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Substituted Corannulenes and Sumanenes as Fullerene Receptors. A Dispersion-Corrected Density Functional Theory Study

Daniela Josa,[†] Jesús Rodríguez-Otero,*[,†] Enrique M. Cabaleiro-Lago,[‡] Lucas A. Santos,[§] and Teodorico C. Ramalho[§]

[†]Centro Singular de Investigación en Química Bolóxica e Materiais Moleculares (CIQUS), Universidade de Santiago de Compostela, Rúa Jenaro de la Fuente, s/n 15782 Santiago de Compostela, Galicia, Spain

[‡]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

[§]Departamento de Química, Universidade Federal de Lavras, Campus Universitário UFLA, 37200-000 Lavras, Minas Gerais, Brazil

S *Supporting Information*

ABSTRACT: Stacking interactions between substituted buckybowls (corannulene and sumanene) with fullerenes (C_{60} and C_{70}) were studied at the B97-D2/TZVP level of theory. Corannulene and sumanene monomers were substituted with five and six Br, Cl, CH_3, C_2H, or CN units, respectively. A comprehensive study was conducted, analyzing the interaction of corannulenes and sumanenes with several faces of both fullerenes. According to our results, in all cases substitution gave rise to larger interaction energies if compared with those of unsubstituted buckybowls. The increase of dispersion seems to be the main source of the enhanced binding, so an excellent correlation between the increase of interaction energy and the increase of dispersion contribution takes place. One of the noteworthy phenomena that appears is the so-called CH···π interaction, which is responsible for the strong interaction of sumanene complexes (if compared with that of corannulene complexes). This interaction also causes the substitution with CH_3 groups (in which one of the H atoms points directly to the π cloud of fullerene) to be the most favorable case. This fact can be easily visualized by noncovalent interaction plots.
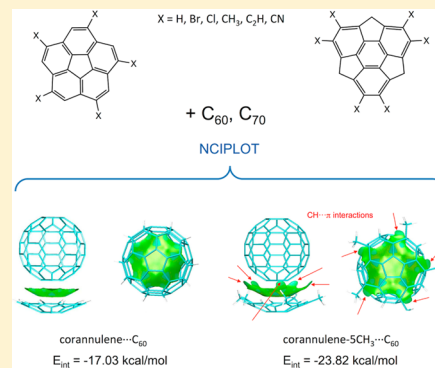
INTRODUCTION

The search for molecular receptors for fullerenes has been a very attractive field of research in recent years.[1] Several compounds have been explored with the goal of finding more effective and selective fullerene receptors.[2−8] A promising strategy to design new molecular receptors for fullerenes is using concave−convex complementarity. In this context, the curved polynuclear aromatic hydrocarbons, also known as buckybowls or fullerene fragments, seem to be ideal candidates because the concave surface of a buckybowl can fit adequately to the convex surface of fullerenes by concave−convex "ball-and-socket" interactions.[4]

The interaction between substituted buckybowls and fullerenes was reported in 2005 by Georghiou et al. for complexes between penta- and decasubstituted corannulenes with C_{60} in toluene solution.[9] Despite the promising results, the experiments did not prove the existence of strong π···π interactions between corannulenes and fullerenes. The association constants obtained were relatively small and highly dependent on substituents, so it could be argued that the true interaction that bound the complex was that taking place between the fullerene and the edge substituents of corannulene and not the π···π interaction between corannulene and fullerene.

Fortunately, two years later, Sygula et al. synthesized the molecular tweezers (a buckycatcher, $C_{60}H_{28}$) made up by two units of corannulene that can trap one fullerene, and they confirmed that the strength of the interaction comes indeed from pure concave−convex π···π interactions between convex faces of fullerene and concave faces of the two subunits of suitably oriented corannulene.[4] Predicting how to modify this buckycatcher to improve their efficiency and selectivity has become a subject of great interest.

Undoubtedly, the success in designing efficient systems requires deep knowledge of the characteristics of the π···π interactions. However, an accurate description of π···π interactions is a challenging task for quantum chemistry methods in general.[10−12]

Although the development of new types of functionals[13,14] and dispersion-corrected density functional theory (DFT-D) methods[15,16] taking into account the dispersion contribution allows the theoretical estimation of the interaction energy for the molecular tweezers designed by Sygula et al.,[4] a huge range

in the estimates (from −21 to −43 kcal/mol) were obtained depending on the DFT model used.[18−20]

Recently, a detailed evaluation of the performance of DFT-D, M05-2X, and M06-2X functionals for studying $\pi\cdots\pi$ interactions was performed.[12] Janowski et al. have performed a benchmark study for corannulene dimers taking the QCISD-(T)/aug-cc-pVTZ level as reference.[21] Both studies show that B97-D2 seems a good approach for studies of concave−convex $\pi\cdots\pi$ interactions. In addition, together with the resolution of identity (RI) approximation,[17] this approach enables excellent results with a noticeably small computational cost. Moreover, recently, for the corannulene dimer, Kennedy et al.[22] showed that the best results (compared with the benchmark performed at the QCISD(T)/aug-cc-pVTZ level[21]) correspond to B3LYP-D3(BJ), but with a very small advantage over B3LYP-D2, M06-2X, and B97-D2. Of these DFT methods, B97-D2 is the best for taking advantage of the noticeable reduction of computational cost that allows the resolution of identity approximation because for nonhybrid functionals the RI procedure speeds up calculations by a factor of 10 at least (as compared to conventional treatments) without sacrificing accuracy.

