A DFT-D study of stacking interactions between substituted buckybowls with fullerenes

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Abstract

Stacking interactions between substituted buckybowls (corannulene and sumanene) with fullerenes (C_{60} and C_{70}) were studied at the B97-D2/TZVP level. Corannulene and sumanene monomers were substituted with five and six Br, Cl, CH_3, C_2H or CN units, respectively. This work was carried out for supplement our previous work of the study of substituent effects in corannulene dimers, in which C_{60}-like ('fullerene copy', corannulene with curvature of buckminsterfullerene, C_{60}) was employed to imitate the concave-convex interactions between substituted corannulenes and fullerene C_{60} (Josa, D.; Rodriguez Otero, J.; Cabaleiro Lago, E. M. *Phys. Chem. Chem. Phys.,* **2011**, 13). Despite the promising results using C_{60}-like, different trends of effects of substituent were obtained for our later calculations using full C_{60}. So, C_{60}-like, does not seem representative to imitate the concave-convex interactions between substituted corannulenes and C_{60}. The calculations with fullerenes show that all substituents

provide a substantial increase of the interaction energy compared with unsubstituted buckybowls, as observed previously. However, substitution with CH_3 groups is more favorable than substitution with CN groups, contrary to that obtained using C_{60}-like. Sumanene substituted with six CH_3 groups caused the largest effect increasing the interaction energy about 11 kcal/mol compared with unsubstituted corannulene for both fullerenes. CH-π interactions seem the great responsible for this increase. 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 to specifically bind one of the fullerenes when exposed to the C_{60}/C_{70} mixture.

1. Introduction

The search for molecular receptors for fullerenes is a very attractive field of research in the last years.[1] Several compounds have been explored in pursuit of more effective and selective fullerene receptors.[2-8] A promising strategy to design new molecular receptors for fullerenes is to use the concave-convex complementarity. In this context, the curved polynuclear aromatic hydrocarbons, also known as buckybowls or fullerene fragments, seem ideal candidates given that the concave surface of one buckybowl can fits highly to the convex surface of the fullerenes by concave-convex 'ball-and-socket' interactions.[4]

The first stacking interaction between buckybowls and fullerenes was reported in 2005 by Georghiou and co-workers for complexes between penta and decasubstituted corannulenes with C_{60} in toluene solution.[9] Despite the promising results, the experiments did not proved the existence of strong $\pi \cdots \pi$ interactions between corannulenes and fullerenes. The association constants obtained were relatively small and highly dependent of substituents, so that one could argue that the true interaction that bound the complex was that taking place between the fullerene and the edge substituents of corannulene and not the $\pi \cdots \pi$ interaction between corannulene and fullerene.

Fortunately, two years later, Sygula and co-workers synthesized the molecular tweezers (a buckycatcher, $C_{60}H_{28}$) made up two units of corannulene that can trap one fullerene and confirmed that the strength of the interaction is indeed from pure concave-convex $\pi \cdots \pi$ interactions between convex faces of fullerene and concave faces

of the two subunits of suitably oriented corannulene.[4] Thenceforth, predicting how to modify this buckycatcher to improve their efficiency and selectivity have been become a subject the great interest.

Undoubtedly, the success in designing of efficient systems requires depth knowledge of the characteristics of the $\pi\cdots\pi$ interactions. However, an accurate description of $\pi\cdots\pi$ interactions is a challenging task for quantum chemistry methods in general.[10-12]

Although the development of new types of functionals[13,14] and 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, we have performed a detailed evaluation of the performance of DFT-D, M05-2X, M06-2X functionals for studying $\pi\cdots\pi$ interactions.[12] On the other hand, Janowski *et al.* have been performed a benchmark for corannulene dimers at the QCISD(T)/aug-cc-pVTZ.[21] Both studies show that B97-D2 seems a good approach for studies of concave-convex $\pi\cdots\pi$ interactions. In addition, together with resolution of identity (RI) approximation,[17] this approach enables excellent results with a noticeably smaller computational cost.

In order to evaluate the effect of the substituents on concave-convex $\pi\cdots\pi$ interactions we have carried out a DFT-D study of a series of complexes between penta-substituted corannulene (Br, Cl, CH_3, C_2H and CN) and C_{60}-like, a 'fullerene copy' of C_{60}.[22] Despite the promising results, different trends were obtained for the effects of substituents regarding to our later study using fullerene C_{60}. Therefore, the goal of the present work is to supplement our previous work.

