

PCCP

Accepted Manuscript



This is an *Accepted Manuscript*, which has been through the Royal Society of Chemistry peer review process and has been accepted for publication.

Accepted Manuscripts are published online shortly after acceptance, before technical editing, formatting and proof reading. Using this free service, authors can make their results available to the community, in citable form, before we publish the edited article. We will replace this *Accepted Manuscript* with the edited and formatted *Advance Article* as soon as it is available.

You can find more information about *Accepted Manuscripts* in the [Information for Authors](#).

Please note that technical editing may introduce minor changes to the text and/or graphics, which may alter content. The journal's standard [Terms & Conditions](#) and the [Ethical guidelines](#) still apply. In no event shall the Royal Society of Chemistry be held responsible for any errors or omissions in this *Accepted Manuscript* or any consequences arising from the use of any information it contains.

Tailoring buckybowls for fullerene recognition. A dispersion-corrected DFT study

Cite this: DOI: 10.1039/x0xx00000x

Daniela Josa,^a Iván González-Veloso,^a Jesús Rodríguez-Otero*^a and Enrique M. Cabaleiro-Lago^b

Received 00th January 2012,
Accepted 00th January 2012

DOI: 10.1039/x0xx00000x

www.rsc.org/

A series of buckybowls with different size and structure have been tested as potential receptors of fullerenes C₆₀, C₇₀ and C₄₀. Among these bowls are corannulene (C₂₀H₁₀), sumanene (C₂₁H₁₂), pinakene (C₂₈H₁₄), hemifullerene (C₃₀H₁₂), circumtrindene (C₃₆H₁₂), pentaindenocorannulene (C₅₀H₂₀) and bowl-shaped hexabenzocoronene derivatives. An exhaustive study taking into account different orientations of fullerenes was performed in order to obtain the most favourable arrangement for interacting with the bowls. Complexes were optimised at the SCC-DFTB-D level and interaction energy were obtained at the B97-D2/TZVP level including. Comparison to full B97-D2/TZVP results (optimisation plus interaction energies) for selected complexes with $\pi \cdots \pi$ interactions suggests that the B97-D2/TZVP/SCC-DFTB-D approach may be a useful screening tool for designing fullerene receptors.

Regarding the "catching" ability of the different buckybowls, it can be concluded that the shape of buckybowl plays a crucial role in its success. So, it seems that addition of *flaps* at the bowl *rim* by benzannelation is an effective strategy to enhance the interaction with fullerenes, providing flexibility enough as to extend the contact surface with the fullerene moiety. In accordance, a bowl-shaped hexabenzocoronene derivative (C₇₂H₂₄) showed the best ability among buckybowls evaluated for catching fullerenes C₆₀, C₇₀ and C₄₀; it is noteworthy that when interacting with C₆₀ the interaction energy is thrice that corresponding to the prototypical buckybowl, corannulene. On the contrary, the more rigid and compact the structure of a buckybowl, the smaller ability for interacting with fullerenes.

Introduction

The discovery of a new form of elemental carbon, buckminsterfullerene (C₆₀)¹, in mid-80s of last century has promoted a lot of research activities in the fields of physics, chemistry and materials science. In addition, this discovery has conducted to a special interest on bowl-shaped polycyclic aromatic hydrocarbons (PAHs), commonly known as *buckybowls* or fullerene fragments. In contrast to others PAHs previously discovered the curvature of buckybowls is not a consequence of addition bulky substituents, but of the impossibility of placing contiguous pentagons and hexagons in a planar sheet. Besides their pure scientific interest, buckybowls also represent chemical entities with future potential applications, especially for host-guest chemistry, such as the *buckycatcher* C₆₀H₂₈² made up by two corannulene units that can encapsulate fullerenes, or its more flexible analogue (C₅₂H₂₈) that can encapsulate solvating molecules of nitrobenzene in the solid state.³

The smallest buckybowl, corannulene (1, Fig. 1) has been the subject of intense experimental and theoretical research in the last years.⁴⁻¹⁷ Recently, Butterfield and co-workers have developed a process for synthesis of corannulene on kilogram scale that reduces material costs by over 2 orders of magnitude

compared to that for the published gram-scale synthesis.¹⁶ Undoubtedly, this find represents a significant step for its future industrial commercialisation.

Nowadays, the design and synthesis of fullerene receptors is a very important field of research. Besides its great importance in the development of new materials in nanotechnology and nanoscience, it also could be crucial for separation of fullerenes. This is because recent studies show that fullerenes and their derivatives represent potential health risks,^{18, 19} and therefore, in the coming years the need for chromatographic separation of fullerenes and its detection at low concentration will surely grow.²⁰

As dispersion plays a major role in $\pi \cdots \pi$ interactions, maximising the host-guest complementarity is particularly important in molecular recognition of fullerenes in terms of both the stability and the selectivity of complexes formed. In this context, the design and synthesis of molecular receptors for fullerenes incorporating buckybowls is very attractive, given that the concave surface of buckybowls can fit highly to the convex surface of the fullerenes through concave-convex "ball-and-socket" $\pi \cdots \pi$ interactions.²

Although several buckybowls with different geometric and electronic properties have been synthesised in the last years,

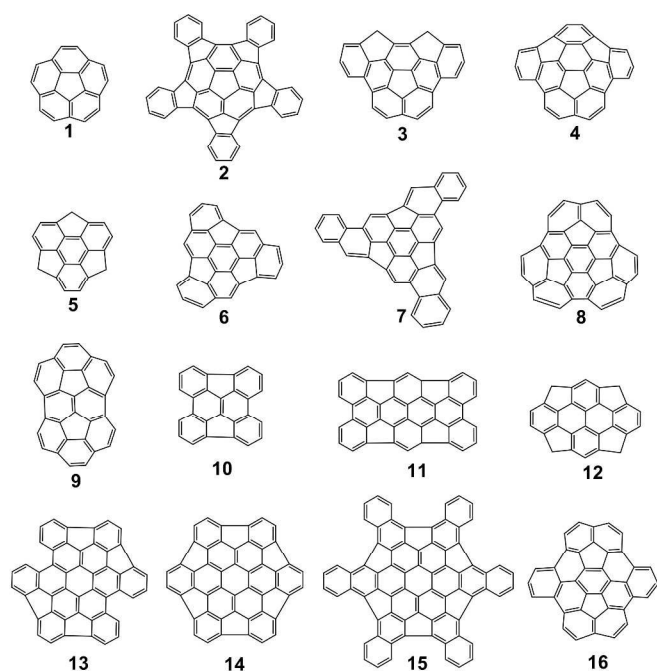


Fig. 1 Buckybowls evaluated in this work.

most stacking interaction studies between buckybowls and fullerenes have focused on corannulene and its derivatives;^{11, 13, 21} To the best of our knowledge, studies with sumanene¹¹, pentaindenocorannulene¹¹ and bowl-shaped hexabenzocoronene derivatives have been reported.²¹⁻²³ On the other hand, it is quite likely that changing the corannulene pincers of the double concave hydrocarbon buckycatcher² by other buckybowls could be a good strategy to improve its efficiency. In this sense, recently, Denis has shown that changing these corannulene pincers by pentaindenocorannulene increases the interaction energy about 15 kcal/mol.^{21, 24} Therefore, the aim of this work is to carry out a comprehensive theoretical study of stacking interactions between a series of buckybowls with different size and structure and fullerenes. Our ultimate goal is finding the best buckybowl to improve the efficiency and/or selectivity of the future *buckycatchers*.