Recently, a DFT-D evaluation of the effect of substituents on the concave−convex $\pi\cdots\pi$ interaction that takes place between pentasubstituted corannulenes (with Br, Cl, CH_3, C_2H, and CN) and fullerene, was performed by our research group.[23] For that purpose, C_{60}-like, a "fullerene copy" of C_{60}, was used instead of the real buckminsterfullerene, C_{60}, to save computation resources. However, the above-mentioned success of the B97-D2 (plus RI) level allows carrying out a comprehensive study of the effects of substituents, using the whole structure of C_{60}. Moreover, the interaction with different faces of C_{60} is taken into account and the complete analysis is extended, including the fullerene C_{70}. In addition, a comprehensive study is carried out for the interaction between hexasubstituted sumanenes and fullerene, for both C_{60} and C_{70}.

COMPUTATIONAL DETAILS

All complexes evaluated were fully optimized at the B97-D2/TZVP level of theory using the resolution of identity approximation implemented in the Turbomole 5.10 program suite.[24]

Counterpoise corrections (CP) were applied to all reported interaction energies to avoid basis set superposition error (BSSE).[25] According to this method, the interaction energy of a system AB (buckybowl···fullerene in our case) is calculated according to

$$E_{int} = E_{AB}^{AB}(AB) - (E_A^{AB}(AB) + E_B^{AB}(AB))$$

where superscript refers to the geometry (that of the system AB) and the parentheses indicates the basis set used. $E_A^{AB}(AB)$ is the energy of monomer A (buckybowl or fullerene) calculated using its geometry in the system AB and the full basis set of the system AB. CP correction was applied to only the optimized geometries of the complexes.

RESULTS AND DISCUSSION

A series of complexes made up by substituted buckybowls (corannulene and sumanene) with fullerenes (C_{60} and C_{70}) were evaluated at the B97-D2/TZVP level. Stacking interactions using both corannulene and sumanene faces of fullerenes were taken into account in this work to obtain the more favorable face of fullerenes for interacting with

buckybowls. In Figure 1 the concepts *cora face* and *suma face* of fullerenes are defined. All complexes were constructed by
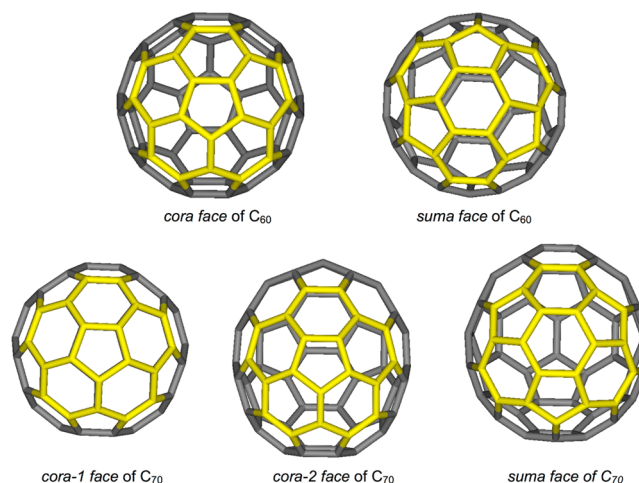

Figure 1. Faces of the fullerenes used to study the stacking interactions with buckybowls.

aligning the central ring of the buckybowl with the central ring of corannulene or sumanene face of fullerenes given in Figure 1. The distance between the centers of these two rings is named d_{eq}.

Unsubstituted Complexes. As can be seen in Table 1, the larger interaction is related with the participation of sumanene structure. Thus, the largest interaction energy corresponds to the complex sumanene···$C_{60/70}$ (with the suma face) which amounts to −20.40/−20.49 kcal/mol. Oppositely, the smallest interaction energy corresponds to the complex corannulene···$C_{60/70}$ (with the cora face) which amounts −17.03/−17.16 kcal/mol. Anyway, the participation of the sumanene structure is clearly more critical for the buckybowl than for the fullerene face chosen to form the complex. These results are similar to those obtained for complexes between corannulene and sumanene.[12] As reported by Denis,[26] sumanene shows three CH_2 groups (absent in corannulene) that can interact through $CH\cdots\pi$ interactions with fullerenes. Therefore, $CH\cdots\pi$ interactions are of great importance for the better catching ability of sumanene compared to corannulene.

