

# Endohedral fullerenes: the importance of electronic, size and shape complementarity between the carbon cages and the corresponding encapsulated clusters<sup>†</sup>

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**Cage-cluster complementarity is of crucial importance in determining the sizes and structures, as well as the properties of endohedral fullerenes. The encapsulated atoms or clusters, which are typically in a positively charged state, are irreversibly, mechanically, and electrostatically trapped inside the typically negatively charged cages. These rather exotic compounds exhibit exquisitely complementary properties between their components. Here, we present a short overview to show that size and shape are crucial in determining the specific structures that are formed, and the presence of electrostatic interactions result in structural motifs that are never observed for pristine fullerene cages. Copyright © 2014 John Wiley & Sons, Ltd.**

**Keywords:** electronic properties; endohedral fullerenes; fullerene and cluster cage sizes; fullerene and cluster shapes

## INTRODUCTION

The discovery and increased interest and to some degree, fascination of trapping and studying atoms and clusters inside the carbon cages began almost immediately after the initial discovery of the fullerenes in 1985,<sup>[1]</sup> with the detection of La@C<sub>60</sub> by Smalley *et al.*,<sup>[2]</sup> the first reported endohedral fullerene. Since then, a wide variety of endohedral systems have been prepared and characterized from compounds encapsulating neutral atom species such as noble gases<sup>[3]</sup> and diatomic and triatomic molecules (H<sub>2</sub> and H<sub>2</sub>O)<sup>[4]</sup> to those with trapped metals and multiatomic clusters inside.<sup>[5–9]</sup> In this article, particular attention is devoted to the metallic nitride and the metallic sulfide families, carefully selecting specific examples that illustrate the complementarity factors that are of primary interest, namely, size, shape, and electronic structures. This is not meant to be a comprehensive review of the endohedral fullerene field, but rather a critical overview of the importance of complementarity between cages and encapsulated species.

The trimetallic nitride family (M<sub>3</sub>N@C<sub>2n</sub>, n = 34–42) was first reported by Stevenson *et al.* in 1999, opening a new and fertile field for future development. They isolated what is today the third most abundant fullerene that can be prepared in an arc reactor (after C<sub>60</sub> and C<sub>70</sub>), namely, Sc<sub>3</sub>N@C<sub>80</sub>.<sup>[10]</sup> They inadvertently produced and isolated this compound as a result of an air leak in their Krätschmer–Huffman arc generator, which introduced N<sub>2</sub> to the reactor chamber. Today, the controlled addition of nitrogen sources to the reactor during the arcing process results in reasonably high yields of Sc<sub>3</sub>N@C<sub>80</sub>. The scandium nitride endohedral fullerene family includes two different isomeric C<sub>80</sub> cages (with I<sub>h</sub> and D<sub>5h</sub> symmetries), one D<sub>3h</sub> symmetric C<sub>78</sub> cage, and one D<sub>3</sub> C<sub>68</sub> carbon cage, all encapsulating the Sc<sub>3</sub>N cluster (Figure 1). Considerable experimental and theoretical efforts have been devoted to explore this endohedral family, to account for their unusual stabilities, and to explain their structural and electronic properties.<sup>[11]</sup> We will address this family as well as others in this article, in an effort to

understand the most important factors involved in determining the specific structures that are observed and their relative importance.

## ELECTRONIC EFFECTS

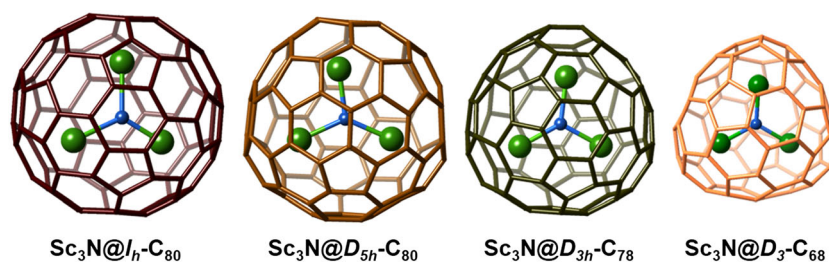
A focal point of interest in this article are fullerene cages that violate the so-called isolated pentagon rule (IPR), which states that five-membered rings are always adjacent to six-membered rings, avoiding fused five-membered rings, or pentalene units.<sup>[12]</sup> To our knowledge, there are no known exceptions of the IPR for neutral pristine fullerenes, but several exceptions have been reported for exohedrally functionalized cages, especially with halogen atoms.<sup>[13]</sup> If an IPR violation occurs as a consequence of the fusion of 2 five-membered rings, the resulting structure, a pentalene unit, destabilizes the corresponding cage by 17–22 Kcal/mol<sup>[14]</sup>, and thus the reason why they have never been observed on pristine carbon cages. However, pentalenes are reasonably common on the cages of many endohedral fullerenes (Table 1).<sup>[13,15]</sup>