2. Computational details

All complexes evaluated were fully optimized at the B97-D2/TZVP level using resolution of identity approximation (RI) implemented in TURBOMOLE 5.10 program suite.[23]

All Counterpoise corrections were applied to reported interaction energies to avoid basis set superposition error (BSSE).[24]

3. Results and discussion

A series of complexes composed by substituted buckybowls (corannulene and sumanene) with fullerenes (C_{60} and C_{70}) were evaluated at the B97-D2/TZVP level. Stacking interactions using corannulene and sumanene face of the fullerenes were taking into account in this work in order to obtain the side of the fullerenes more favorable for interacting with buckybowls. All complexes were constructed by aligning of central ring of buckybowl with central ring of corannulene or sumanene face of fullerenes given in Figure 1.

Unsubstituted complexes

As can be seen from Table 1, sumanene bowl in both concave (in the interacting side of fullerenes) and convex (buckybowl) side increases the interaction regarding to corannulene. However, the effect the sumanene in the convex side is more favorable. These results are similar than obtained for buckybowls complexes between corannulene and sumanene. [12]

As reported previously by Denis,[25] sumanene show three hydrogen atoms in CH_2 groups absent in corannulene than can interact through CH-π interactions with fullerenes. So, CH-π interactions are largely responsible by a better catcher ability of sumanene compared to corannulene.

A series of stacking interactions between unsubstituted corannulene and sumanene with different faces of C_{70} were also evaluated in this work. Values of interaction energy of -17.16, -18.00, -17.33, -18.57, -19.53 and -20.49 kcal/mol were obtained for corannulene···C_{70}(cora-1 face), corannulene···C_{70}(cora-2 face), corannulene···C_{70}(suma face), sumanene···C_{70}(cora-1 face), sumanene···C_{70}(cora-2 face) and sumanene···C_{70}(suma face), respectively. Unfortunately, these results are quite similar to that obtained with C_{60} (Table 1). Therefore, it is not expected that buckybowls evaluated to specifically bind one of the fullerenes when exposed to the C_{60}/C_{70} mixture.

Despite previous work of the stacking interactions between buckybowls and fullerenes also show an increase in the interaction of the sumanene···C_{60} complex regarding to corannulene···C_{60}. Similar interaction energy was obtained for corannulene and sumanene complexes with C_{70} at the M06-2X/6-311G level with BSSE

uncorrected.[25] On the other hand, calculations at the same level with BSSE-corrected have shown similar trends than those obtained in this work. These results confirm that disregarding of the BSSE correction for curved complex may lead to unreliable interaction energies. In fact, the underestimation of M06-2X is not due to the BSSE correction. It is due to the weakness of M06-2X for studying complexes with curved monomers, as discussed in detail in our previous study.[12]

Substituted complexes

Nowadays, predict how to modify the traditional tweezers to improve their efficiency and selectivity is the great interest. The modification of the 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, we have studied the substituent effects on corannulene using C_{60}-like, a 'fullerene copy' to imitate the concave-convex interaction between substituted corannulene and C_{60}.[22] Our results showed that introduction of substituents in the structure of buckybowls with different acceptor/donor character can change substantially the interaction. In addition, corannulenes substituted with five alternating Br, Cl, CH_3, C_2H and CN units behave as a better buckycatcher than the unsubstituted corannulene. Although C_{60}-like proposed by Sygula and co-workers[26] provide a considerable computational cost reduction, different catchers ability were obtained in our later work using the fullerene C_{60}. So, C_{60}-like, does not seem representative to imitate the concave-convex interaction between substituted corannulene and C_{60}. Therefore, a supplementary work using the buckminsterfullerene, C_{60} is very advisable.

A series of stacking interactions between substituted buckybowls (corannulene and sumanene) with fullerenes (C_{60} and C_{70}) were evaluated in this work in order to known the true ability of substituted buckybowls as fullerene receptors. Corannulene and sumanene monomers were substituted with five and six Br, Cl, CH_3, C_2H or CN units, respectively. Figure 2 shows one of complexes investigated and Table 1 summarizes the interaction energies and equilibrium distances values obtained at the B97-D2/TZVP level.