From Table 1 it is clear that interaction energies for C_{60} are very similar to those for C_{70}; only a very slight difference favors C_{70}. Therefore, unfortunately, it is not expected that the buckycatcher binds very specifically to one of the fullerenes when exposed to the C_{60}/C_{70} mixture.

Substituted Complexes. Nowadays, predicting how to modify the traditional buckycatchers to improve their efficiency and selectivity is studied with great interest. Modification of tweezers by a different functionalization of buckybowls, which constitute the main part of tweezers, could improve their efficiency and selectivity. In this context, substituents may exert a modulatory effect and enable a better concave−convex interaction with fullerenes.

Recently, substituent effects on the concave−convex interaction between corannulene and C_{60} were studied by our research group (using C_{60}-like, a "fullerene copy" to imitate C_{60}).[23] The results showed that introduction of substituents with different acceptor−donor character in the structure of buckybowls can substantially change the interaction. Thus, corannulenes substituted with five Br, Cl, CH_3, C_2H, and CN

Table 1. Interaction Energies, E_{Int} (kcal/mol), and Equilibrium Distances, d_{eq} (Å), for Complexes between Buckybowls and Fullerenes[a]

| | X=C$_{60}$ | | | | X=C$_{70}$ | | | |
| | cora face of C$_{60}$ | | suma face of C$_{60}$ | | cora face of C$_{70}$[b] | | suma face of C$_{70}$ | |
	E_{Int}	d_{eq}	E_{Int}	d_{eq}	E_{Int}	d_{eq}	E_{Int}	d_{eq}
corannulene···X	−17.03 (−14.16)	3.456 (3.51)	−17.26	3.563	−17.16 [−18.00]	3.447 [3.453]	−17.33	3.574
corannulene-5Br···X	−23.06 (−20.44)	3.399 (3.45)	−22.90	3.523	−23.04	3.385		
corannulene-5Cl···X	−20.60 (−18.56)	3.414 (3.47)	−20.49	3.534	−20.58	3.408		
corannulene-5CH$_3$···X	−23.82 (−19.23)	3.394 (3.44)	−23.90	3.512	−23.87	3.378		
corannulene-5C$_2$H···X	−22.31 (−18.06)	3.426 (3.47)	−22.17	3.554	−22.20	3.410		
corannulene-5CN···X	−22.28 (−23.35)	3.442 (3.43)	−21.91	3.593	−22.10	3.434		
sumanene···X	−18.47	3.502	−20.40	3.450	−18.57 [−19.53]	3.494 [3.489]	−20.49	3.453
sumanene-6Br ···X	−25.40	3.528	−26.50	3.507			−27.03	3.496
sumanene-6Cl···X	−22.34	3.532	−23.40	3.512			−23.78	3.505
sumanene-6CH$_3$···X	−26.43	3.511	−27.61	3.459			−28.10	3.446
sumanene-6C$_2$H···X	−24.67	3.534	−25.88	3.510			−26.51	3.508
sumanene-6CN···X	−25.51	3.521	−26.36	3.537			−27.02	3.511

[a]All calculations were performed at the B97-D2/TZVP level. Calculations at the B97-D2/6-31+G* level using C$_{60}$-like[23] are given in parentheses for comparison. [b]With cora-1 face and cora-2 face (in square brackets).

units behave as better buckycatchers than the unsubstituted corannulene. C$_{60}$-like proposed by Sygula et al.[27] provide a considerable computational cost reduction; however, according to Table 1, it seems clear that results obtained with this procedure (in parentheses in Table 1) are somewhat poor when compared with those using the whole C$_{60}$ structure. Thus, not only absolute differences appear but also relative differences are remarkable. So, for instance, substitution with CH$_3$ is the most favorable when full C$_{60}$ is used, whereas substitution with CN is the most favorable when C$_{60}$-like is used. Therefore, C$_{60}$-like does not seem representative for imitating the concave–convex interaction between substituted corannulene and C$_{60}$. Therefore, a supplementary work using the whole C$_{60}$ is very advisable. In the present work the study is fully completed as follows. First, not only the cora face of C$_{60}$ is taken into account, but also the suma face is analyzed. Second, not only corannulene is studied, but also sumanene is used as a buckycatcher of fullerene. Finally, not only fullerene C$_{60}$ is included, but also an almost parallel study for C$_{70}$ is carried out.