The commonly accepted explanation for the existence of fused five-membered rings in endofullerenes involves the combination of the following: (i) extensive negative charge transfer from the encapsulated entity to the carbon cage; (ii) substantial negative charge localization predominantly on the pentalene

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**Figure 1.** Scandium nitride endohedral fullerene family ( $M_3N@C_{2n}$ ,  $n = 34\text{--}40$ ).

**Table 1.** Reported non-isolated pentagon rule endohedral fullerenes

Endohedral Fullerene	Symmetry	# Pentalenes	$e^-$ transfer from metal to cage	Cage #
$\text{Sc}_2@C_{66}$ [16]	$C_{2v}$	2	2	4348
$\text{Sc}_3\text{N}@C_{68}$	$D_3$	3	6	6140
$\text{Sc}_2\text{C}_2@C_{68}$	$C_{2v}$	2	4	6073
$\text{Sc}_3\text{N}@C_{70}$	$C_{2v}$	3	6	7854
$\text{Sc}_2\text{S}@C_{70}$ [17]	$C_2$	2	4	7892
$\text{La}@C_{72}$ [18]	$C_2$	1	3	10612
$\text{La}_2@C_{72}$	$D_2$	2	6	10611
$\text{DySc}_2\text{N}@C_{76}$ [19]	$C_5$	2	6	17490
$\text{Yb}@C_{76}$ [20]	$C_{2v}/C_1$	1	2	19138/17459
$M_3\text{N}@C_{78}$ ( $M = \text{Tm, Dy, Gd}$ )	$C_2$	2	6	22010
$\text{Gd}_3\text{N}@C_{82}$	$C_5$	1	6	39663
$M_3\text{N}@C_{84}$ ( $M = \text{Gd, Tb, Tm}$ )	$C_5$	1	6	51365

units,<sup>[21]</sup> (iii) electrostatic stabilization of the negative charge on the pentalenes by the cationic metals or clusters inside; and (iv) aromatization of the pentalene units when gaining electrons.<sup>[11,22]</sup> Whether pentalene units exist or not on the endohedral fullerene cages, extensive negative charge is always transferred from the cluster to the cage, leading to what is referred to as the ionic model, which for  $\text{Sc}_3\text{N}@C_{80}$  is best represented as a six electron transfer that formally leads to  $[\text{Sc}_3\text{N}]^{6+}[\text{C}_{80}]^{6-}$ .<sup>[15–17]</sup> This model is widely accepted and has been verified and tested both experimentally and theoretically.<sup>[23]</sup>

For those endohedral fullerene compounds where pentalene units are present on the cages, it has been found that most of the negative charge on the cage is localized on them, for example, about 76% of the total cage charge is estimated to reside on the three pentalene units present on  $\text{Sc}_3\text{N}@C_{68}$  (6140), which possesses a  $D_3$  symmetric cage.<sup>[11]</sup> Thus  $[\text{Sc}_3\text{N}]^{6+}[\text{C}_{68}]^{6-}$  has the majority of the cage charge localized on the three pentalenes and, not coincidentally, the three Sc ions, each being formally  $\text{Sc}^{3+}$ , whereas the N is formally  $3^-$ , are all exactly adjacent to these pentalene surface motifs, providing electrostatic stabilization to the overall structure.<sup>[11]</sup> The combination of the intrinsic cage stabilization that results upon transfer of six electrons from the cluster to the cage, which leads to a closed-shell high HOMO-LUMO gap structure, together with the intramolecular electrostatic stabilization provided by the three trivalent cations leads to these stable endohedral compounds. As far as we are aware, all endohedral compounds that possess pentalene units on the surface always have endohedral cationic metal centers that are very proximal to the pentalenes and, typically, very close to the bond where the 2 five-membered rings are fused. Only one exception to these observations was

recently reported based on a computational study about  $\text{Sc}_2\text{C}_2@C_{70}$ , which is proposed to exist as  $\text{Sc}_2@C_{70}$ , not  $\text{Sc}_2\text{C}_2@C_{68}$ , as previously reported. More details about this unique exception are presented in the succeeding text in the “shape” section.<sup>[17]</sup>