Computational details

All complexes evaluated were optimised by the self-consistent charge density functional tight-binding method using an empirical correction to the dispersion (SCC-DFTB-D). DFTB+ code was applied for this method together with mio-1-1 parameter set.²⁵⁻²⁸ Interaction energies were obtained at the B97-D2/TZVP level using the resolution of identity approximation (RI) as implemented in TURBOMOLE 5.10 program suite.²⁹ This level seems appropriate for this kind of study.¹⁷

Counterpoise corrections were applied to all reported interaction energies to avoid basis set superposition error (BSSE).³⁰ Furthermore, some selected complexes were also optimised at the B97-D2/TZVP level in order to assess the performance of the B97-D2/TZVP//SCC-DFTB-D calculations for studying $\pi \cdots \pi$ interactions.

The visualisation of non-covalent interactions regions was conducted using the NCIPLOT-3.0 program,^{31, 32} and then

graphics of the concave-convex $\pi \cdots \pi$ interactions were obtained using the VMD 1.9.1 software.³³ NCI enables identification of non-covalent interactions and is based on the peaks that appear in the reduced density gradient (RDG) at low densities. When an RDG isosurface for a low value of RDG is plotted, the non-covalent regions clearly appear in the supramolecular complex. These interactions correspond to both favourable and unfavourable interactions. To differentiate between them, the sign of the second density Hessian eigenvalue times the density is colour-mapped onto the isosurface; bonding interactions can be identified by the negative sign. To save computation time, promolecular densities have been used, as was done previously with good results.³⁴

Results and discussion

A series of stacking interactions between buckybowls and fullerenes (C_{60} , C_{70} and C_{40}) were evaluated in this work. Fig. 1 shows the buckybowls studied, most of them previously synthesised.^{22, 35-46} The first group (compounds 1-4) comprises the most popular buckybowl, corannulene (1), and three structures built from the central unit of corannulene. The second group includes sumanene (5) and three structures built from the central unit of it (6-8). In the third group the geometrical centre of the structure is not a ring but a C-C bond; the central unit is a pyracyclene and it is expanded in a central position (compounds 9 and 10) or in a lateral position (compounds 11 and 12). The fourth group has a central unit of coronene. Coronene is a fully planar structure, but the addition of five-membered external rings leads to a bowl-shaped geometry (compounds 13-15). Finally, a slightly different kind of buckybowl was taken into account: compound 16. The prototypical buckybowls (as corannulene or sumanene) corresponds to a fragment of fullerene C_{60} . However, compound 16 corresponds to a fragment of C_{70} . The structure of this latter compound could be considered as a fusion of two corannulene units, and it would be interesting to analyse its ability for supplying a different environment for binding to fullerene. To the best of our knowledge, only compound 15 has not been synthesised yet; this compound has been devised by us for trying to improve the "catching ability" of 14.

Complexes were optimised at the SCC-DFTB-D level and interaction energy calculations were performed at the B97-D2/TZVP level. Different faces of fullerenes and spatial dispositions were also taken into account in this study. All complexes were constructed by aligning of the central ring of the buckybowl with the central ring of the faces of fullerenes given in Fig. S1 (Supplementary Information). Fig. S2 explains the "building" and the naming of complexes.

Performance of B97-D2//SCC-DFTB-D for studying $\pi \cdots \pi$ interactions

According to several studies, B97-D2 seems a good approach for studying $\pi \cdots \pi$ interactions.^{10, 12, 13, 17, 47-50} However, B97-D2 is still quite time-consuming to be employed in the systematic search of suitable strategies for improving the efficiency and/or selectivity of fullerene receptors, especially for studying complexes without any symmetry.

Recently, Sygula and Collier have suggested the use of molecular mechanics (MM) methods as rapid screening tool for designing molecular tweezers and clips.²⁰ Although their results are fairly acceptable, a most accurate description of the concave-convex $\pi \cdots \pi$ interactions could be very useful in the

Table 1. Interaction energies, E_{int} , (kcal/mol) and equilibrium distances, d_{eq} , (Å) for different complexes studied previously with $\pi \cdots \pi$ interactions.⁴⁹ The percentage of error of the B97-D2/TZVP//SCC-DFTB-D interaction energy (less favourable interaction) regarding to the B97-D2/cc-pVTZ one is shown in parentheses.

	B97-D2/cc-pVTZ ^a		B97-D2/TZVP//SCC-DFTB-D	
	d_{eq}	E_{int}	d_{eq}	E_{int}
Planar complexes				
Benzene dimer	3.90	-1.60	3.55	-0.53 (67%)
Naphthalene dimer	3.77	-4.12	3.54	-2.70 (35%)
Anthracene dimer	3.73	-6.83	3.54	-5.12 (25%)
Pyrene dimer	3.69	-8.93	3.53	-7.20 (19%)
Coronene dimer	3.64	-16.30	3.53	-14.13 (13%)
Curved complexes				
1 \cdots 1	3.62	-16.06	3.73	-14.95 (7%)
5 \cdots 5	3.62	-21.09	3.94	-18.02 (15%)
1 \cdots 5	3.63	-16.89	3.80	-15.20 (10%)
5 \cdots 1	3.70	-18.18	3.94	-16.40 (10%)
Curved and planar complexes				
Coronene \cdots 1	3.25	-17.17	3.36	-15.65 (9%)
Coronene \cdots 5	3.18	-17.10	3.28	-14.85 (13%)

^a Data from reference 49.

Table 2. Interaction energies, E_{int} , (kcal/mol) and equilibrium distances, d_{eq} , (Å) for different cases of curved complexes with C_{60} . The percentage of error of the B97-D2/TZVP//SCC-DFTB-D interaction energy (less favourable interaction) regarding to the B97-D2/cc-pVTZ one is shown in parentheses.

