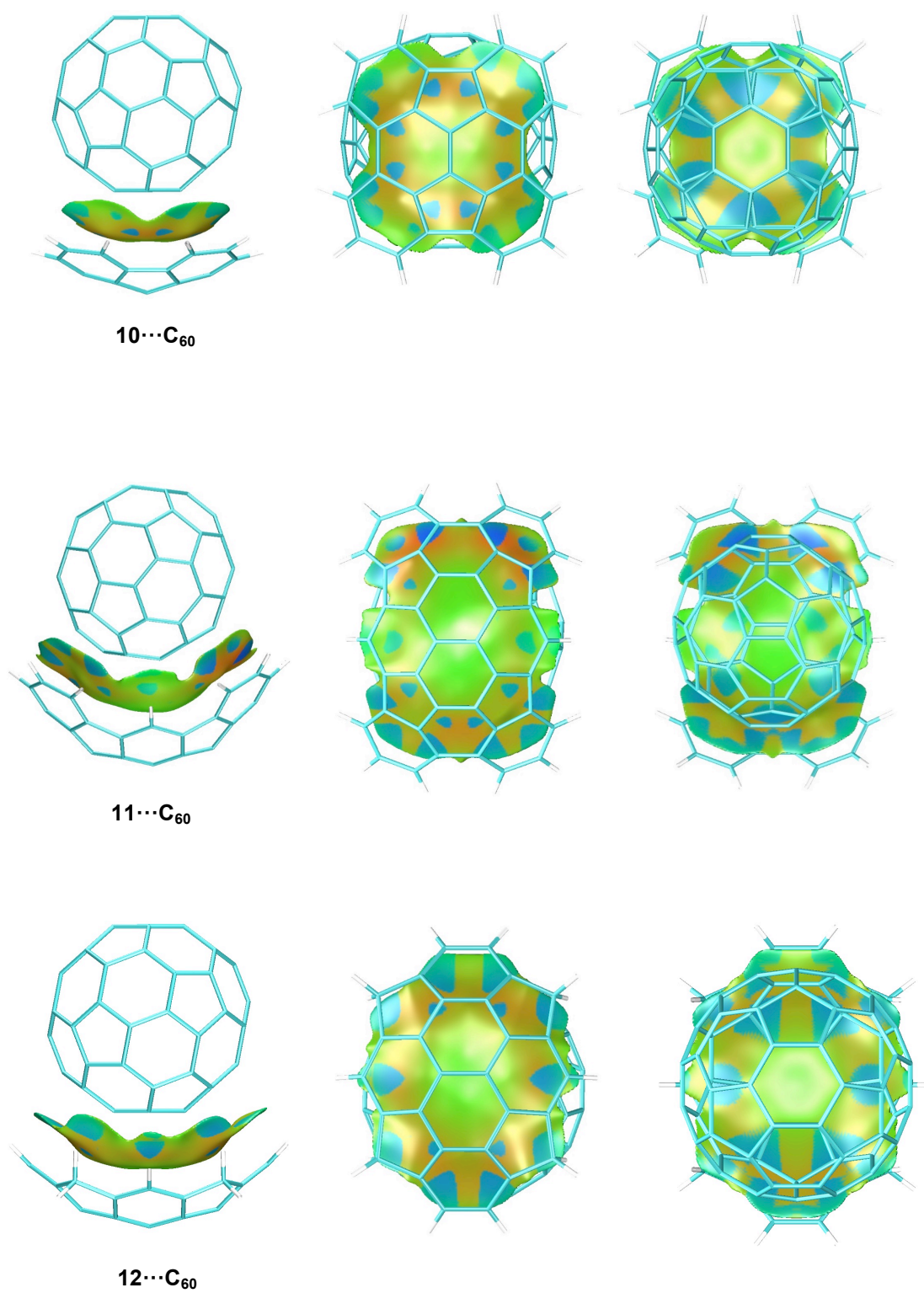


Figure C.5: (cont.)