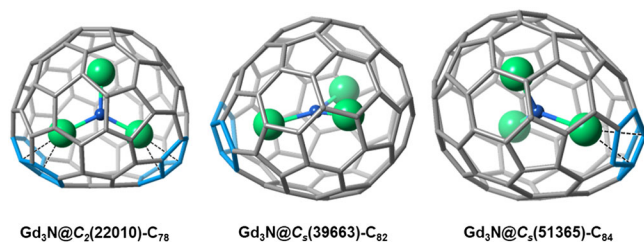
In addition to the intrinsic stabilization of the cage that results upon addition of the extra electrons from the cluster that fill the degenerate highest occupied molecular (HOMO) orbitals and the intramolecular electrostatic interactions, aromaticity has also been proposed as an additional factor in the overall stabilization.<sup>[11,17]</sup> Sola *et al.* have recently proposed aromaticity as the single most important parameter to predict the stabilities of endohedral fullerene derivatives,<sup>[17,24]</sup> then the combination of all of these factors plays a crucial role in determining the overall stabilities of endohedral fullerenes.

One important consideration is the relative contribution of these factors; what is the balance between the instability resulting from introducing a pentalene unit on a fullerene cage ( $\sim 20$  Kcal/mol) versus the stabilization that results from the electrostatic interactions that occur with the encapsulated cations and the gain in aromaticity? If the latter interactions were dominant then one would expect all endohedral metallofullerenes to possess pentalene structures as a means of added stabilization, but this is not the experimentally observed case because non-IPR compounds, though reasonably common in the endohedral fullerene world, are not totally ubiquitous. This observation leads one to believe that pentalenes occur at a net energy cost to the compound and is thus not a general feature of endohedral metallofullerenes.

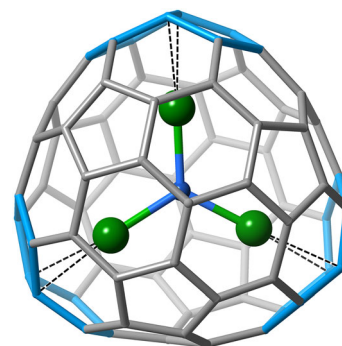
Recent theoretical report by Zhao *et al.* proposed that  $\text{Gd}_2@C_{98}$  should preferentially exist as a non-IPR  $C_1$ (168785) cage

with one pentalene unit, and the authors state that the reason is partially due to the interaction between the encapsulated metals and the fused pentagons, as described previously.<sup>[25]</sup> This result is rather interesting and somewhat counterintuitive because only one pentalene is present on cage 168785; therefore, if the electrostatic stabilization is the reason for observing the pentalene in the first place, two pentalenes should have been preferred, which is not the theoretically predicted structure. This is particularly true in this case because the two gadolinium ions are not bonded and have no fixed shape.<sup>[16]</sup> It is also interesting to note that before this report appeared in 2012, the largest experimentally determined cage exhibiting a non-IPR structure corresponded to  $C_{84}$ . All other known non-IPR cages have 84 or fewer carbon structures.<sup>[26]</sup>