	B97-D2/TZVP		B97-D2/TZVP//SCC-DFTB-D	
	d_{eq}	E_{int}	d_{eq}	E_{int}
1 \cdots C ₆₀ (F ₁ -e)	3.456	-17.03	3.636	-16.42 (4%)
2 \cdots C ₆₀ (F ₁ -s ₃₆)	4.086	-37.95	4.313	-36.56 (4%)
5 \cdots C ₆₀ (F ₂ -s ₆₀)	3.450	-20.40	3.856	-17.77 (13%)
6 \cdots C ₆₀ (F ₂ -e)	4.005	-22.53	4.206	-21.52 (5%)
6 \cdots C ₆₀ (F ₂ -s ₃₀)	4.091	-22.29	4.221	-21.62 (3%)
6 \cdots C ₆₀ (F ₂ -s ₆₀)	3.977	-22.96	4.238	-21.70 (6%)
8 \cdots C ₆₀ (F ₂ -e)	5.054	-19.76	5.062	-19.53 (1%)
8 \cdots C ₆₀ (F ₂ -s ₃₀)	4.885	-22.69	5.011	-22.26 (2%)
8 \cdots C ₆₀ (F ₂ -s ₆₀)	5.094	-19.41	5.063	-19.13 (2%)
10 \cdots C ₆₀ (F ₁ -1)	3.529	-22.58	3.786	-21.12 (7%)
10 \cdots C ₆₀ (F ₁ -2)	3.527	-22.63	3.786	-21.12 (7%)
10 \cdots C ₆₀ (F ₂ -1)	3.637	-22.58	3.873	-21.60 (4%)
10 \cdots C ₆₀ (F ₂ -2)	3.599	-22.91	3.867	-21.40 (7%)
14 \cdots C ₆₀ (F ₁)	4.483	-29.54	4.729	-27.98 (5%)
14 \cdots C ₆₀ (F ₂ -1)	4.463	-30.30	4.685	-28.77 (5%)
14 \cdots C ₆₀ (F ₂ -2)	4.577	-26.55	4.641	-25.06 (6%)
15 \cdots C ₆₀ (F ₂ -1)	4.130	-49.80	4.223	-49.47 (1%)
C ₆₀ H ₂₈ \cdots C ₆₀		-39.92		-38.55 (4%)

selection of suitable strategies to design new fullerene receptors. On the other hand, the recent SCC-DFTB-D approach not only shows outstanding time/performance efficiency in several studies, but also does not require large amounts of empirical parameter fields to describe molecular properties.^{51, 52} Therefore, taking into account the limitations of MM methods, we believe that SCC-DFTB-D approach could be a more balanced and suitable screening tool.

Thus, the performance of the B97-D2//SCC-DFTB-D regarding the full B97-D2 has been evaluated for four groups of complexes with $\pi \cdots \pi$ interactions: (1) complexes with eclipsed PAHs; (2) complexes with curved PAHs; (3) mixed complexes made up by planar and curved PAHs; (4) complexes made up by curved PAHs and C₆₀. Table 1 shows the results for the three

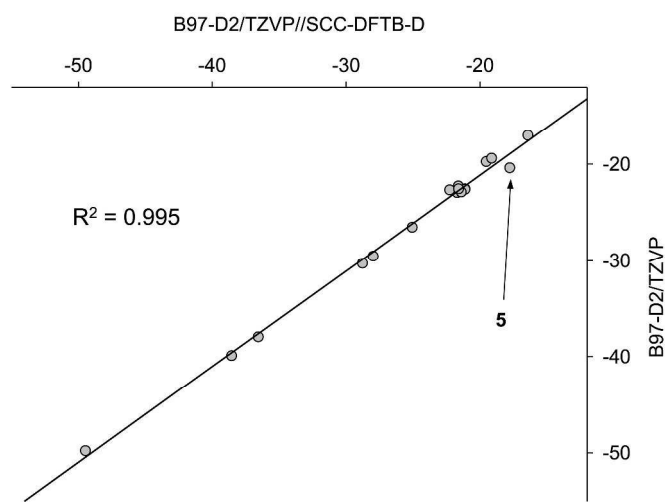


Fig. 2 B97-D2/TZVP vs. B97-D2/TZVP//SCC-DFTB-D interaction energy in (kcal/mol). Linear fit gave $E_{\text{int}}(\text{B97-D2/TZVP}) = 0.9942E_{\text{int}}(\text{B97-D2/TZVP//SCC-DFTB-D}) - 1.271$ with an R^2 value of 0.995.

first groups, obtained previously by us at the B97-D2/cc-pVTZ level⁴⁹ and Table 2 shows the results for the last group performed at the B97-D2/TZVP level. Complexes of Table 2 are chosen trying to select a diverse set of buckybowls and including several faces of fullerenes.

Regarding the geometry of dimers, the results of Tables 1-2 show a moderate increase in the equilibrium distance between monomers (taken as the distance between the centre of the buckybowls' central ring and the centre of the ring of the fullerene directly faced to it) obtained at the SCC-DFTB-D level relative to that obtained at the B97-D2 level. There are only two clear exceptions to this trend: planar complexes where the trend is opposite and complexes 8 \cdots C₆₀ where equilibrium distances are very similar with the two calculation levels (only a difference of about a tenth of angstrom arises). As it will be discussed later, this distinctive feature of compound 8 is related to its particular structure (closed and deep): this fact leads to very distant fullerenes, regardless the level of calculation.

Obviously the quality of the interaction energies obtained using the SCC-DFTB-D geometries is directly related to the quality of these geometries, which seem not too bad as they lead to rather satisfactory interaction energies. The worst results correspond to complexes formed by planar monomers, but even in this case the results improve as the size grows, reaching a moderate error (about 2 kcal/mol, 13 %) for the coronene dimer. Thereby, B97-D2/TZVP//SCC-DFTB-D calculations could also seem appropriate for studying large $\pi \cdots \pi$ planar complexes. For complexes with curved monomers the energetic results are much better and even errors of only 1 % are obtained. Moreover, the correlation between interaction energies is excellent ($R^2 = 0.995$) as shown in Fig. 2, which includes the results for the complexes with C₆₀ of Table 2. Only complex 5 \cdots C₆₀ deviates slightly of the linear behaviour, although not much. This is also directly related with the outstanding energetic error of Table 2 (13 %), which in turn is consequence of the largest difference in equilibrium distance (more than 4 tenths of angstrom). On the opposite side, complexes 8 \cdots C₆₀ are found, with very small errors of 1-2 %, as expected from their good geometries. It certainly happens something similar with the complex 15 \cdots C₆₀, with an error of 1 %, as a result of a difference smaller to a tenth of angstrom in the equilibrium distance.

Table 3. Equilibrium distances (Å) for the most stable conformation of the studied complexes. All optimisations were performed at the SCC-DFTB-D level.