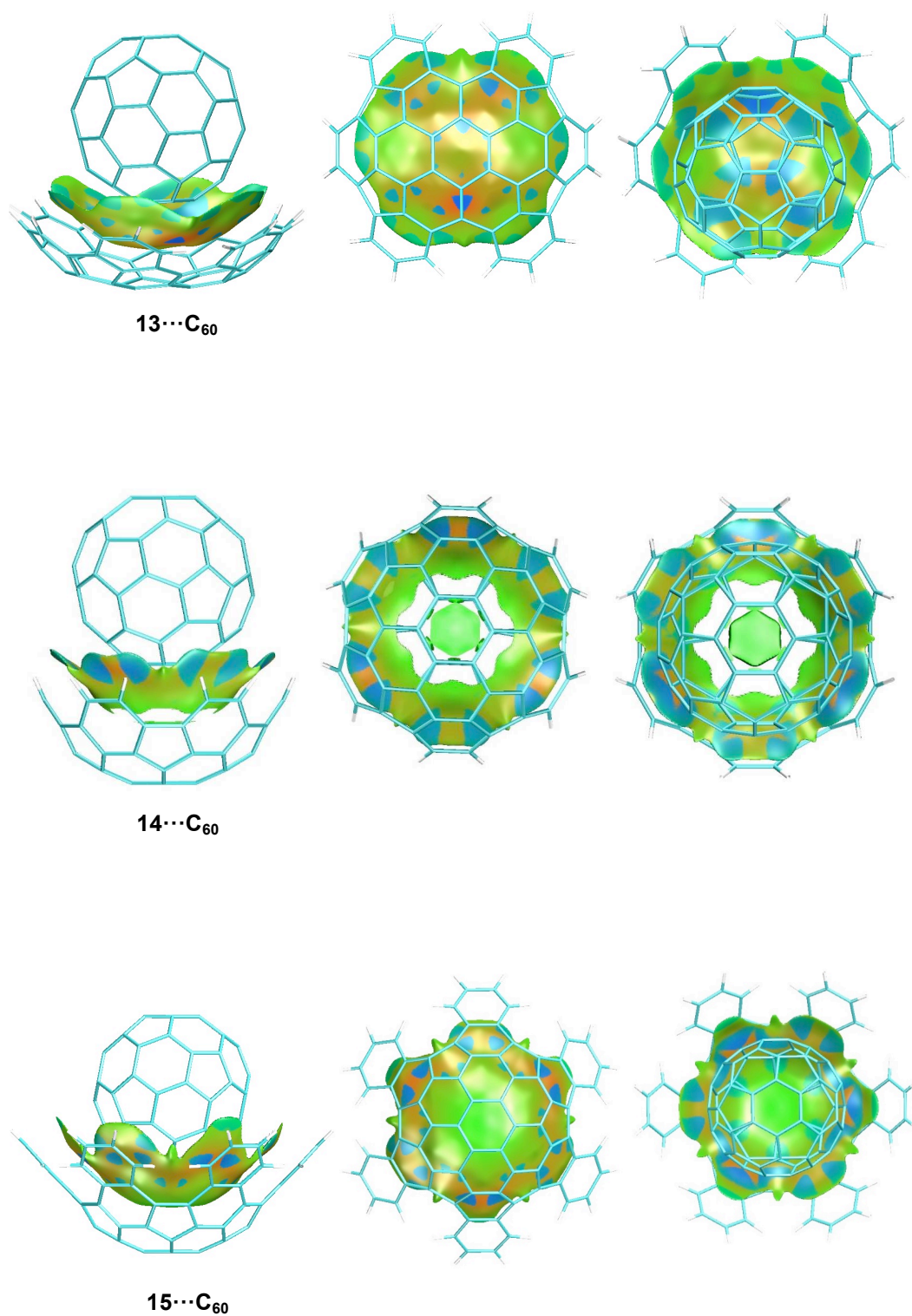
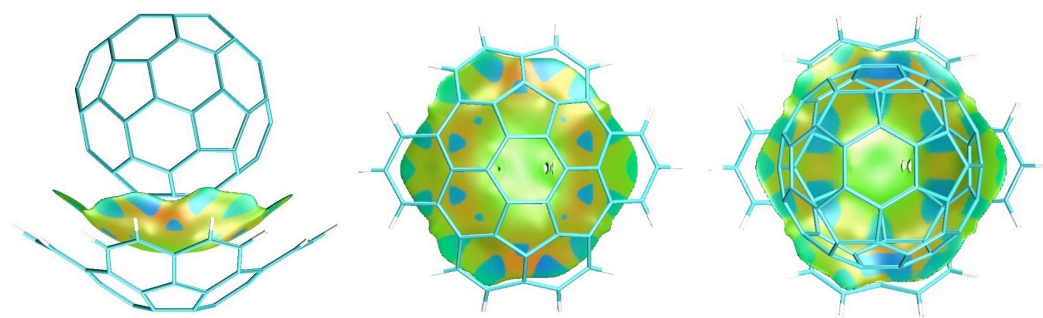


Figure C.5: (cont.)



**16...C<sub>60</sub>**

**Figure C.5:** (cont.)



## Appendix D

### Supporting information for Chapter 9

#### *D.1. Interaction energies using different DFT-D methods*

Table D.1: B97-D2/TZVP, B97-D3/TZVP, and B97-D3(BJ)/TZVP interaction energies (in kcal/mol)

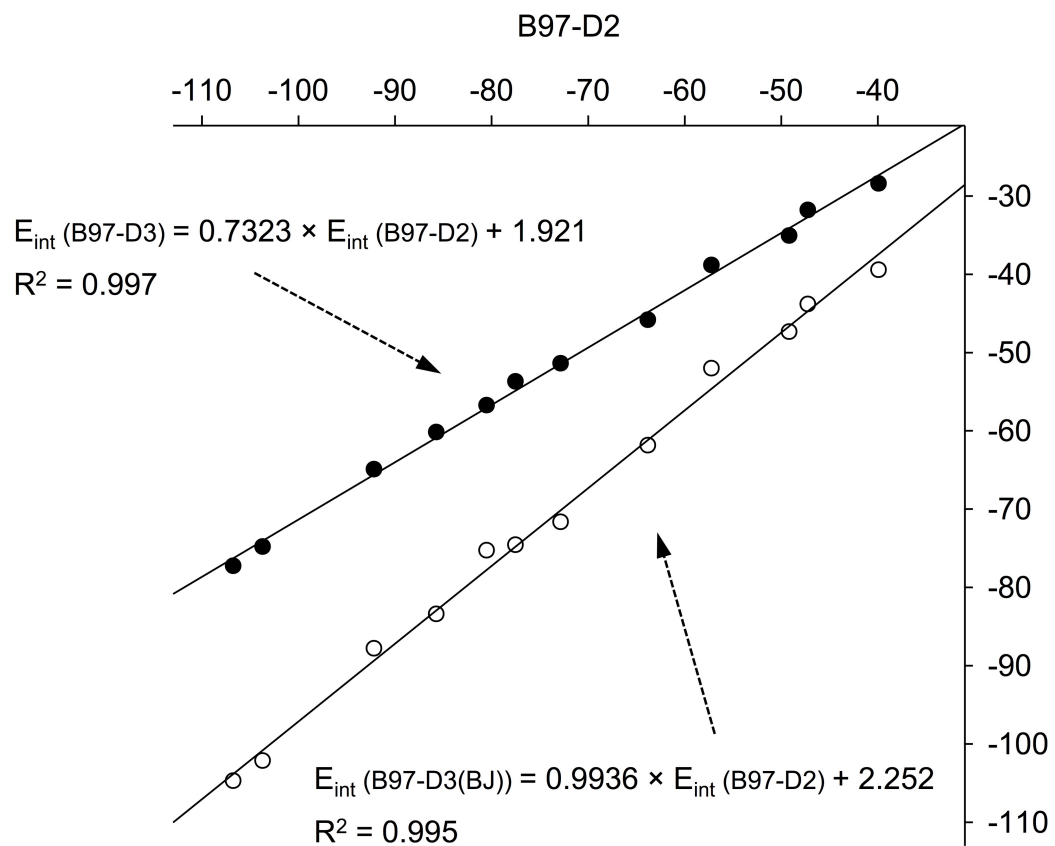
	B97-D2/TZVP	B97-D3/TZVP <sup>a</sup>	B97-D3(BJ)/TZVP <sup>a</sup>
1a···C <sub>60</sub>	-39.92	-28.43	-39.46
1b···C <sub>60</sub>	-49.18	-35.08	-47.34
2a···C <sub>60</sub>	-47.26	-31.80	-43.82
2b···C <sub>60</sub>	-57.23	-38.84	-52.03
3a···C <sub>60</sub>	-72.86	-51.38	-71.64
3b···C <sub>60</sub>	-85.73	-60.18	-83.40
4a···C <sub>60</sub>	-63.83	-45.82	-61.86
4b···C <sub>60</sub>	-80.52	-56.73	-75.28
5a···C <sub>60</sub>	-77.53	-53.70	-74.58
5b···C <sub>60</sub>	-92.19	-64.91	-87.79
6a···C <sub>60</sub>	-103.72	-74.80	-102.14
6b···C <sub>60</sub>	-106.76	-77.27	-104.72