In order to analyze the effect of substitution, corannulene and sumanene monomers were substituted with five and six Br, Cl, CH$_3$, C$_2$H, or CN units, respectively. Figure 2 shows one of the complexes investigated, and Table 1 summarizes interaction energies and equilibrium distances obtained. To save time and avoid a superfluous accumulation of data (because trends seem sufficiently clear), a full analysis of buckybowl substitution for the interaction with C$_{70}$ is not performed; only the interaction of corannulenes with the cora face and the interaction of sumanene with the suma face are considered, i.e, only stacking interactions using a face of C$_{70}$ equivalent to the buckybowl are evaluated. As stated above, very similar results are obtained for complexes with fullerenes C$_{60}$ and C$_{70}$; therefore, an exhaustive study for C$_{70}$ seems unnecessary. In the case of corannulene···C$_{70}$ (cora face) only the cora-1 face is chosen because this case leads to complexes with symmetry higher than the that of case of the cora-2 face, providing a considerable reduction of the computational cost.

According to values of Table 1, the ranking of buckybowls relative to the added substituents is CH$_3$ > Br > C$_2$H ≈ CN ≫ Cl ≫ H for all the corannulene···fullerene complexes. This
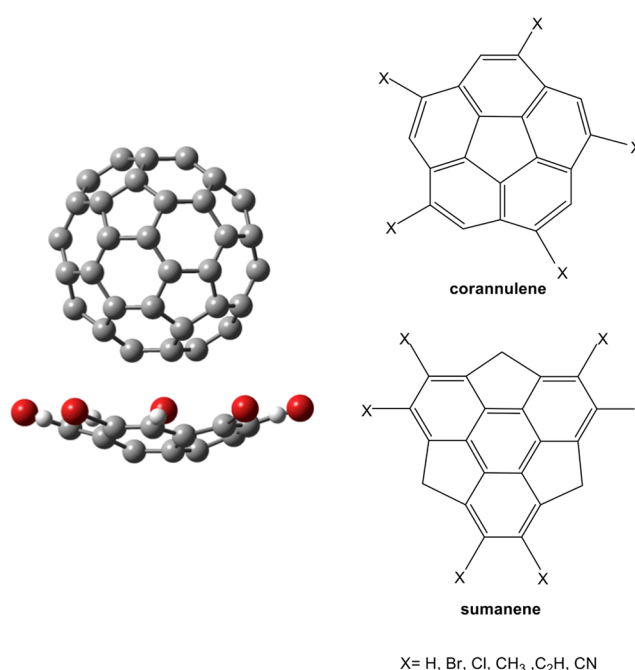
Figure 2. Structure of complex corannulene-5Br···C$_{60}$ (*cora face of* C$_{60}$) (left panel). Substituted corannulene and sumanene studied (right panel).

ranking is rather different than that obtained previously using C$_{60}$-like:[23] CN ≫ Br > CH$_3$ > Cl > C$_2$H ≫ H.

When sumanene···fullerene complexes are considered, the ranking is mainly the same and suffers only a slight modification: CH$_3$ > Br ≈ CN > C$_2$H ≫ Cl ≫ H; that is, basically substitution with CN is strengthened and moves up, relative to corannulene complexes.

Sumanene substituted with six CH$_3$ groups is the best fullerene receptor (E_{int} = −28.10 kcal/mol), with an increase greater than 11 kcal/mol relative to the unsubstituted corannulene (about a 65% of increase of "fullerene catching" ability). Almost certainly, the ability of sumanene-6CH$_3$ is directly related to the important role of CH···π interactions in this kind of complex.

Table 2. Geometric Parameter, R (Å), and POAV Angles at the *Hub* Position (degrees) of Buckybowls Obtained at the B97-D2/TZVP Level[a]

| | X=C_{60} | | | | X=C_{70} | | | |
| | cora face of C_{60} | | suma face of C_{60} | | cora-1 face of C_{70} | | suma face of C_{70} | |
	R	POAV	R	POAV	R	POAV	R	POAV
corannulene⋯X	0.902	8.38	0.894	8.28, 8.31, 8.34	0.909	8.42		
corannulene-5Br⋯X	0.882	8.26	0.871	8.11, 8.18, 8.19, 8.21	0.878	8.22		
corannulene-5Cl⋯X	0.881	8.25	0.873	8.12, 8.17, 8.21	0.888	8.30		
corannulene-5CH$_3$⋯X	0.914	8.51	0.904	8.36, 8.41, 8.42, 8.45, 8.48	0.915	8.51		
corannulene-5C$_2$H⋯X	0.921	8.52	0.906	8.33, 8.42, 8.43, 8.44	0.910	8.44		
corannulene-5CN⋯X	0.924	8.55	0.911	8.34, 8.46, 8.47, 8.49, 8.51	0.916	8.51		
sumanene⋯X	1.093	8.42, 8.57, 8.64	1.067	8.43			1.076	8.46, 8.49, 8.51
sumanene-6Br ⋯X	1.096	8.63, 8.71	1.058	8.50			1.061	8.50, 8.52, 8.53
sumanene-6Cl⋯X	1.098	8.61, 8.69, 8.70	1.063	8.49			1.065	8.50, 8.52
sumanene-6CH$_3$⋯X	1.115	8.59, 8.74, 8.77	1.091	8.59			1.091	8.60, 8.61
sumanene-6C$_2$H⋯X	1.138	8.79, 8.84	1.104	8.68			1.108	8.68, 8.70
sumanene-6CN⋯X	1.126	8.75, 8.76, 8.79	1.101	8.68			1.102	8.66, 8.68, 8.70

[a]When different values of POAV are found, they are indicated.