The  $Gd_3N@C_{2n}$  family provides a self-consistent set to probe the existence of IPR exceptions. In this family, the observed  $C_{78}$  compound exhibits two pentalenes (cage 22010),<sup>[27]</sup> whereas the corresponding  $C_{82}$  and  $C_{84}$  compounds exhibit only one (cages 39663 and 51365, respectively), in agreement with computational studies that have shown that the number of pentalene units decreases for the larger carbon cages.<sup>[16,26,28]</sup> In all three non-IPR cases, the  $Gd^{3+}$  ions are directly adjacent to the center bond of the pentalene units, again suggesting that the stabilization results from pentalene-cluster ion interactions (Figure 2). These interactions provide some stabilization when the cages are sufficiently small to accommodate the planar clusters. Consistent with this interpretation,  $Gd_3N@C_{86}$ , which has a larger cage, is observed to possess a  $D_3$ -symmetric IPR cage where the cluster fits in planar form.<sup>[29]</sup> The generalization abstracted from these observations is that for large enough cages ( $>C_{84}$ ) there is likely to be an IPR cage available where the cluster can exist in its most stable, planar geometry and thus no pentalenes occur. In perfect agreement with these generalizations is the structure of  $Sc_3N@C_{68}$ , which exhibits not two but three pentalenes in a  $D_3$  symmetric cage (cage 6140), and each Sc ion in the cluster sits close to each fused pentagon bond in the pentalenes, whereas the cluster is planar, (Figure 3). Although introducing the three pentalenes costs about 60 Kcal/mol, this is partially offset by the electrostatic stabilization and increase of aromaticity. There are many other endohedral fullerene examples that corroborate these conclusions, consequently, Zhao *et al.* prediction of a non-IPR  $C_{98}$  cage is very surprising, based on all available experimental evidence thus far. The largest endohedral compound characterized experimentally thus far,  $Sm_2@D_{3d}(822)-C_{104}$ ,<sup>[30]</sup> as well as other large-cage endohedral compounds ( $C_{86}$ - $C_{100}$  cages) all exhibit IPR cages,<sup>[31]</sup> in agreement with the concept that the stabilization resulting from pentalene-cation interactions only partially offsets the energy cost of introducing the pentalenes in the first place. Thus



**Figure 2.** Gadolinium nitride endohedral fullerene non-isolated pentagon rule family ( $M_3N@C_{2n}$ ,  $n = 39-42$ ).

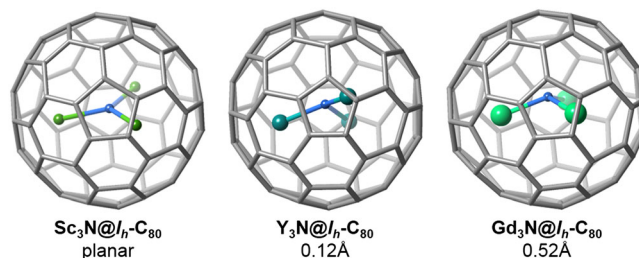


**Figure 3.**  $Sc_3N@D_3-C_{68}$  exhibits three pentalenes in a symmetric cage (cage 6140) and each Sc ion sits close to each fused pentagon bond in the pentalenes, while the cluster is planar.

pentalenes should occur only on small cages where there are no IPR isomers available to allow for a perfect fit of the planar cluster. The case of  $C_{70}$ -based endohedrals is discussed in the succeeding text; within the context of cluster shape and cage geometries, although they obviously also involve considerable electronic interactions. It will be very important to obtain experimental evidence to substantiate the non-IPR claim for  $Gd_2@C_{98}$ , which in our opinion is unexpected and somewhat controversial.

## SIZE EFFECTS

Separating electronic from size and shape effects is simply a convenient way to introduce the concepts, because these factors are closely correlated and contribute simultaneously to determine the observed structures. A lot has been said about cluster size effects in determining the size of the corresponding cages,<sup>[32]</sup> as well as their specific geometries,<sup>[33]</sup> to illustrate the effects mainly due to size we have selected the sequence of lanthanide-based trimetallic nitrides, going from the smallest  $Lu_3N$  to the largest  $La_3N$ .  $M_3N$  clusters with  $M = Sc, Y$ , or with lanthanide metals between Gd-Lu select the  $C_{80}$  icosahedral cage preferentially, even though the metal radius increases monotonically in the lanthanide series from Lu to Gd. Although  $Sc_3N$  fits perfectly and is planar inside  $C_{80}$  ( $I_h$ ),  $Y_3N$  exhibits a slight degree of pyramidalization, at 0.12 Å, measured as the distance between the plane defined by the three Y nuclei and the center of the N atom. This pyramidalization results as a consequence of the larger ionic radius of Y relative to that of Sc, hence the cluster folds like an umbrella in order to fit inside the cage (Figure 4). It is interesting to note that the added strain and electrostatic repulsion between the cationic metal centers upon pyramidalization are apparently not sufficient to favor the



**Figure 4.** Increased pyramidalization of different metal clusters inside of an icosahedral  $C_{80}$  cage.

formation of a larger cage where  $Y_3N$  could be encapsulated more comfortably and in planar form. This must be a consequence of the tremendous stabilization of the  $C_{80}$  ( $I_h$ ) cage upon the transfer of the six electrons from the cluster to the triply degenerate HOMO of the cage, which dominates the selection of this cage.