<sup>a</sup> Calculated using the optimized B97-D2/TZVP geometries.

D2: reference 47. D3: S. Grimme, J. Antony, S. Ehrlich, H. Krieg, *J. Chem. Phys.*, 2010, **132**, 154104.

D3(BJ): S. Grimme, S. Ehrlich, L. Goerigk, *J. Comput. Chem.*, 2011, **32**, 1456–1465.

Figure D.1 shows the correlation between B97-D2/TZVP interaction energy with B97-D3/TZVP, and B97-D3(BJ)/TZVP interaction energies.



**Figure D.1:** B97-D2/TZVP interaction energy vs. B97-D3/TZVP, and B97-D3(BJ)/TZVP interaction energies (in kcal/mol).

## D.2. BSSE

Table D.2: B97-D2/TZVP interaction energies, BSSE and percentage of BSSE (kcal/mol)

	$E_{\text{int}}^{\text{a}}$	BSSE	% <sup>b</sup>	$E_{\text{int}}^{\text{c}}$
1a...C <sub>60</sub>	-44.53	4.61	10.4	-39.92
1b...C <sub>60</sub>	-54.47	5.29	9.7	-49.18
2a...C <sub>60</sub>	-52.96	5.70	10.8	-47.26
2b...C <sub>60</sub>	-63.86	6.63	10.4	-57.23
3a...C <sub>60</sub>	-81.32	8.46	10.4	-72.86
3b...C <sub>60</sub>	-95.35	9.62	10.1	-85.73
4a...C <sub>60</sub>	-71.14	7.31	10.3	-63.83
4b...C <sub>60</sub>	-89.59	9.07	10.1	-80.52
5a...C <sub>60</sub>	-86.68	9.15	10.6	-77.53
5b...C <sub>60</sub>	-102.59	10.40	10.1	-92.19
6a...C <sub>60</sub>	-115.48	11.76	10.2	-103.72
6b...C <sub>60</sub>	-118.29	11.53	9.7	-106.76

<sup>a</sup> Without CP correction

<sup>b</sup>  $(-\text{BSSE}/E_{\text{int}}^{\text{a}}) \times 100$

<sup>c</sup> With CP correction

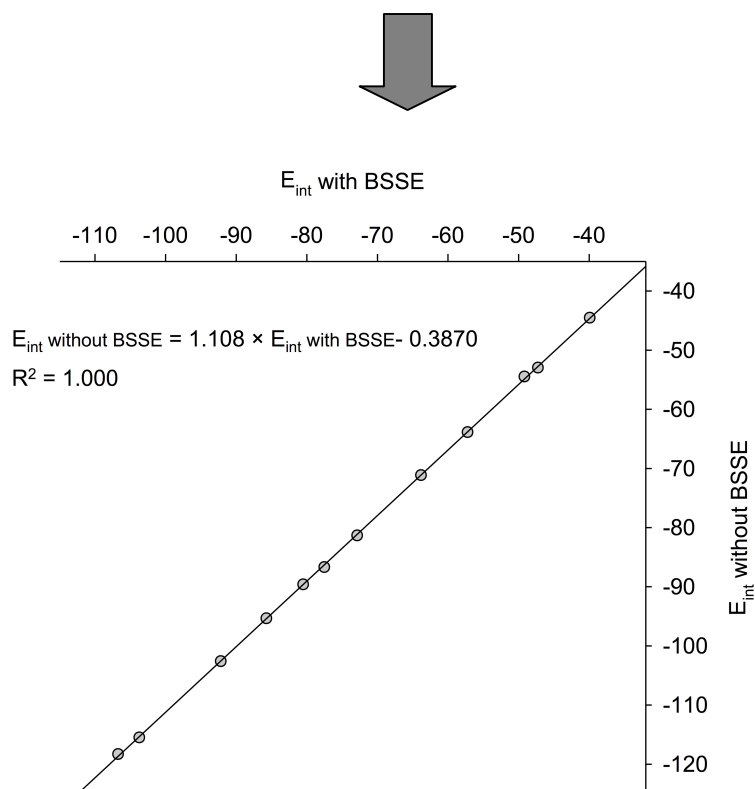
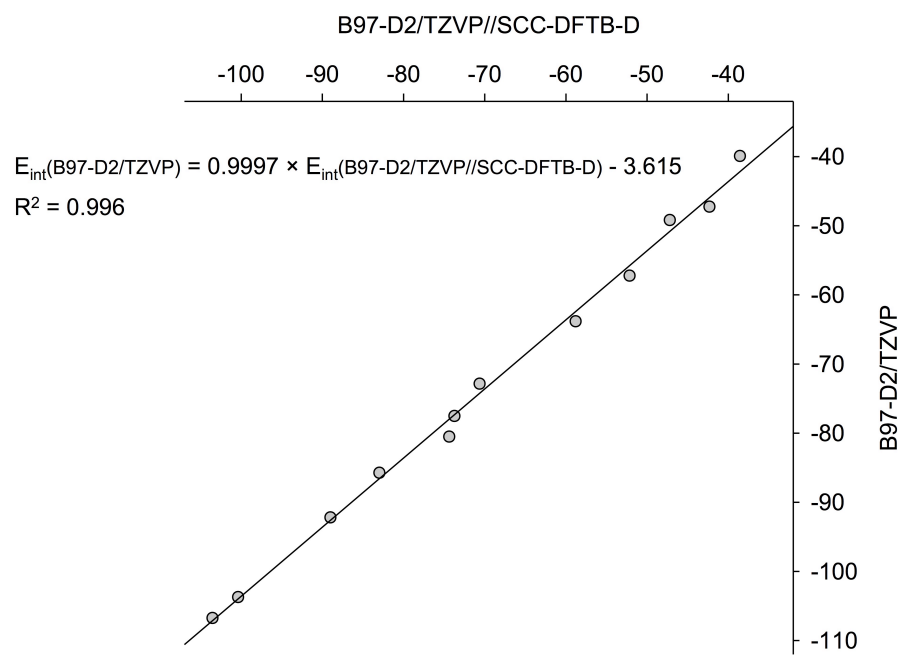