As commented above, similar results were obtained for complexes with fullerenes C_{60} and C_{70}. So, only stacking interactions using equivalent face of C_{70} that

buckybowl interacting were evaluated in this work. Although, complexes using cora-2 face of C_{70} showed interaction energies about 1 kcal/mol higher than those obtained with cora-1 face. Only, complexes with cora-1 face (higher symmetry) were evaluated for substituted corannulenes, which provides a considerable reduction of the computational cost.

Unfortunately, a different ranking of catchers was obtained for substituted corannulene complexes with C_{60} and C_{60}-like (Table 1). In fact, calculations using C_{60} show that substitution with CH_3 groups is more favorable than substitution with CN groups, obtained using C_{60}-like. Again, our results show that CH-π interaction plays an important role to improve the recognition of fullerenes.

Sumanene substituted with six CH_3 groups causes the large effect, increasing the interaction energy about 11 kcal/mol, compared with unsubstituted corannulene. Although sumanene shows a better catcher ability than corannulene for stacking interaction with both fullerenes evaluated, the introduction of substituents in their structure provides similar effects than those obtained for corannulene.

As can be seen in Table 1 there is a substantial increase in the interaction energy of complexes when different substituents were placed in corannulene and sumanene monomers. However, only very small differences in the equilibrium distance were found. In general, the introduction of substituents on corannulene stacking interactions with fullerenes C_{60} and C_{70} produces a slight decrease in the equilibrium distance values, except for corannulene-5CN$\cdots C_{60}$(sumanene face of C_{60}). On the other hand, the introduction of substituents on sumanene yields a slight increase, except for CH_3 groups that show very similar equilibrium distances than using unsubstituted sumanene.

On the other hand, comparison between equilibrium distances obtained in this work for complexes between substituted corannulenes with C_{60} and those obtained previously using C_{60}-like shows a slight shortening of equilibrium distances, except for corannulene with CN groups that increases the equilibrium distance.

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, respectively; it represents the bowl depth. POAV is the pyramidalization angle (π-orbital axis vector) as proposed by Haddon.[27] The POAV angle allows 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. Geometric results indicate that

substituents give rise to small changes in the curvature of corannulene and sumanene bowls. So, there was not a clear relationship between the curvature of bowl and the changes on the interaction energy generated by addition of substituents in the bowl.

In order 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. So, 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 very important role in the interaction energy of complexes.

The ranking of the catchers show a strong relationship with dispersion, except for CN substituents that show similar or slight higher catcher ability and smaller dispersion contribution that obtained with C_2H. Despite substitution with CN groups does not cause the largest effect on interactions with fullerenes evaluated, the results show a most favorable pure B97 interaction energy for this substitution compared to the others substitutions evaluated, as obtained previously.[22] These results show that both dispersive and electrostatic effects are important to justify the behavior of substituents in concave-convex $\pi\cdots\pi$ interactions.

4. 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 known the ability of these substituted buckybowls as 'buckycatchers'.

All substituted buckybowls evaluated behave as a better buckycatcher than the unsubstituted buckybowls. Sumanene substituted with six CH_3 group was the most stable complex. CH-π interactions are largely responsible by this result.

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

The ranking of the catchers show a strong relationship with dispersion. On the other hands, the dispersion is not only factor responsible by interaction energy. As can be observed, sumanene-6CN monomer shows a better catcher ability than

sumanene-$6C_2H$. However, sumanene-$6C_2H$ shows a higher dispersion than sumanene-$6CN$.

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 substituted corannulene and C_{60}. The weakness of the C_{60}-like can be due the small size of this 'fullerene copy' (corannulene with curvature of C_{60}, $C_{20}H_{10}$). Moreover, possibly, the ten hydrogen atoms attached to the dangling bonds of C_{60}-like can interact with the substituents of the corannulene. Additionally, C_{60}-like shows a different molecular electrostatic potential map than that obtained for the real C_{60}.