	X=C ₆₀	X=C ₇₀	X=C ₄₀
1...X	3.636	3.644	3.649
2...X	4.313	4.361	4.328
3...X	4.075 ^a		
4...X	3.862 ^a		
5...X	3.856	3.912	3.596 ^a
6...X	4.238	4.047 ^a	4.128
7...X	4.197		
8...X	5.011	5.003	4.907
9...X	4.412		
10...X	3.873	3.907	3.804
11...X	4.300 ^a		
12...X	4.084		
13...X	3.373 ^a		
14...X	4.685		
15...X	4.223	4.096 ^a	3.836
16...X	4.101		

^a In these complexes the bucky bowl's central ring is very displaced from the centre of the face of fullerene used to build the complex; therefore, d_{eq} is taken as the distance between the centre of the bucky bowl's central ring and the closest atom of fullerene.

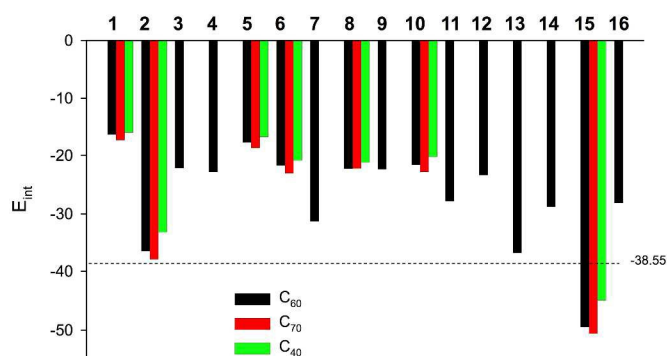


Fig. 3 B97-D2/TZVP//SCC-DFTB-D interaction energy (kcal/mol) for complexes bucky bowl...fullerene.

As already mentioned the worst result in Table 2 and Fig. 2 corresponds to the 5...C₆₀ complex (the complex between sumanene and fullerene), but if Table 1 is analysed at the same time (for complexes with curved monomers) is easy to realise that the worst results correspond to those cases involving sumanene; especially when it is doubly involved (5...5, 15 %). However, corannulene participation leads to clearly better results: between 7 (corannulene dimer) and 10 % of error. In the same way the complex designed by Sygula², C₆₀H₂₈...C₆₀ (which incorporates two corannulene units) shows an error of only 4%.

In summary, for complexes with curved monomers B97-D2/TZVP//SCC-DFTB-D calculations lead to very reasonable interaction energies if compared with the full B97-D2 ones. With the only exception of complexes with sumanene, the difference in interaction energy ranges from 0.26 to 1.56 kcal/mol (which corresponds to an error of 1-7 %). When sumanene is involved the results are slightly worse, with a difference of 2.56 kcal/mol (13 %) for the complex with C₆₀. At first sight, inspection of the structure of bucky bowls of Table 2 leads to a first hypothesis: only sumanene includes *sp*³ carbon atoms, *i.e.*, only this bucky bowl has the ability to establish C-H... π interactions with fullerene. This kind of interaction can play a quite important role as shown recently since it takes

place especially for compounds with saturated rings, where the internal hydrogen atom of the CH₂ group points directly to the π cloud of fullerenes.¹⁷ It would not be surprising that SCC-DFTB-D method was not able to account for this subtle effect. For that reason, the monomers are not close enough and the reproduction of interaction energy is slightly less accurate when sumanene participates.

In brief, despite some limitations, the B97-D2/TZVP//SCC-DFTB-D approach provides sufficiently accurate results so that it can be used as a useful tool for a rapid selection of suitable strategies for rational design of molecular clips and tweezers. Moreover, SCC-DFTB-D method also can be very useful to provide start guess for more accurate calculations of the largest π ... π complexes.

Stacking interactions between bucky bowls with fullerene C₆₀, C₇₀, and C₄₀

Dispersion interactions play the most prominent role in the association of bucky bowls with fullerenes.¹⁷ So, it seems very obvious that increasing the bucky bowl size will lead to an enhancement of the interaction with fullerene. However, the key question is: how to increase the bucky bowl size to maximise fullerene recognition? In order to answer this question, the stacking interaction between a series of bucky bowls and fullerene C₆₀ has been evaluated.

First, the stacking interaction taking into account different faces of fullerene C₆₀ was evaluated in order to obtain the most favourable face for interacting with bucky bowls. According to our results, the stacking interaction with different faces of C₆₀ leads to differences ranging from 0.31 to 3.71 kcal/mol (Table S1, Supplementary Information). Therefore, it seems that the choice of the face is not relevant in some cases, but it is crucial to get the correct results in others. A similar analysis was performed with fullerenes C₇₀ and C₄₀, but only with some selected bucky bowls: 1 and 5, the most popular bucky bowls, corannulene and sumanene; 2 and 6, a variant of the above two; 8, a very particular bucky bowl (a very closed bowl with a very large depth); 10, the most simple example of bucky bowls derived from pyracylene; and 15, an example of the coronene derived structures, and clearly the best buckycatcher for C₆₀. According to our results (Table S1, Supplementary Information) comparable conclusions to those obtained with C₆₀ are achieved. The main difference is that for complexes with these two fullerenes the choice of the face is more critical: there are no cases where this selection is irrelevant since always leads to differences higher than 1 kcal/mol in interaction energy. In general these differences (especially with C₇₀, ranging from 1.61 to 3.93 kcal/mol) are always higher if compared with those of the same complexes with C₆₀. This is a pretty reasonable result since C₆₀ is the most spherical fullerene and therefore the particular face for binding to the bowl should be less relevant.

Taking into account only the best case (largest interaction energy) for each bucky bowl...fullerene complex, Table 3 summarises the equilibrium distances, d_{eq} , at the SCC-DFTB-D level, and Fig. 3 shows a comparison of the calculated interaction energies. As expected, none general correlation between equilibrium distance and interaction energy was found (Fig. S5, Supplementary Information), because differences in structure of bucky bowls are too large. Only for the case of compound 13 with C₆₀, a significantly shorter equilibrium distance than for 1, corannulene, was found. Compound 8 leads to the complexes with the largest d_{eq} , which is consequence of

Table 4. B97 component of the interaction energy and dispersion contribution (kcal/mol) for the most stable complexes (optimised at the SCC-DFTB-D level) calculated at the B97-D2/TZVP level.

	X=C ₆₀		X=C ₇₀		X=C ₄₀	
	B97	Dispersion	B97	Dispersion	B97	Dispersion
1...X	11.59	-28.01	12.05	-29.41	10.97	-27.02
2...X	24.30	-60.86	26.00	-63.92	22.41	-55.54
3...X	18.48	-40.63				
4...X	16.90	-39.71				
5...X	12.00	-29.77	12.73	-31.42	12.19	-29.00
6...X	16.43	-38.13	17.96	-40.99	16.35	-37.21
7...X	20.55	-51.82				
8...X	17.22	-39.48	17.99	-40.20	15.98	-37.16
9...X	16.04	-38.37				
10...X	12.85	-34.45	14.52	-37.31	12.86	-33.06
11...X	22.60	-50.43				
12...X	15.44	-38.77				
13...X	22.61	-59.43				
14...X	20.89	-49.66				
15...X	30.46	-79.93	35.99	-86.59	30.04	-74.95
16...X	19.85	-48.00				

the closed and deep structure of this buckybowl, as already commented above.