Figure D.2: Interaction energy with BSSE vs. interaction energy without BSSE (kcal/mol).

### D.3. B97-D2/TZVP//SCC-DFTB-D vs. B97-D2/TZVP interaction energy



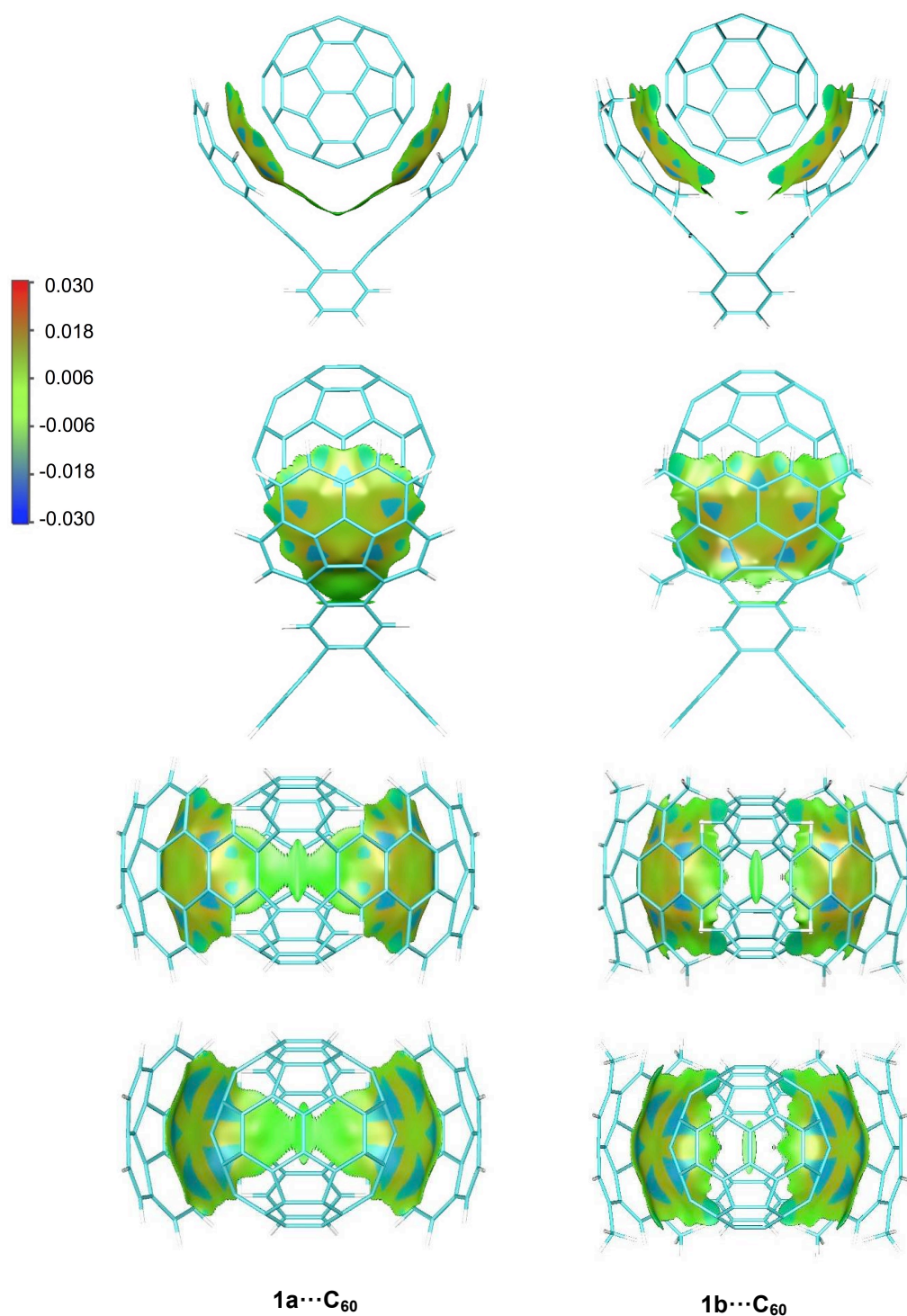
**Figure D.3:** B97-D2/TZVP//SCC-DFTB-D vs. B97-D2/TZVP interaction energy (in kcal/mol).