Table 3. B97 Interaction Energy and Dispersion Contribution for Complexes Obtained at the B97-D2/TZVP Level (kcal/mol)

| | X=C_{60} | | | | X=C_{70} | | | |
| | cora face of C_{60} | | suma face of C_{60} | | cora-1 face of C_{70} | | suma face of C_{70} | |
	B97	dispersion	B97	dispersion	B97	dispersion	B97	dispersion
corannulene⋯X	16.17	−33.20	16.43	−33.69	16.21	−33.37		
corannulene-5Br⋯X	21.07	−44.13	20.77	−43.67	21.10	−44.14		
corannulene-5Cl⋯X	19.36	−39.96	19.12	−39.61	19.53	−40.11		
corannulene-5CH$_3$⋯X	21.39	−45.21	21.44	−45.34	21.78	−45.65		
corannulene-5C$_2$H⋯X	20.10	−42.41	19.71	−41.88	19.83	−42.03		
corannulene-5CN⋯X	18.60	−40.88	18.33	−40.24	18.24	−40.34		
sumanene⋯X	19.17	−37.64	20.47	−40.87			20.65	−41.14
sumanene-6Br ⋯X	23.66	−49.06	25.69	−52.19			26.22	−53.25
sumanene-6Cl⋯X	21.70	−44.04	23.97	−47.37			24.23	−48.01
sumanene-6CH$_3$⋯X	25.93	−52.36	26.94	−54.55			27.67	−55.77
sumanene-6C$_2$H⋯X	22.98	−47.65	25.30	−51.18			25.30	−51.81
sumanene-6CN⋯X	20.79	−46.30	22.16	−48.52			23.13	−50.15

As can be seen in Table 1, although there is a substantial increase in the interaction energy of complexes when different substituents are placed in corannulene and sumanene monomers, only very small differences in the equilibrium distance are found. For complexes with corannulene, in general, the introduction of substituents gives a slight decrease in the equilibrium distance values, with a vague trend in which an increase of interaction energy corresponds to a shortening of d_{eq} (with complexes with corannulene-5CN being the most notorious exception to this trend). For complexes with sumanene, differences in equilibrium distances are even more insignificant and exhibit a trend that is even more unclear.

As a way of checking the changes introduced in the bowls by the substituents, Table 2 lists the values of two important geometric parameters. R is the interplanar distance between the planes formed by *hub* and *rim* atoms of the buckybowl; it represents the bowl depth. POAV is the pyramidalization angle (π-orbital axis vector) as proposed by Haddon.[28] The POAV angle allows for the description of local curvature of a conjugated system and is defined as the angle between the C−C bond and the vector perpendicular to the pyramidal base of three idealized C−C bonds. The greater depth of the bowl (greater R) is usually related to the greater curvature of carbons of the *hub* (greater POAV). According to results shown in

Table 2, it is clear that substituents give rise to very small changes in the curvature of corannulene and sumanene bowls: no noteworthy difference relative to the unsubstituted buckybowl is found. Therefore, there was not a clear relationship between the curvature of bowl and the changes in the interaction energy generated by addition of substituents in the bowl.

To analyze in more detail the balance of energy contributions to the stability of the complexes, the interaction energy was decomposed according to a simple method. Therefore, the two 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 3 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, dispersion is responsible for the binding in the complexes. Second, and more noteworthy, the ranking of interaction energies is directly related to the ranking of dispersion contributions. This fact is absolutely true for corannulene complexes and mainly true for sumanene complexes, with both C_{60} and C_{70}. It is worth noting that, regarding dispersion contributions, corannulene complexes behave exactly the same as sumanene complexes. The relationship between the dispersive contribution and the

interaction energy can be clearly visualized in Figure 3, which includes all the complexes of Table 3 and shows a good
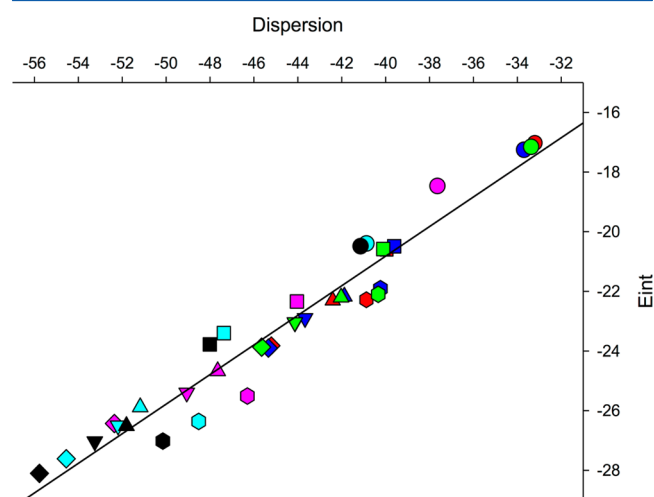