In the lanthanide series, the observed trend is the same, increasing the size of the metal radio when going from Lu to Gd results in an increased pyramidalization, which for  $Gd_3N$  is 0.52 Å, as previously defined, but the  $C_{80}$  ( $I_h$ ) continues to be the one preferentially templated (Figure 4).<sup>[34]</sup> However, when the ionic radius continues to increase beyond Gd, a new cage is preferentially selected,  $C_{88}$ , and this is observed starting with Nd, and also for Pr and Ce.<sup>[32]</sup> The  $C_{80}$  cage is observed for  $Nd_3N$  and  $Pr_3N$ , but not at all for  $Ce_3N$ , but for all three, the preferred cage is  $C_{88}$ . It is interesting to note that progressively increasing the size of the encapsulated metal in this series of trimetallic nitride endohedrals results in a discontinuous preferential cage selection, which goes from a preferred  $C_{80}$  cage to  $C_{88}$ . Although  $C_{82}$ ,  $C_{84}$ , and  $C_{86}$  cages are also observed, they are obtained in much lower concentrations. Not surprisingly, when  $La_3N$  is encapsulated, it preferentially selects an even larger cage,  $C_{96}$ , confirming the importance of cluster-cage size complementarity.<sup>[32]</sup> Although  $C_{90}$ ,  $C_{92}$ , and  $C_{94}$  cages are also observed (especially for  $Ce_3N$  and  $La_3N$ ), the progression is again discontinuous because going from  $Ce_3N$  to  $La_3N$  changes the cage preference from  $C_{88}$  to  $C_{96}$ , another increase of eight carbon atoms. We believe that these observations provide clear evidence for the importance of cluster-cage size complementarity effects, or simply stated size matters.

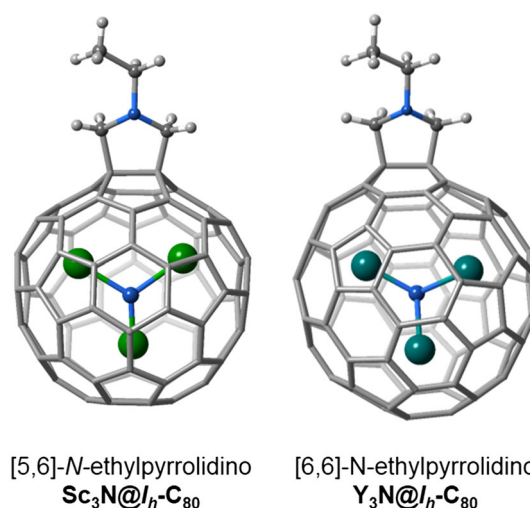
One reported example seems to deviate and almost contradict these observations, a compound with the formula  $La_3N@C_{79}N$ , which was detected by matrix-assisted laser desorption/ionization mass spectrometry as the preferentially templated cage using the so-called chemically adjusting plasma temperature, energy, and reactivity synthetic method.<sup>[35]</sup> The authors tried to explain this apparent contradiction with the other results on the basis of electronic, as opposed to size, effects, given that the size of the  $C_{79}N$  cage should be very similar to that of  $C_{80}$ . Unfortunately, this article did not report high performance liquid chromatography traces or other analytical data to evidence the preference of  $La_3N@C_{79}N$  over  $La_3N@C_{2n}$ , except for the matrix-assisted laser desorption/ionization (MALDI) spectrum. Given our frequent observations of very widely differing abilities of endohedrals to desorb under MALDI conditions, we wonder if the apparent preponderance of the  $C_{79}N$  cage over that of  $C_{96}$ , which the authors also observed in the spectrum, is the result of such a difference. Perhaps, the  $C_{79}N$  cage is desorbed much more easily and appears to be the preferred product, a situation we have frequently encountered in our own work. Although this example seems to contradict the cluster-cage size complementarity arguments presented earlier, assuming that the quantitation by MALDI is correct, it may be more a reflection of the balance between size and electronic factors, which is certainly possible. As stated previously, these effects occur simultaneously and one can easily become dominant over the other, as the  $C_{80}$  cage predilection of all the metal nitrides between Lu and Gd clearly show that size can be overcome by electronic factors.