#### D.4. B97-D2/TZVP//SCC-DFTB-D Results

Table D.3: Complexation energy ( $E_{\text{complex}}$ ), deformation energy ( $E_{\text{def}}$ ) in kcal/mol. Calculations was performed at the B97-D2/TZVP//SCC-DFTB-D level

	$E_{\text{complex}}$	$E_{\text{def}}$
1a...C <sub>60</sub>	-37.86	0.69
1b...C <sub>60</sub>	-47.78	-0.59
2a...C <sub>60</sub>	-37.55	4.76
2b...C <sub>60</sub>	-45.69	6.46
3a...C <sub>60</sub>	-63.98	6.64
3b...C <sub>60</sub>	-76.55	6.43
4a...C <sub>60</sub>	-57.05	1.75
4b...C <sub>60</sub>	-73.97	0.40
5a...C <sub>60</sub>	-74.77	-1.05
5b...C <sub>60</sub>	-87.93	1.07
6a...C <sub>60</sub>	-94.92	5.46
6b...C <sub>60</sub>	-95.64	7.89

### D.5. NCI PLOTS



**Figure D.4:** Front, side, bottom, and top views of the NCI PLOT gradient isosurface (0.35 a.u.). The surfaces are coloured on a blue-green-red scale according to the strength and type (attractive or repulsive) of interaction. Blue indicates strong attractive interactions, green indicate weak VdW interactions, and red indicates strong nonbonded overlap.

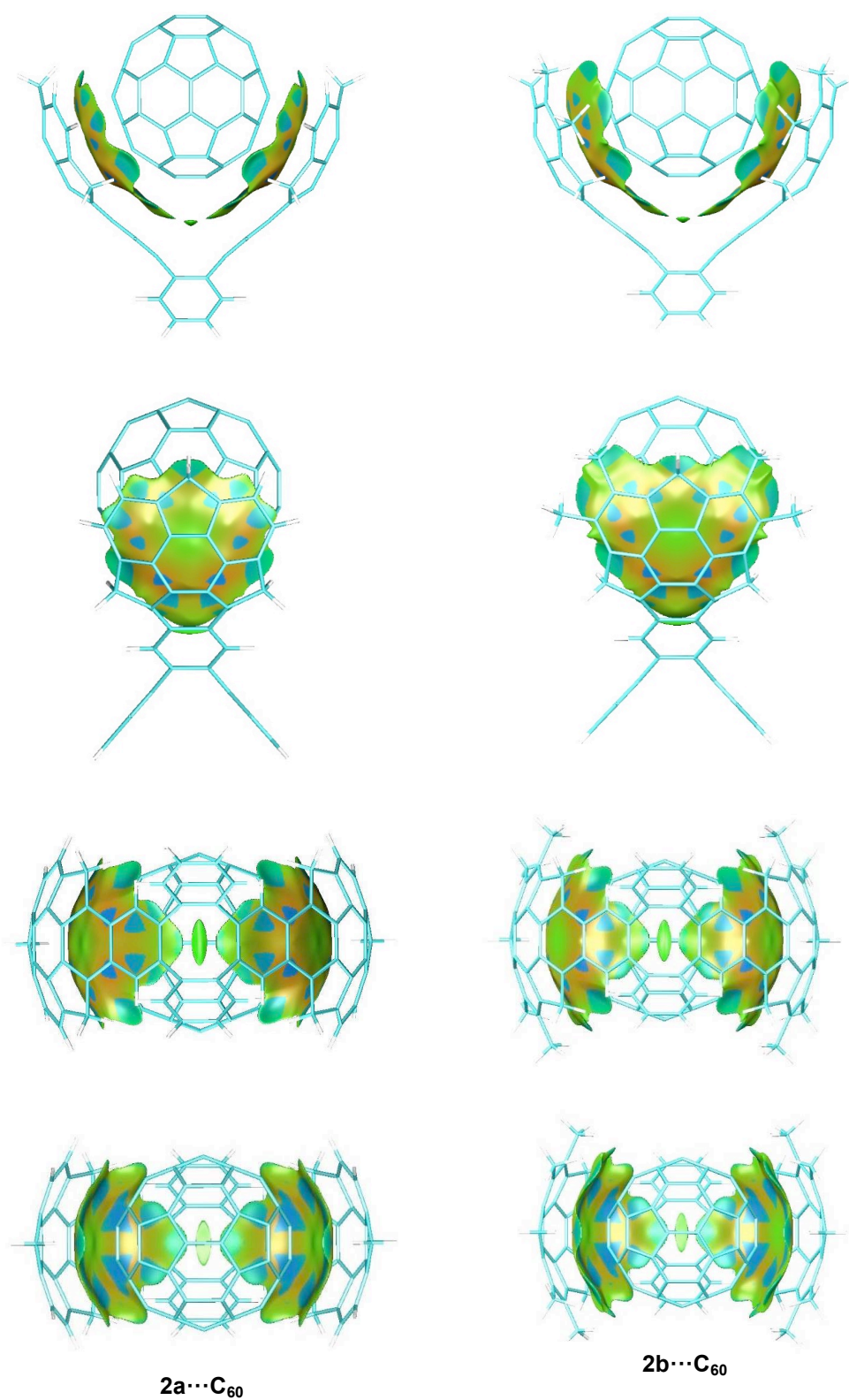


Figure D.4: (cont.)