Figure 3. Dispersion contribution versus interaction energy (in kilocalories per mole). Corannulene⋯C_{60} (cora face), red; corannulene⋯c_{60} (suma face), dark blue; corannulene⋯c_{70} (cora-1 face), green; sumanene⋯c_{60} (cora face), pink; Sumanene⋯C_{60} (suma face), light blue; sumanene⋯c_{70} (suma face), black. Buckybowl (corannulene or sumanene), circle; buckybowl-5Br, triangle down; buckybowl-5Cl, square; Buckybowl-5CH$_3$, diamond; buckybowl-5C$_2$H, triangle up; Buckybowl-5CN, hexagon. $E_{int} = 0.4960\,\mathrm{Disp} - 0.9773$; $R^2 = 0.95$.

correlation. Only in the cases of complexes with buckybowl-5(6)CN (hexagons in Figure 3) does a very slight deviation appear; interaction energies larger than those corresponding to their dispersion contributions are obtained. Table 3 shows that these enhanced interaction energies are due to the small repulsion of the pure B97 functional (the least repulsive of the substituted corannulenes). Thus, if complexes with CN substitutions are not taken into account, the correlation is even better, R^2 going from 0.95 to 0.98 (Figure S1 of Supporting Information).

The partition of the interaction energy in two components (functional plus dispersion) could be questionable because B97-D was constructed as a whole, optimizing the functional form in the presence of a dispersion correction. However, this fact does not necessarily imply that the two components are unbalanced. To check that the partition used is appropriate and that it can lead to fully valid results, several single-point calculations at the B3LYP-D3(BJ)/TZVP//B97-D2/TZVP level were carried out (Figure S2 of Supporting Information). The conclusions are the same as those obtained with B97-D2.

As stated above, the buckycatcher ranking previously obtained using C_{60}-like[23] for mimicking the whole molecule fails. Where is the source of the error? As shown in the top panel of Figure 4, the fault does not lie in the dispersive contribution; the correlation between contributions obtained using the whole C_{60} and using C_{60}-like[23] is excellent. On the contrary, if contributions of the pure functional are compared, the correlation is awful, as shown in the bottom panel of Figure 4; the awful correlation occurs with the formerly calculated values for C_{60}-like[23] and also with the recalculated values with the TZVP basis set. The contribution of the pure functional includes the components corresponding to repulsion, electrostatics, and induction. Obviously, according to the bottom panel of Figure 4, these components are very different for C_{60}
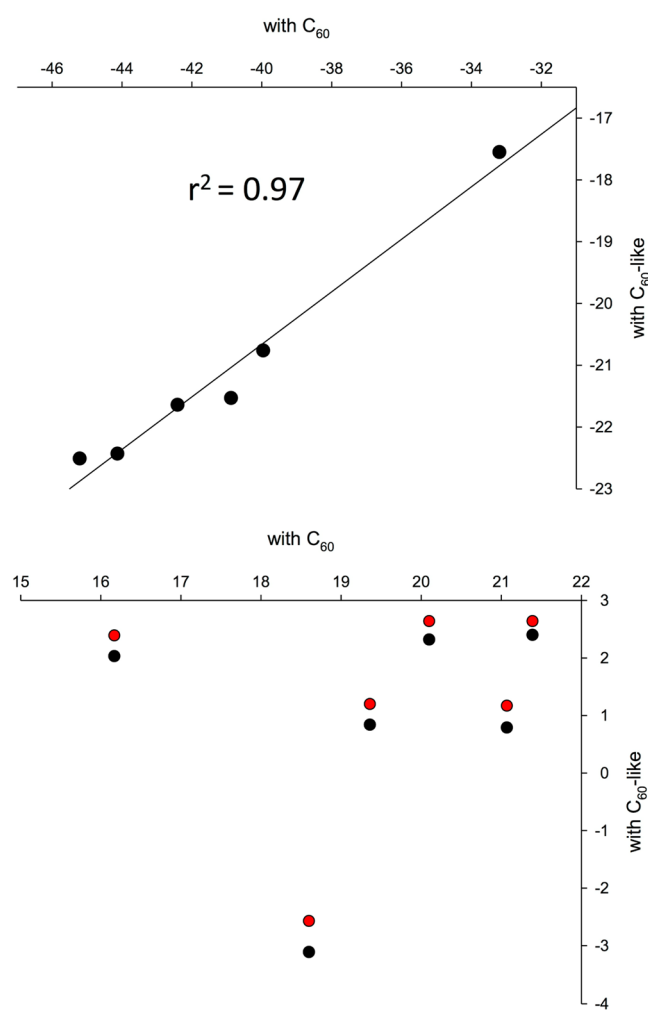