Another interesting series that nicely exemplifies the cluster-cage size complementarity is the change in  $C_{78}$  cage isomers that are preferentially formed as the cluster size increases,

reported by Dunsch *et al.*<sup>[30]</sup> Although  $Sc_3N@C_{78}$  preferentially selects the  $D_{3h}$  (24109) symmetric cage, in which the cluster fits well and in planar form, increasing the size of the cluster by increasing the ionic radius of the encapsulated metals results in the preferential formation of a non-IPR cage  $C_2$  (22010), where the clusters fit better and in their planar form. This was found to be the case computationally for the  $Y_3N$  and  $Lu_3N$  clusters. This interesting work was mainly based on computational studies, but they also performed vibrational spectroscopic analyses of experimentally isolated  $Tm_3N@C_{78}$  and  $Dy_3N@C_{78}$ , which corroborated the assignments. Later on, we were able to confirm the cage symmetry by X-Ray crystallographic analysis of  $Gd_3N@C_{78}$ , which clearly showed it to be cage 22010, see in the previous text.<sup>[26]</sup> One could reasonably argue that electronic factors likely play an important role in the selection of this cage, which possesses two pentalene units and two of the encapsulated metal centers are adjacent to the fused bonds between the five-membered rings, as discussed in the electronic effects section.

We feel that these two examples provide very strong evidence for the importance of cluster-cage size complementarity effects in determining the formation of endohedral fullerenes.

An additional and subtle effect of cluster size was revealed by the chemical reactivity of endohedral compounds and the observation of isomeric exohedral adducts.<sup>[36–41]</sup> Although a 1,3-dipolar cycloaddition reaction led exclusively to the observation of pyrrolidine attachment to a [5, 6] bond on  $Sc_3N@I_h-C_{80}$ ,<sup>[36]</sup> the same reaction conditions led exclusively to [6,6] pyrrolidine addition on the analogous Y-based compound,  $Y_3N@I_h-C_{80}$ , (Figure 5).<sup>[37]</sup> Therefore, just a slight change in the size of the encapsulated cluster was significant enough to result in totally different and selective exohedral addition sites, although it was later shown that the [6,6] addition compound corresponded to the kinetic product which eventually thermalizes to the thermodynamically preferred [5,6] isomer derivative.<sup>[42]</sup> Very similar results were later reported by Chen *et al.*<sup>[38]</sup> who showed that both [5,6] and [6,6] exohedral addition products were observed for pyrrolidine additions to  $Sc_xGd_{3-x}N@C_{80}$  ( $I_h$ ) ( $x=0-3$ ), but the  $ScGd_2N@C_{80}$  pyrrolidine derivatives resulted exclusively in the [5,6] isomer derivative



**Figure 5.** N-ethyl-pyrrolidine attached to a [5,6] bond on  $Sc_3N@I_h-C_{80}$  and a [6,6] bond on  $Y_3N@I_h-C_{80}$ .

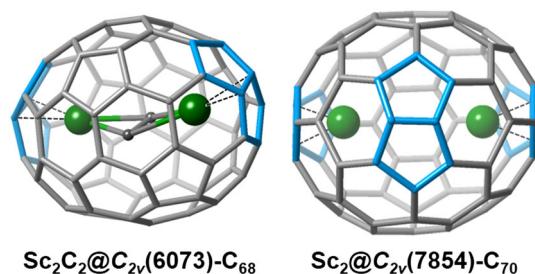


upon thermalization, whereas the  $\text{Gd}_3\text{N@C}_{80}$  pyrrolidine derivatives resulted exclusively in the [6,6] isomer. An even more recent example reported the first observation of reversible isomerization between [5,6] and [6,6] pyrrolidine adducts on  $\text{Y}_3\text{N@C}_{80}$  ( $I_h$ ) and  $\text{Gd}_3\text{N@C}_{80}$  ( $I_h$ ), which exist in equilibrium.<sup>[43]</sup> The effect of the cluster size is not only observed for  $I_h$ - $\text{C}_{80}$  cages, computational studies by Solà *et al.* showed significant differences between  $\text{Sc}_3\text{N@D}_{3h}\text{-C}_{78}$  and  $\text{Y}_3\text{N@D}_{3h}\text{-C}_{78}$  toward Diels–Alder reaction.<sup>[39]</sup>