Fig. 3 shows that in general interaction with C₇₀ is slightly more favourable than with C₆₀; however, the interaction with C₄₀ is meaningfully less favourable. Consequently, it is not expected that these buckybowls to specifically bind one of the fullerenes when exposed to a C₆₀/C₇₀ mixture, since the major difference for catching C₆₀ and C₇₀ is only about 1.3 kcal/mol for compounds 2 and 6. With C₄₀ the differences, relative to C₆₀, are higher reaching 3.43 and 4.56 kcal/mol for compounds 2 and 15; thus some selectivity could be found, especially when compound 15 is exposed to a C₆₀/C₄₀ mixture (but this combination is not very common, since usually C₆₀ is mixed with larger fullerenes).

According to Fig. 3, compounds 2, 7, 13, and 15 lead to the most favourable cases (interaction energy stronger than -30 kcal/mol). Compounds 2, 7, and 15 show a rather interesting particularity: they are the only ones that have a ring that shares only a bond with the rim of the bowl; that external ring might be called a *flap*. As can be seen, these three buckybowls show a noteworthy improvement in the fullerene recognition compared to buckybowls of the same group without *flaps*. It could be argued that this improvement might be simply caused by the increase of the size of the bowl with the subsequent increase of dispersion. This issue has no simple answer, but if the behaviour of compounds 14 and 15 are compared (the only case where the same structure with and without *flaps* is available), then it can be observed that an increase of the bowl size (from 48 to 72 carbon atoms, 50 %) leads to a significantly higher increase of the interaction energy with C₆₀ (from -28.77 to -49.47 kcal/mol, 72 %). Compound 13 leads to one of the highest interaction energies (-36.26 kcal/mol with C₆₀) but it does not have *flaps*, as they were described above. However, this compound has four external hexagonal rings that act in a similar manner. They are less able to bend as the case of the real *flaps* (the anchoring to the rim of the bowl is by sharing two bonds), but its structure is flexible enough for "embracing" the fullerene to some extent. This ability leads to an increase of the interaction energy with C₆₀ of 26 % if compared with that of compound 14, having both compounds very similar sizes. Moreover, it is worth noting that only for this compound 13 the equilibrium distance in the complex with C₆₀, d_{eq} , is smaller than that of corannulene, 1.

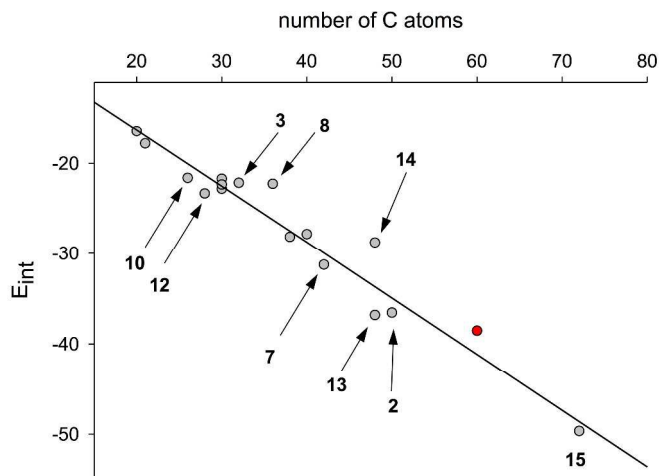


Fig 4. Relationship between the bowl size (given by the number of carbons, N_c) and the interaction energy: $E_{int} = -0.6218N_c - 3.859$ with an R^2 value of 0.937. The red point corresponds to the tweezers designed by Sygula *et al.*²

As already noted, a possible way to measure the efficiency of a receptor is comparing its size with the interaction energy that it causes. This is because simply increasing the size of a receptor an increase of the dispersion energy is achieved when this receptor binds to fullerene. Although the number of C atoms of a structure is not a very reliable measure of the size of this structure, it may account for the relevance of dispersion. As expected, Fig. 4 shows a rather good correlation between the number of C atoms of a bowl and the interaction energy with C₆₀ ($R^2 = 0.937$). Nevertheless, the most important thing is detecting the deviations of the linear behaviour looking for the most efficient receptors; that is to say, the best receptors that produce large interaction energies without a large increase of size. In this respect, it seems clear that compounds 2, 7, 10, 12, 15, and especially 13, are efficient receptors with larger interaction energy than predicted by their size. Compounds 2, 7, 13, and 15 (with some kind of *flaps*) were already commented above, and thus Fig. 4 reinforces the previous conclusions. Compounds 10 and 12 also work rather well, with large interaction energy than predicted by their size. However, due to their small size, this good performance in relative terms is not so good in absolute terms. Compounds 3, and especially 8 and 14 are found in the opposite situation, with smaller interaction energy than predicted by their size. They are very rigid and compact structures with little ability to "embrace" the fullerenes. Especially poor is the performance of compound 14, a large bowl with rather modest "catching" aptitude. Addition of *flaps* to this structure leads to buckybowl 15 (proposed here, but not yet synthesised): clearly the strongest fullerene receptor obtained. It almost triplicates the interaction produced by corannulene, 1, and leads to an increase of about 11 kcal/mol in the interaction energy if compared with that of the tweezers designed by Sygula *et al.*² These tweezers (shown in red in Fig. 4) do not have a high efficiency relative to the number of C atoms, but this is not surprising since in this case not all the C atoms face directly the fullerene (as it is the case of a significant part of the tetrabenzocyclooctatetraene tether).

In summary, an important conclusion could be that addition of *flaps* at the bowl rim seems a promising strategy for designing more effective fullerene receptors. The addition of these *flaps* not only increases the size of the π -system, but also does so in an advantageous manner since the slight flexibility of the *flaps* favours the "embrace" of fullerenes. Although this flexibility is