Figure 4. Top panel: dispersion contribution calculated with the whole C_{60} versus the dispersion contribution calculated previously with C_{60}-like.[23] Bottom panel: contribution of the functional calculated with the whole C_{60} versus the contribution of the functional calculated previously with C_{60}-like (the formerly calculated values are in black,[23] and calculated values with the TZVP basis are in red). Both figures refer to corannulene-5X⋯C_{60} complexes (X = H, Br, Cl, CH$_3$, C$_2$H, CN). Values are in kilocalories per mole.

and for C_{60}-like. Without conducting an exhaustive analysis, it is clear that the electrostatic characteristics of these two species are rather different. While the convex face of C_{60}-like is basically negative,[23] the face of C_{60} shows an almost neutral molecular electrostatic potential (MEP) and an even slightly positive MEP on top of the five-membered rings (Figure S3 of Supporting Information). C_{60}-like is a highly polar structure ($\mu = 4.13$ D at the ωB97XD/6-311G* level[23]), while the first nonvanishing multipole moment is the 64-pole one for C_{60}. In summary, C_{60}-like reproduces rather well only the dispersive contribution in the complexes, failing completely from the electrostatic point of view. For complexes with C_{60} (and C_{70}), the interaction energies are almost fully controlled by dispersion (Table 3 and Figure 3); therefore, electrostatics plays a very secondary role. However, C_{60}-like erroneously confers to electrostatics much more importance than it actually has because its dipole leads to an important dipole−dipole interaction with buckybowls, all of them with nonzero dipole moment.

It is worth noting that corannulene-5CN clearly shows the highest dipolar moment among all substituted corannulenes:
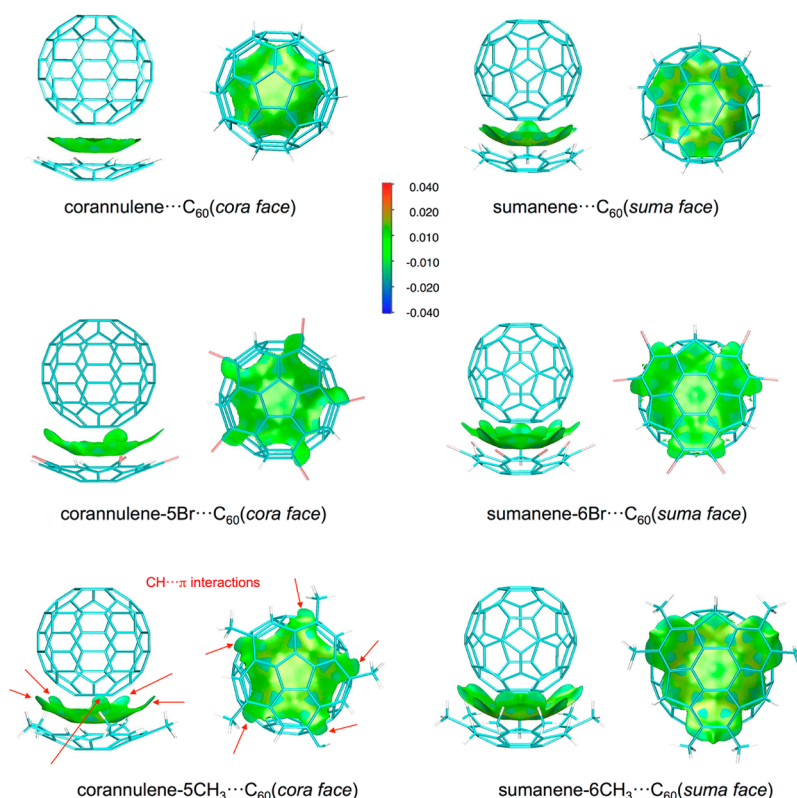
Figure 5. Front and bottom views of the NCIPLOT gradient isosurface (0.3 au). The surfaces are colored on a blue−green−red scale according to the strength and type (attractive or repulsive) of interaction. Blue indicates strong attractive interactions, green weak vdW interactions, and red (they do not appear in the current cases) strong nonbonded overlap.