All of these examples clearly show how sensitive the structures of these compounds and those of their corresponding derivatives are to subtle electronic and size differences. In addition to these parameters, the shapes of the clusters also play a definitive role in selecting appropriate cages with complementary motifs.

## SHAPE EFFECTS

We select only a few examples that clearly illustrate the effects of cluster-cage shape complementarity, thus we restrict the discussion mainly to  $\text{C}_{70}$  and  $\text{C}_{72}$  cages. As far as we are aware, there are only three reported endohedral fullerene compounds that exhibit three violations of the IPR,  $\text{Sc}_3\text{N@C}_{68}$  ( $D_3$ ), which was already mentioned,  $\text{Sc}_3\text{N@C}_{70}$   $\text{C}_{2v}$  (7854),<sup>[44]</sup> and a very recent report of the same  $\text{C}_{2v}$  (7854) cage incorporating two Sc ions,  $\text{Sc}_2\text{@C}_{70}$ ,<sup>[22]</sup> although Shinohara *et al.* earlier reported that  $\text{Sc}_2\text{C}_70$  corresponded to a metallic carbide compound,  $\text{Sc}_2\text{C}_2\text{@C}_{68}$   $\text{C}_{2v}$  (6073).<sup>[45]</sup> Of the three, only  $\text{Sc}_3\text{N@C}_{68}$  ( $D_3$ ) was characterized by X-Ray crystallography, the others were mainly characterized by spectroscopic methods and the structures assigned based on theoretical calculations. The proposed  $\text{Sc}_2\text{C}_2\text{@C}_{68}$   $\text{C}_{2v}$  (6073) exhibits a perfectly complementary match between the cluster and the two pentalenes on the cage, with the shape of the cluster providing optimal interaction between the two Sc ions and the two existing pentalenes on this cage, (Figure 6). On the other hand, the computationally proposed alternate structure for  $\text{Sc}_2\text{@C}_{70}$   $\text{C}_{2v}$  (7854) has two Sc ions adjacent to two pentalenes on the cage, but there is a third pentalene that is not stabilized by the proximity of an endohedral ion, (Figure 6). As stated earlier, to our knowledge, this is the only proposed pentalene on an endohedral structure which does not have a proximal cation inside. The authors propose that the pentalenes are stabilized by increased aromaticity induced by the negative charges, which nominally transform the  $8\pi$  antiaromatic pentalenes into  $10\pi$  aromatic structures. However, as stated earlier, if charge transfer and aromatization of the pentalenes is strongly stabilizing, then pentalenes would be ubiquitous, especially if no endohedral counterions are required for their electrostatic stabilization and can exist as free standing units. In



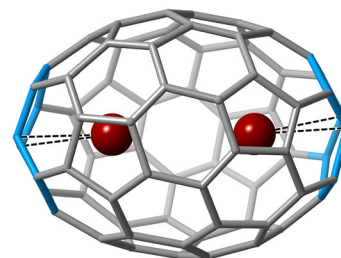
**Figure 6.** Comparison of two computational proposed structures of  $\text{Sc}_2\text{C}_70$ .

the case of  $\text{Sc}_3\text{N@C}_{70}$   $\text{C}_{2v}$  (7854),<sup>[44]</sup> which has the same cage symmetry, the three pentalenes are perfectly complemented by the three proximal Sc ions in the cluster, very similar to the size and shape fit exhibited by  $\text{Sc}_3\text{N@C}_{68}$  ( $D_3$ ). The originally proposed  $\text{Sc}_2\text{C}_2\text{@C}_{68}$   $\text{C}_{2v}$  (6073) is more congruent with the size-shape complementarity idea presented in this article, but further experimentation, hopefully an X-Ray single crystal structure, will be required to solve these conflicting observations.