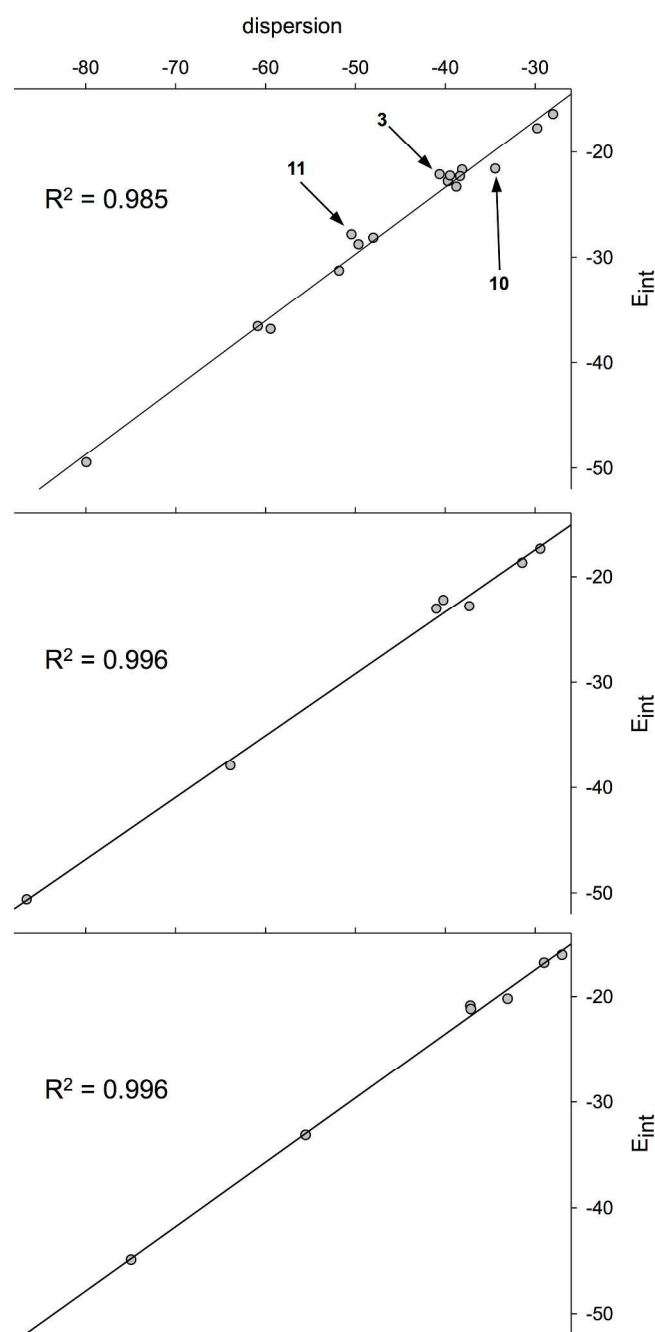


Fig. 5 Interaction energy vs. dispersion component (kcal/mol). Top: complexes with C₆₀; $E_{int} = 0.6337E_{disp} + 1.983$, $R^2 = 0.985$. Middle: complexes with C₇₀; $E_{int} = 0.5867E_{disp} + 0.1327$, $R^2 = 0.996$. Bottom: complexes with C₄₀; $E_{int} = 0.6082E_{disp} + 0.8041$, $R^2 = 0.996$.

rather small, is strong enough to modify significantly the distance between the external rings and the fullerene, thereby modifying the dispersion effects (see page 4 of Supplementary Information). If the bowl does not have any kind of *flaps*, at least it should have some flexibility to be an efficient fullerene receptor. Therefore, in general, large rigid structures can be good receptors but with an efficiency much lesser than predicted by their size.

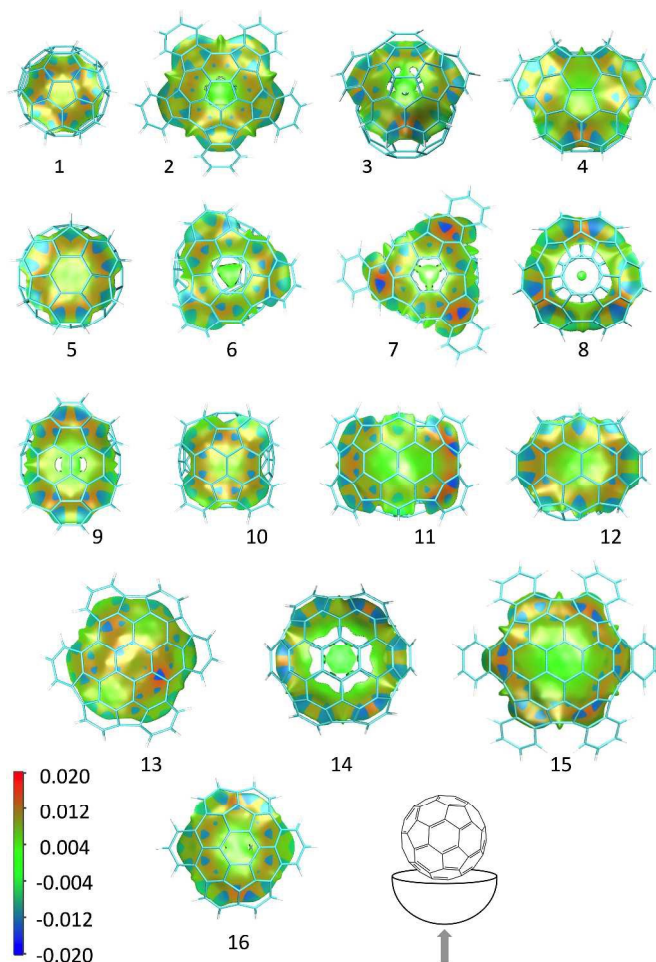


Fig. 6 Bottom views (following the arrow) of the NCIPlot gradient isosurface (0.4 a.u.). The surfaces are coloured on a blue-green-red scale according to the strength and type (attractive or repulsive) of interaction. Blue indicates strong attractive interactions, green indicate weak vdW interactions, and red indicates strong nonbonded overlap. Front and top views of NCIPlot are available in the Supplementary Information.

In order to analyse in more detail the balance of energy contributions to the stability of the complexes, the interaction energy was decomposed according to a very simple method. So, the two main contributions of the model employed were taken into account; that is, the pure B97 interaction energy and the empirical dispersion contribution to the interaction energy. Results in Table 4 show that dispersion plays a crucial role in the interaction energy of complexes. First, because the contribution of the pure B97 functional is clearly repulsive, so dispersion is responsible for the binding in complexes. And second, and more noteworthy, because as can be seen in Fig. 5, there is an excellent correlation between dispersion and interaction energies for complexes evaluated (with $R^2 = 0.985$, 0.996, and 0.996 for complexes with C₆₀, C₇₀, and C₄₀, respectively). Only bowls 3, 10, and 11 when complexed with C₆₀ deviate from the perfectly linear behaviour by a somewhat appreciable difference: compound 10 leads to larger interaction energy than that predicted by dispersion; compounds 3 and 11 lead to an opposite condition. In order to explain these minimal discrepancies, a qualitative analysis based on the contribution of electrostatics to interaction energy (similar to that performed previously in a recent paper¹⁷) has been carried out (see Supplementary Information).