dipolar moments of 2.23, 0.29, 0.21, 2.47, 1.82, and 3.59 D at the B97-D2/TZVP level for corannulene-5X, with X = H, Br, Cl, CH_3, C_2H, and CN, respectively. This fact could explain the above-mentioned slight deviation suffered by the complexes formed between this buckybowl and fullerene (Figure 3). Its strong dipole makes perceptible the favorable electrostatic interaction with fullerene, which reduces the repulsive contribution of the pure B97 functional (Table 3). Moreover, the dipole moment of corannulene-5CN not only is the largest one in magnitude, but also has a clear difference with the other ones: the direction of $\vec{\mu}$ is exactly opposite to that of the others, going from the convex to the concave face of the bowl (from outside to inside). This is due to the huge electron acceptor character of CN groups, which are able to invert the electron distribution of corannulene (electron deficient at the *rim* of the bowl because of the electropositive character of the hydrogen atoms). On the other hand, in the case of sumanene derivatives, the dipole of the CN-substituted compound is even more different from the rest: 2.52, 0.53, 0.78, 3.14, 1.76, and 7.65 D for sumanene-6X, with X = H, Br, Cl, CH_3, C_2H, and CN, respectively. Therefore, this more relevant electrostatic interaction with sumanene-6CN could explain the above-mentioned ranking for sumanene···fullerene complexes in which substitution with CN is strengthened and moves up.

Finally, to obtain more information about the interaction in the buckybowl···fullerene complexes, the plotting of non-covalent interaction regions was performed using the recently developed NCIPLOT program.[29,30] This method enables identification of noncovalent 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 noncovalent regions clearly appear in the supramolecular complex. These interactions correspond to both favorable and unfavorable interactions. To differentiate between them, the sign of the second density Hessian eigenvalue times the density is color-mapped onto the isosurface; bonding interactions can be identified by the negative sign. Figure 5 shows several NCI plots using an isosurface of 0.3 au; blue, green, and red indicate strongly attractive, weak, and strongly repulsive interactions, respectively (with a scale running from −0.040 to 0.040 au). To save computation time, promolecular densities have been used[30] after verifying in a couple of complexes that results are very similar to those obtained with SCF densities. According to NCI plots, the common interaction that takes place in all the complexes is the $\pi···\pi$ interaction between the *spokes* of buckybowl and fullerene. This interaction is clearly the most important one in the complex corannulene···C_{60} (cora face). In the complex sumanene···C_{70} (suma face), an additional interaction appears: that between CH_2 groups and the fullerene π cloud. Specifically, these are the so-called C−H···π interactions, found in different molecular systems including organic crystals, proteins, and nucleic acids.[31] One of the substituents that results in larger interaction energy is Br (Table 1), and this is shown in Figure 5 (according to Table 1, the increase of dispersion is the source of this fact). The largest effect corresponds to the inclusion of CH_3 groups in the buckybowl. It increases dispersion, but an additional interaction also emerges: the C−H···π interaction. The H atom of the CH_3 group that points to fullerene is responsible for this interaction, as shown in Figure 5. In the complex sumanene-6CH$_3$···C_{60} (suma face), nine such interactions take place: six are from the

CH_3 groups, and three are from the sumanene itself, all of which can be observed in Figure 5.

CONCLUSIONS

Stacking interactions between substituted buckybowls (corannulene and sumanene) with fullerenes (C_{60} and C_{70}) were studied at the B97-D2/TZVP level in order to assess the ability of these substituted buckybowls as "buckycatchers".

All substituted buckybowls evaluated behave as better buckycatchers than the unsubstituted buckybowls. Sumanene substituted with six CH_3 groups was the most favorable complex. $CH\cdots\pi$ interactions are largely responsible for this result; up to nine interactions of this kind can be found.

Regarding the face of fullerene involved in the interaction, overall, corannulenes prefer to bind by the cora face of fullerene, whereas sumanenes prefer to bind by the suma face of fullerene. This preference is weak for corannulenes (differences smaller than 1 kcal/mol), but it is considerably larger for sumanenes (about 3 kcal/mol).

Stacking interactions between buckybowls and fullerene C_{70} show interaction energies quite similar to those obtained with C_{60}. Therefore, it is not expected that buckybowls evaluated bind very specifically to one of the fullerenes when exposed to the C_{60}/C_{70} mixture.

According to our results, the interaction energy of the complexes is directly related to the dispersion contribution. Only very small deviations of this behavior are found for buckybowls substituted with CN groups: in this case a significant electrostatic effect emerges that modulates the strong dispersive effect.

The results of this work show that C_{60}-like, used in our previous work, does not seem representative for reproducing the concave···convex interactions between buckybowls and fullerenes. The weakness of the C_{60}-like comes from the inability of this structure to reproduce the electrostatic characteristics of the whole C_{60}. However, results using C_{60}-like are not too bad because C_{60}-like is able to reproduce rather well the dispersive effect (which is the most important contribution) of the real C_{60}.

ASSOCIATED CONTENT

(S) Supporting Information

Modified Figure 3, comparison between the partition of the interaction energy using B97-D2 and B3LYP-D3(BJ), MEP of C_{60} and C_{70}, and optimized geometries of the complexes. This material is available free of charge via the Internet at http://pubs.acs.org.

AUTHOR INFORMATION

Corresponding Author
*E-mail: r.otero@usc.es. Phone: +34-881815706.

Notes
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