Consistent with the shape complementarity observations for  $\text{C}_{70}$  cages is the recently reported  $\text{Sc}_2\text{S@C}_{70}$   $\text{C}_2$  (7892),<sup>[46]</sup> which has two pentalene units whose positions on the cage nicely complement the shape of the cluster to provide close contacts with the encapsulated Sc ions. By using computational methods, the most stable empty tetraanionic cage  $\text{C}_{70}^{4-}$  corresponds to that of the only IPR isomer (8149) possible, but upon encapsulation of  $\text{Sc}_2\text{S}$  the most stable cage is 7892, by 18.6 Kcal/mol compared with the next in stability, cage 7924, which also possesses two pentalene units.

Perhaps one of the most striking examples of shape complementarity is provided by the  $\text{C}_{72}$  endohedral fullerene cage family. In a very comprehensive article by Popov and Dunsch,<sup>[21]</sup> they computed the stabilities of many fullerene cages in their hexaanionic form and then after encapsulation of the  $\text{Sc}_3\text{N}$  cluster. The most stable  $\text{C}_{72}^{6-}$  cage is the  $D_2$  (10611), which is 17 Kcal more stable than the next one, and has opposing pentalenes on a linear arrangement across the cage, (Figure 7). Cage 10528 is about 19 Kcal/mol less stable in its hexaanionic form but it becomes the most stable after encapsulation of  $\text{Sc}_3\text{N}$ , whereas cage 10611 is about 13 Kcal/mol less stable after cluster encapsulation. The shape of the cluster provides a better fit in the 10528 cage because two of the Sc ions can interact with the two existing pentalenes on this cage (Figure 7). No available cage with three perfectly complementary pentalenes exists, the closest being cage 10482, but the fit is not perfect, thus why 10528 is preferred. It is virtually impossible for the triangular cluster to provide close proximity of two Sc ions with the linearly disposed pentalenes on cage 10611, thus why it is relatively destabilized.

Interestingly, what if the encapsulated species had the ability to donate six electrons but possess a different shape, or better still have no specific shape at all, meaning that it could adjust to the cage structure essentially at will? Under those conditions, it would be expected that cage 10611 would predominate, because it is the most stable in its hexaanionic state. This is exactly what is observed experimentally for  $\text{La}_2\text{@C}_{72}$ , which exclusively selects the 10611, because the two  $\text{La}^{3+}$  ions can independently interact with the corresponding pentalenes on opposing ends (Figure 7). We believe that this is a striking and significant example of the importance of shape selectivity in endohedral fullerene compounds.



**Figure 7.**  $\text{La}_2\text{@D}_2\text{-C}_{72}$  exclusively select cage 10611, where each La ion sits close to the pentalenes at the poles.

## CONCLUSIONS

The presence of pentalene units in endohedral fullerenes results from a combination of several factors such as charge transfer from the encapsulated entity to the carbon cage, localization of negative charge at the pentalene units, and aromatization of the pentalene units upon gaining electrons. These factors make the pentalenes reasonably common on endohedral fullerene cages, even though each one destabilizes the cage by 17–22 Kcal/mol.

As far as we are aware, very little is known about the relative and opposite contributions that arise from introducing pentalene units on a fullerene cage versus the stabilization that results from the electrostatic interactions with the encapsulated cations and the gain in aromaticity.

The only case of a cage pentalene that does not have a proximal endohedral metal ion stabilization was recently proposed based on computational studies for  $Sc_2@C_{70}$ , which has three pentalene units, and two of them have proximal Sc ions, but the other pentalene does not. Further experimental results are needed to confirm such an unusual structure.

When the cages are sufficiently small to accommodate planar clusters, the presence of pentalene units is observed, but in larger cages; IPR cages typically exist that can accommodate the planar clusters.

The tremendous stabilization of the  $C_{80}$  ( $I_h$ ) cage upon the transfer of six electrons from the cluster to the triply degenerate HOMO of the cage is able to offset the strain that results as the metal radius increases and pyramidalization of the cluster occurs. This is not the case when the metal radius of the trimetallic nitride cluster is sufficiently large, as for La, Ce, Pr, and Nd.

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