Finally, a qualitative non-covalent interactions (NCI) analysis has been performed to obtain more information about $\pi\cdots\pi$ interactions and more data about the behaviour of the different bowls. The visualisation of $\pi\cdots\pi$ interactions between the two monomers in the real space was drawn using VMD software³³ with an isosurface of 0.4 a.u. and scale running from -0.020 (min) to 0.020 a.u. (max): blue, green and red indicate strongly attractive, weak and strongly repulsive interactions, respectively. Fig. 6 shows the NCI plots for complexes with C₆₀ (Fig. S3 in the Supplementary Information includes more views of the NCI plots). The first thing that catches the eye in this figure is that compounds 8 and 14 (which are the most inefficient ones in relation to their size, as discussed above) are precisely those that show more significant discontinuities in their RDG isosurfaces. This is undoubtedly related to the fact, as previously commented, that these two bowls have very compact and deep structures, which leads to the longest equilibrium distances (4.685 Å for 14 \cdots C₆₀, and especially 5.011 Å for 8 \cdots C₆₀). For this reason, for these two compounds the interaction with fullerene is much more important with the walls than with the bottom of the bowl. Even so, for compound 14 the interaction is still rather important due to the considerable size of the surface (consequence of the size of compound) and the significant attractive zones. In general, the best receptors in absolute terms as 2, 7, 11, 13, 15, and 16 or in relative terms (in relation to its size) also including 10 and 12, are related to large and continuous RDG surfaces with important attractive zones (blue). Compound 7 is the only exception to this trend: in this case the small discontinuity of the surface is compensated by the presence of three strong attractive areas. The surface of the 11 \cdots C₆₀ clearly shows the displacement of fullerene to the right side of the bowl, weakening the interaction in the other side. Comparison of NCI plots of 14 \cdots C₆₀ and 15 \cdots C₆₀ shows the huge difference between these two cases: the addition of *flaps* not only increases the interaction surface but it also removes the discontinuities of it. This causes a huge shortening of the equilibrium distance: 0.462 Å. In summary, NCI plots reinforce the conclusion that shape of bucky bowl plays a fundamental role for the enhancement of the fullerene recognition.

Conclusions

According to our results, the B97-D2/TZVP//SCC-DFTB-D approach seems to be a useful tool for a rapid selection of suitable strategies for rational evaluation and design of fullerene receptors. Fullerene orientation relative to the bowl has very little importance in some cases, but in others it is essential to get the proper results (differences of almost 4 kcal/mol can be obtained).

Dispersion plays a crucial role on the interaction energy in these complexes: it is responsible for the binding in them, showing an excellent correlation with the interaction energies (the minimal deviations can be explained by a qualitative analysis based on the contribution of electrostatics to interaction energy). As expected, the increase on dispersion energy shows a fairly good correlation with the increase on bowl size. However, there are some substantial deviations that can be attributed to the shape of the bowl. In this way, compounds whose structure possesses *flaps* at the *rim* of the bowl show an enhanced ability for interacting with fullerenes. On the contrary, compounds with very rigid and compact structures show little ability to "embrace" the fullerenes.

The largest interaction corresponds to complexes with the devised compound 15, a bowl-shaped hexabenzocoronene derivative. This bucky bowl has a large size and added *flaps*, which allows obtaining interaction energies of about 50 kcal/mol (triple than that achieved with corannulene). However, in relation to its size, the most efficient receptor is compound 13, which also has a kind of *flaps*. This type of appendix not only increases the size of the π -system, but also does so in an advantageous manner since their slight flexibility favours the "embrace" of fullerenes. If the bowl does not have any kind of *flaps*, at least should have some flexibility to be an efficient fullerene receptor. For that reason, large compounds with a very rigid structure can be good receptors but with an efficiency much smaller than predicted by their size.

NCI plots reinforce the conclusion that the shape of the bucky bowl plays a fundamental role for the enhancement of fullerene recognition. The best receptors are related to large and continuous RDG surfaces with important attractive zones.

Finally, it is worth mentioning that the interaction energy for the complexes with C₇₀ shows only small increases with respect to that obtained with C₆₀. On the other hand, complexes with C₄₀ show a significant decrease in the interaction energy regarding to C₆₀ and C₇₀. The greatest differences take place for bucky bowls 2 and 15 that show a decrease of 3.43 and 4.56 kcal/mol regarding to C₆₀, respectively. Curiously, bucky bowls 2 and 15 are the only (studied with C₄₀) having *flaps* in their structure. So, the addition of *flaps* on the *rim* of the bowl perhaps could also be a useful strategy for designing bucky bowls for the selective separation of fullerenes from mixtures.

Acknowledgements

We are extremely grateful to Prof. Hélio A. Duarte and his research group at the *Universidade Federal de Minas Gerais* (Brazil), especially to Dr. Maurício C. Silva, for introducing D.J. to the SCC-DFTB method and for allowing part of calculations were done by means of their computing facilities.

This research has been supported by the Xunta de Galicia (project INCITE09209103PR). The authors want to express their gratitude to the CESGA (Centro de Supercomputación de Galicia) for the use of their computers. D.J. thanks the Spanish Ministry of Education for FPU scholarship.

^a Centro Singular de Investigación en Química Biolóxica e Materiais Moleculares. Universidade de Santiago de Compostela, Rúa Jenaro de la Fuente, s/n 15782, Santiago de Compostela, Galicia (Spain).

^b Departamento de Química Física, Facultad de Ciencias, Universidade de Santiago de Compostela, Campus de Lugo, Av. Alfonso X El Sabio, s/n 27002 Lugo, Galicia (Spain).

Electronic Supplementary Information (ESI) available: NCI plots, MEPS, full interaction energies, full geometries. See DOI: 10.1039/b000000x/

References

1. H. W. Kroto, J. R. Heath, S. C. O'Brien, R. F. Curl and R. E. Smalley, *Nature*, 1985, **318**, 162-163.
2. A. Sygula, F. R. Fronczek, R. Sygula, P. W. Rabideau and M. M. Olmstead, *J. Am. Chem. Soc.*, 2007, **129**, 3842-3843.
3. L. Kobryn, W. P. Henry, F. R. Fronczek, R. Sygula and A. Sygula, *Tetrahedron Lett.*, 2009, **50**, 7124-7127.
4. T. J. Seiders, K. K. Baldrige, G. H. Grube and J. S. Siegel, *J. Am. Chem. Soc.*, 2001, **123**, 517-525.
5. K. Kavitha, M. Manoharan and P. Venunalingam, *J. Org. Chem.*, 2005, **70**, 2528-2536.
6. A. K. Kandalam, B. K. Rao and P. Jena, *J. Phys. Chem. A*, 2005, **109**, 9220-9225.