5. Acknowledgments

Table 1. Interaction energies, E_{Int}, (kcal/mol) and equilibrium distances, d_{eq}, (Å) for complexes between buckybowls with corannulene or sumanene face of fullerenes. All calculations were performed at the B97-D2/TZVP level. Calculations at the B97-D2/6-31+G* using C_{60}-like are given in parentheses for comparison.

| | 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} | |
	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	3.447		
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-5CH₃···X	-23.82 (-19.23)	3.394 (3.44)	-23.90	3.512	-23.87	3.378		
Corannulene-5C₂H···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			-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-6CH₃···X	-26.43	3.511	-27.61	3.459			-28.10	3.446
Sumanene-6C₂H···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

Table 2. Geometric parameter R (in Å), and POAV angles at the hub position (degrees) obtained at the B97-D2/TZVP level.

| | 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, 8.5
Sumanene-6Br ⋯X	1.096	8.63, 8.71	1.058	8.50			1.061	8.50, 8.52, 8.5
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, 8.7

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$\cdots$X	16.17	-33.20	16.43	-33.69	16.21	-33.37		
Corannulene-5Br$\cdots$X	21.07	-44.13	20.77	-43.67	21.10	-44.14		
Corannulene-5Cl$\cdots$X	19.36	-39.96	19.12	-39.61	19.53	-40.11		
Corannulene-5CH$_3\cdots$X	21.39	-45.21	21.44	-45.34	21.78	-45.65		
Corannulene-5C$_2$H$\cdots$X	20.10	-42.41	19.71	-41.88	19.83	-42.03		
Corannulene-5CN$\cdots$X	18.60	-40.88	18.33	-40.24	18.24	-40.34		
Sumanene$\cdots$X	19.17	-37.64	20.47	-40.87			20.65	-41.14
Sumanene-6Br $\cdots$X	23.66	-49.06	25.69	-52.19			26.22	-53.25
Sumanene-6Cl$\cdots$X	21.70	-44.04	23.97	-47.37			24.23	-48.01
Sumanene-6CH$_3\cdots$X	25.93	-52.36	26.94	-54.55			27.67	-55.77
Sumanene-6C$_2$H$\cdots$X	22.98	-47.65	25.30	-51.18			25.30	-51.81
Sumanene-6CN$\cdots$X	20.79	-46.30	22.16	-48.52			23.13	-50.15
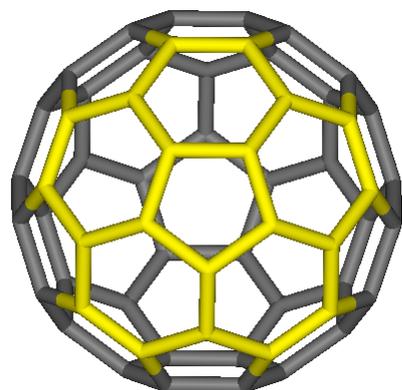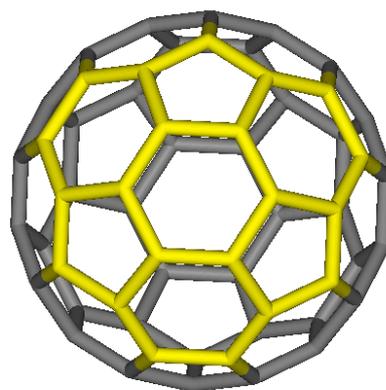
Cora face of C$_{60}$ **Suma face of C$_{60}$**
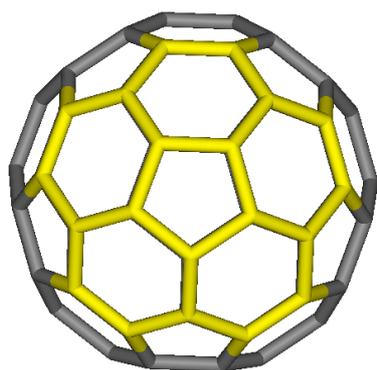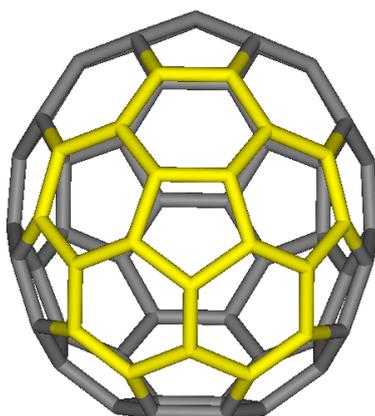
Cora-1 face of C$_{70}$ **Cora-2 face of C$_{70}$**   **Suma face of C$_{70}$**
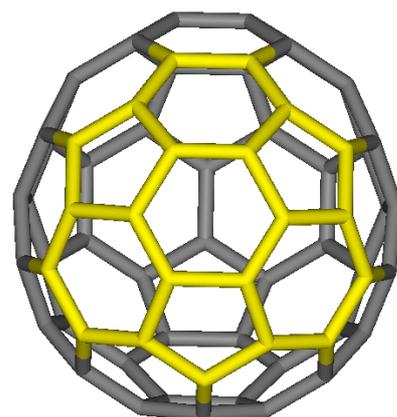
Figure 1. Faces of the fullerenes used in the stacking interactions with buckybowls.