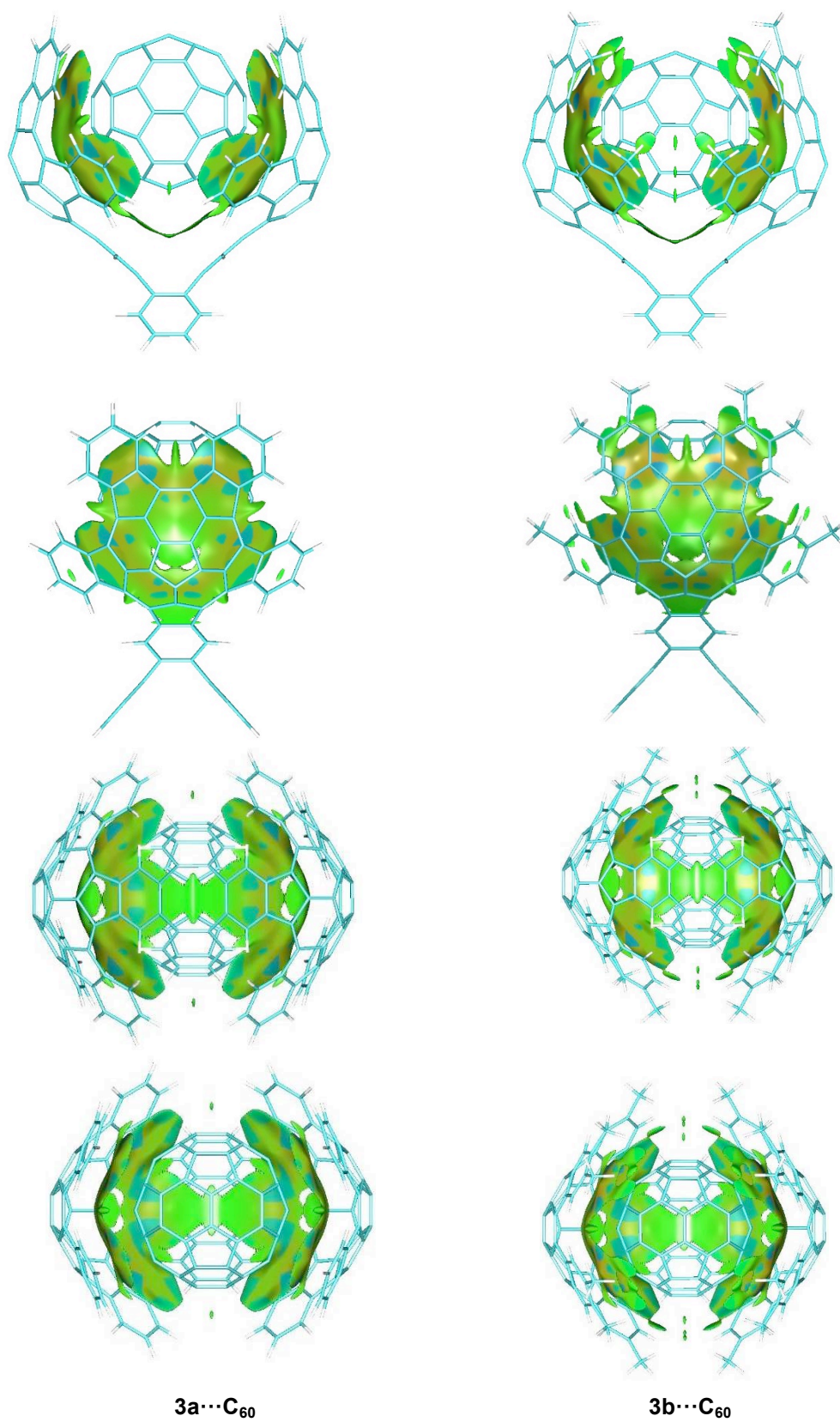


Figure D.4: (cont.)