7. P. A. Denis, *J. Mol. Struct. (Theochem)*, 2008, **865**, 8-13.
8. M. A. Petrukhina, K. W. Andreini, J. Mack and L. T. Scott, *J. Org. Chem.*, 2005, **70**, 5713-5716.
9. A. Sygula and S. Saebo, *Int. J. Quantum Chem.*, 2009, **109**, 65-72.
10. T. Janowski, P. Pulay, A. A. Sasith Karunarathna, A. Sygula and S. Saebo, *Chem. Phys. Lett.*, 2011, **512**, 155-160.
11. P. A. Denis, *Chem. Phys. Lett.*, 2011, **516**, 82-87.
12. D. Josa, J. Rodríguez Otero and E. M. Cabaleiro Lago, *Phys. Chem. Chem. Phys.*, 2011, **13**, 21139-21145.
13. I. Welsh and M. Lein, *J. Comput. Chem.*, 2014, **35**, 181-191.
14. M. Rellán Piñero, J. Rodríguez Otero, E. M. Cabaleiro Lago and D. Josa, *J. Mol. Model.*, 2013, **19**, 2049-2055.
15. M. R. Kennedy, L. A. Burns and C. D. Sherrill, *J. Phys. Chem. A*, 2012, **116**, 11920-11926.
16. A. M. Butterfield, B. Gilomen and J. S. Siegel, *Org. Process Res. Dev.*, 2012, **16**, 664-676.
17. D. Josa, L. Azevedo dos Santos, I. González-Veloso, J. Rodríguez-Otero, E. M. Cabaleiro-Lago and T. de Castro Ramalho, *RSC Adv.*, 2014, **4**, 29826-29833.
18. J. Gao, H. L. Wang, A. Shreve and R. Iyer, *Toxicol. Appl. Pharmacol.*, 2010, **244**, 130-143.
19. E. J. Park, H. Kim, Y. Kim, J. Yi, K. Choi and K. Park, *Toxicol. Appl. Pharmacol.*, 2010, **244**, 226-233.
20. A. Sygula and W. E. Collier, in *Fragments of Fullerenes and Carbon Nanotubes: Designed Synthesis, Unusual Reactions, and Coordination Chemistry*, ed. M. A. Petrukhina and L. T. Scott, John Wiley & Sons, Inc., Hoboken, NJ, USA, 2012, ch. 1, pp. 1-40.
21. P. A. Denis, *RSC Adv.*, 2013, **3**, 25296-25305.
22. A. C. Whalley, K. N. Plunkett, A. A. Gorodetsky, C. L. Schenck, C.-Y. Chiu, M. L. Steigerwald and C. Nuckolls, *Chem. Sci.*, 2011, **2**, 132-135.
23. G. Casella and G. Saielli, *New J. Chem.*, 2011, **35**, 1453-1459.
24. P. A. Denis, *Chem. Phys. Lett.*, 2014, **591**, 323-327.
25. M. Elstner, D. Porezag, G. Jungnickel, J. Elsner, M. Haugk, T. Frauenheim, S. Suhai and G. Seifert, *Phys. Rev. B*, 1998, **58**, 7260-7268.
26. M. Elstner, T. Frauenheim and S. Suhai, *Phys. Status Solidi B*, 2000, **217**, 357-376.
27. M. Elstner, P. Hobza, T. Frauenheim, S. n. Suhai and E. Kaxiras, *J. Chem. Phys.*, 2001, **114**, 5149-5155.
28. M. Elstner, K. J. Jalkanen, M. Knapp-Mohammady, T. Frauenheim and S. Suhai, *Chem. Phys.*, 2001, **263**, 203-219.
29. R. Ahlrichs, M. Bär, M. Häser, H. Horn and C. Kölmel, *Chem. Phys. Lett.*, 1989, **162**, 165-169.
30. S. F. Boys and F. Bernardi, *Mol. Phys.*, 1970, **19**, 553-566.
31. E. R. Johnson, S. Keinan, P. Mori-Sánchez, J. Contreras-García, A. J. Cohen and W. Yang, *J. Am. Chem. Soc.*, 2010, **132**, 6498-6506.
32. J. Contreras-García, E. R. Johnson, S. Keinan, R. Chaudret, J. P. Piquemal, D. N. Beratan and W. Yang, *J. Chem. Theory Comput.*, 2011, **7**, 625-632.
33. W. Humphrey, A. Dalke and K. Schulten, *J. Mol. Graphics*, 1996, **14**, 33-38.
34. D. Josa, J. Rodríguez-Otero, E. M. Cabaleiro-Lago, L. A. Santos and T. C. Ramalho, *J. Phys. Chem. A*, 2014, **118**, 9521-9528.
35. W. E. Barth and R. G. Lawton, *J. Am. Chem. Soc.*, 1966, **88**, 380-381.
36. E. A. Jackson, B. D. Steinberg, M. Bancu, A. Wakamiya and L. T. Scott, *J. Am. Chem. Soc.*, 2007, **129**, 484-485.
37. T. C. Wu, H. J. Hsin, M. Y. Kuo, C. H. Li and Y. T. Wu, *J. Am. Chem. Soc.*, 2011, **133**, 16319-16321.
38. H. Sakurai, T. Daiko and T. Hirao, *Science*, 2003, **301**, 1878.
39. S. Hagen, M. S. Bratcher, M. S. Erickson, G. Zimmermann and L. T. Scott, *Angew. Chem. Int. Ed. Engl.*, 1997, **36**, 406-408.
40. S. Higashibayashi and H. Sakurai, *Chem. Lett.*, 2011, **40**, 122-128.
41. L. T. Scott, M. S. Bratcher and S. Hagen, *J. Am. Chem. Soc.*, 1996, **118**, 8743-8744.
42. G. Mehta and G. Panda, *Chem. Commun.*, 1997, 2081-2082.
43. L. T. Scott, *Pure & Appl. Chem.*, 1996, **68**, 291-300.
44. A. Sygula, *Eur. J. Org. Chem.*, 2011, **2011**, 1611-1625.
45. G. Mehta, G. Panda, R. D. Yadav and K. Ravikumar, *Indian J. Chem., Sect. B: Org. Chem. Incl. Med. Chem.* 1997, **36 (B)**, 301-302.
46. T. C. Wu, M. K. Chen, Y. W. Lee, M. Y. Kuo and Y. T. Wu, *Angew. Chem. Int. Ed.*, 2013, **52**, 1289-1293.
47. C. Mück-Lichtenfeld, S. Grimme, L. Kobryn and A. Sygula, *Phys. Chem. Chem. Phys.*, 2010, **12**, 7091-7097.
48. S. Grimme, *J. Comput. Chem.*, 2006, **27**, 1787-1799.
49. D. Josa, J. Rodríguez-Otero, E. M. Cabaleiro-Lago and M. Rellán-Piñero, *Chem. Phys. Lett.*, 2013, **557**, 170-175.
50. S. Grimme, C. Mück-Lichtenfeld and J. Antony, *J. Phys. Chem. C*, 2007, **111**, 11199-11207.
51. G. Zheng, S. Irle and K. Morokuma, *Chem. Phys. Lett.*, 2005, **412**, 210-216.
52. M. Gaus, Q. Cui and M. Elstner, *WIREs Comput. Mol. Sci.*, 2014, **4**, 49-61.