corannulene

sumanene

X= H, Br, Cl, CH$_3$,C$_2$H, CN
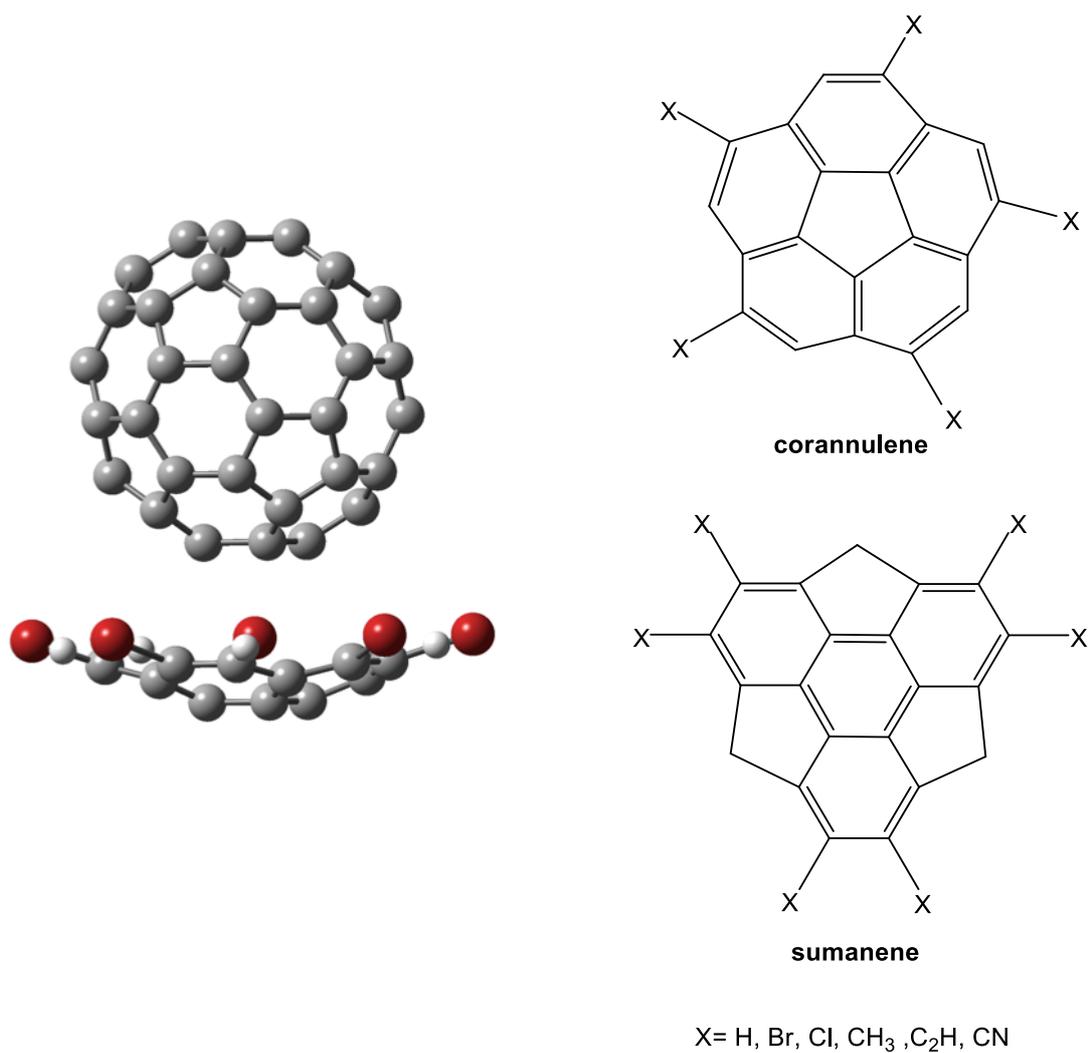
Figure 2. A Complex formed by corannulene-5Br and fullerene (cora face of C$_{60}$) (left). Substituted corannulene and sumanene monomer studied (right).

6. References

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