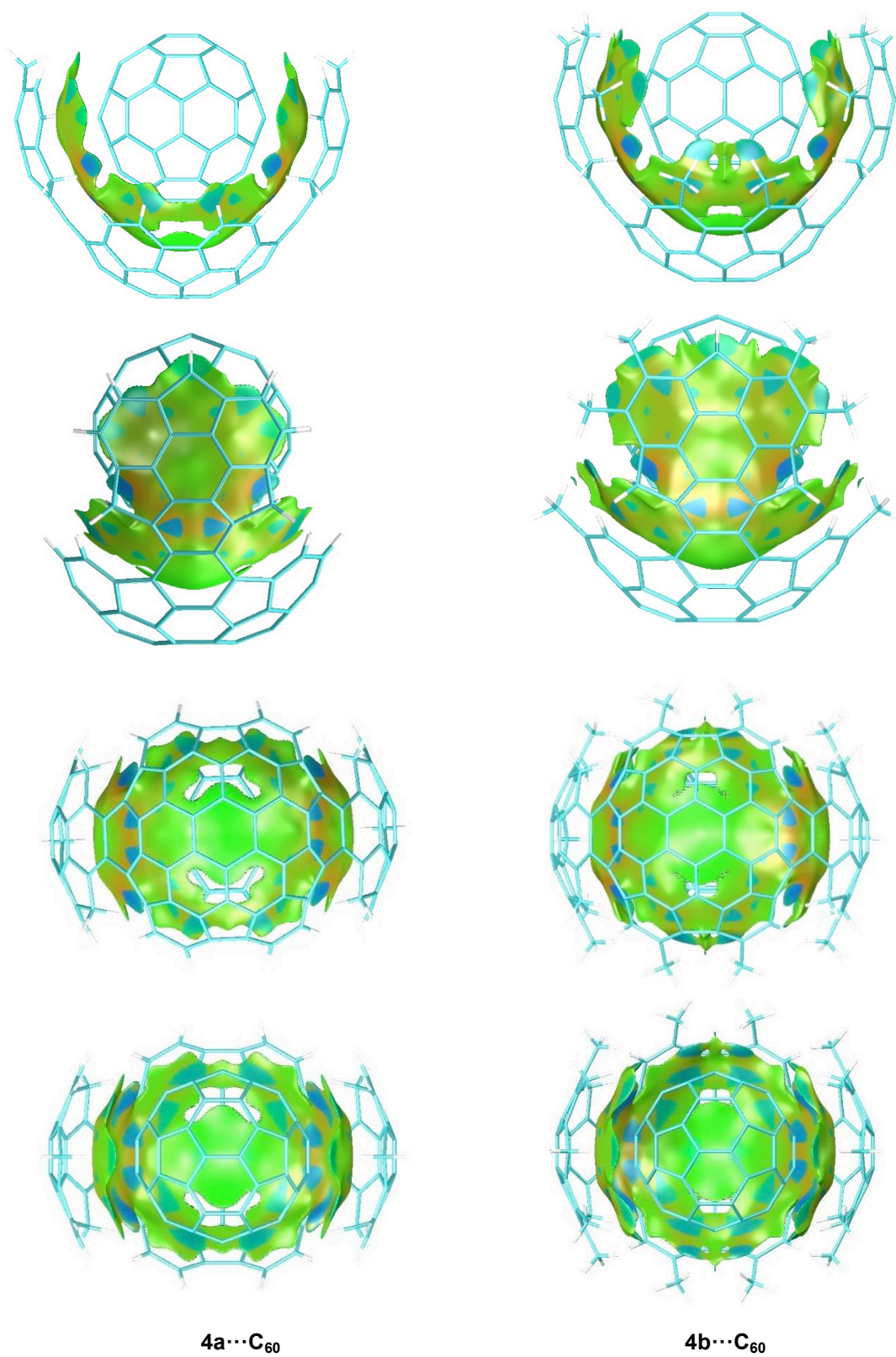


Figure D.4: (cont.)

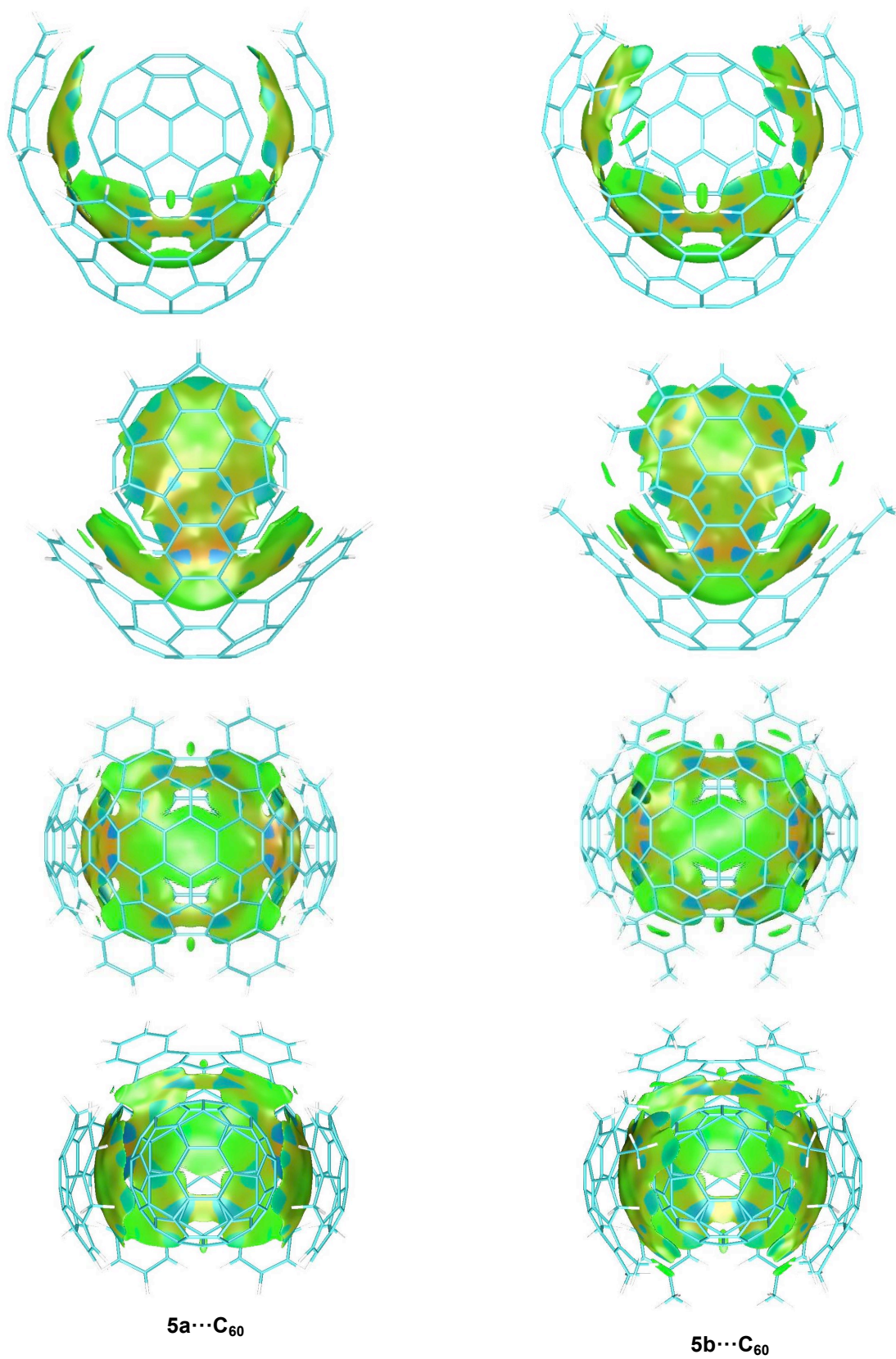


Figure D.4: (cont.)

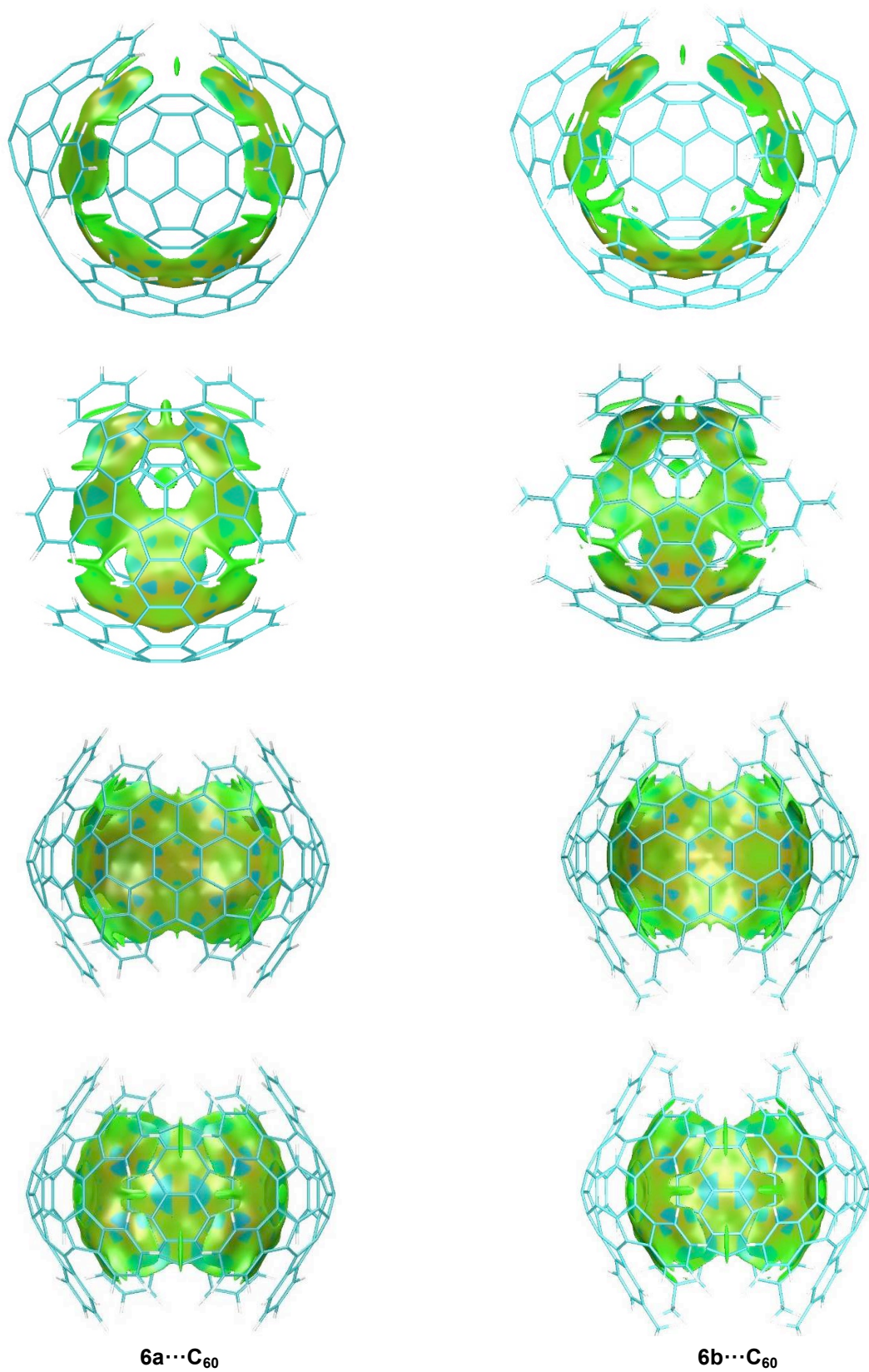
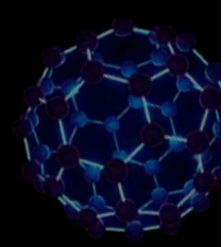


Figure D.4: (cont.)





Nearly 30 years after their discovery, fullerenes, the third allotrope of carbon, remain attracting the interest of many researchers worldwide due their unique properties and applications in wide ranging fields from material science to medicine. Nowadays, the design and synthesis of fullerenes receptors is a very attractive field of research. Besides their great importance in the development of new materials in nanotechnology and nanoscience, fullerene receptors also could be crucial for separation of fullerenes. A promising strategy to design new molecular receptors for fullerenes is using the concave-convex complementarity. Nevertheless, the examples of concave fullerene receptors are relatively scarce since curved molecules are not always an easy synthetic target due their tensioned structures. In this context, bowl-shaped polycyclic aromatic hydrocarbons, commonly known as *buckybowls* or fullerene fragments seem very attractive because several buckybowls have been synthesized in recent years and their concave surface can fit adequately to the convex surface of fullerenes through concave-convex "ball-and-socket"  $\pi \cdots \pi$  interactions. In 2007, Sygula and co-workers introduced a novel type of molecular tweezers (a buckycatcher,  $C_{60}H_{28}$ ) with buckybowl pincers that have attracted a substantial interest of researchers due their ideal architecture for recognizing fullerenes and their potential future applications, in particular as stationary phases in liquid chromatography for the separation of fullerenes or as buckycatcher-fullerene complexes in photovoltaic devices (A. Sygula *et al.* *J. Am. Chem. Soc.* **2007**, *129*, 3842). Despite their great interest, the number of theoretical studies of concave-convex  $\pi \cdots \pi$  interactions between buckybowls and fullerenes are limited due to the recent discovery of these structures, to their large size and, especially, to the fact that until a few years ago there were no satisfactory options for the precise calculation of the non-covalent interactions between large molecules. For that reason, the goal of this doctoral thesis is to carry out an exhaustive theoretical study of the concave-convex  $\pi \cdots \pi$  interactions between buckybowls and fullerenes in order to get a better understanding of the supramolecular systems existing and guiding the design of new systems more effective and/or selective. The methodology of quantum chemistry will be used for this purpose. This methodology has proved to be a powerful tool for understanding phenomena of many kinds. It can provide valuable information, both interpretative, since it can provide a better knowledge of the intimate properties of matter, and predictive, since results can be an important aid for designing appropriate molecules that make use of interactions involving these species.

