

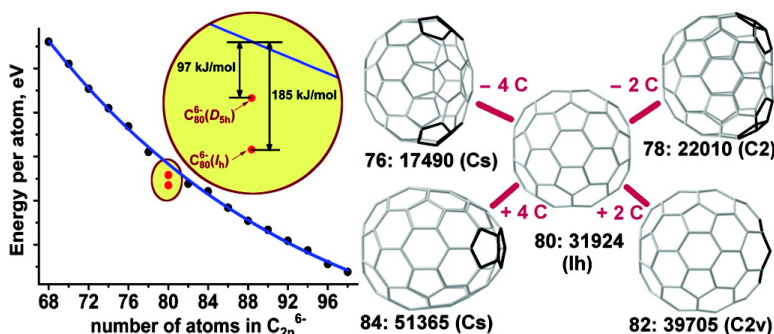
Article

Structure, Stability, and Cluster-Cage Interactions in Nitride Clusterfullerenes $MN@C$ ($M = Sc, Y; 2n = 68-98$): a Density Functional Theory Study

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Structure, Stability, and Cluster-Cage Interactions in Nitride Clusterfullerenes $M_3N@C_{2n}$ ($M = Sc, Y$; $2n = 68-98$): a Density Functional Theory Study

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Abstract: Extensive semiempirical calculations of the hexaanions of IPR (isolated pentagon rule) and non-IPR isomers of $C_{68}-C_{88}$ and IPR isomers of $C_{90}-C_{98}$ followed by DFT calculations of the lowest energy structures were performed to find the carbon cages that can provide the most stable isomers of $M_3N@C_{2n}$ clusterfullerenes ($M = Sc, Y$) with Y as a model for rare earth ions. DFT calculations of isomers of $M_3N@C_{2n}$ ($M = Sc, Y$; $2n = 68-98$) based on the most stable C_{2n}^{6-} cages were also performed. The lowest energy isomers found by this methodology for $Sc_3N@C_{68}$, $Sc_3N@C_{78}$, $Sc_3N@C_{80}$, $Y_3N@C_{78}$, $Y_3N@C_{80}$, $Y_3N@C_{84}$, $Y_3N@C_{86}$, and $Y_3N@C_{88}$ are those that have been shown to exist by single-crystal X-ray studies as $Sc_3N@C_{2n}$ ($2n = 68, 78, 80$), $Dy_3N@C_{80}$, and $Tb_3N@C_{2n}$ ($2n = 80, 84, 86, 88$) clusterfullerenes. Reassignment of the carbon cage of $Sc_2@C_{76}$ to the non-IPR C_5 : 17490 isomer is also proposed. The stability of nitride clusterfullerenes was found to correlate well with the stability of the empty 6-fold charged cages. However, the dimensions of the cage in terms of its ability to encapsulate M_3N clusters were also found to be an important factor, especially for the medium size cages and the large Y_3N cluster. In some cases the most stable structures are based on the different cage isomers for Sc_3N and Y_3N clusters. Up to the cage size of C_{84} , non-IPR isomers of C_{2n}^{6-} and $M_3N@C_{2n}$ were found to compete with or to be even more stable than IPR isomers. However, the number of adjacent pentagon pairs in the most stable non-IPR isomers decreases as cage size increases: the most stable $M_3N@C_{2n}$ isomers have three such pairs for $2n = 68-72$, two pairs for $n = 74-80$, and only one pair for $n = 82, 84$. For C_{86} and C_{88} the lowest energy IPR isomers are much more stable than any non-IPR isomer. The trends in the stability of the fullerene isomers and the cluster-cage binding energies are discussed, and general rules for stability of clusterfullerenes are established. Finally, the high yield of $M_3N@C_{80}$ (I_h) clusterfullerenes for any metal is explained by the exceptional stability of the C_{80}^{6-} (I_h : 31924) cage, rationalized by the optimum distribution of the pentagons leading to the minimization of the steric strain, and structural similarities of C_{80} (I_h : 31924) with the lowest energy non-IPR isomers of C_{76}^{6-} , C_{78}^{6-} , C_{82}^{6-} , and C_{84}^{6-} pointed out.

Introduction

The world of endohedral fullerenes has been largely expanded in the past decade by the introduction of nitride clusterfullerenes with a variety of carbon cages and encaged clusters.¹⁻³ Historically, the first member of nitride clusterfullerenes was $Sc_3N@C_{80}$ (I_h : 31924), isolated and structurally characterized by Stevenson et al.⁴ in 1999. It remains the most abundant structure of this clusterfullerene family up until now. The class of Sc_3N -based clusterfullerenes also includes D_{3h} - $Sc_3N@C_{68}$,^{5,6}

D_{3h} - $Sc_3N@C_{78}$,⁷ the isomer of $Sc_3N@C_{80}$ with D_{5h} -symmetric carbon cage,⁸⁻¹⁰ and the recently reported compound $Sc_3N@C_{70}$.¹¹ Significantly, $Sc_3N@C_{68}$ and $Sc_3N@C_{70}$ are based on fullerene isomers that do not obey the isolated pentagon rule (IPR). Substantial efforts by several groups to synthesize different nitride clusterfullerenes resulted in the isolation of $M_3N@C_{80}$ ($M = Y$ and all lanthanides from Gd to Lu),¹²⁻¹⁷ a series of

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mixed $\text{Er}_x\text{Sc}_{3-x}\text{N}@C_{68}$ ($x = 1, 2$)⁵ and $\text{M}_x\text{Sc}_{3-x}\text{N}@C_{80}$ clusterfullerenes ($\text{M} = \text{Er}^{4,12}$ or Gd^{18} , $x = 1, 2$; $\text{M} = \text{Ce}$, $x = 1$)¹⁹, and even $\text{ScYErN}@C_{80}$,²⁰ a clusterfullerene with three different metals. Development of the reactive gas atmosphere methodology made the isolation of a larger variety of cluster fullerenes possible, including the families $\text{Gd}_3\text{N}@C_{2n}$ ($2n = 80-88$),¹⁶ $\text{Tm}_3\text{N}@C_{2n}$ ($2n = 78-88$),¹³ and $\text{Dy}_3\text{N}@C_{2n}$ ($2n = 76-98$).²¹ In addition, the isolation of $\text{Tb}_3\text{N}@C_{2n}$ ($2n = 80, 84-88$) clusterfullerenes was recently reported.^{22,23}

Unambiguous structural characterization of clusterfullerenes, at least in terms of the cage isomer present, can be provided by single-crystal X-ray diffraction in some cases. Clusterfullerenes based on the C_{80} (I_h : 31924) cage isomer remain the most studied ones: single-crystal X-ray structures were reported for $\text{Sc}_3\text{N}@C_{80}$,⁴ $\text{Lu}_3\text{N}@C_{80}$,²⁴ $\text{Dy}_3\text{N}@C_{80}$,²⁵ $\text{Tb}_3\text{N}@C_{80}$,²³ $\text{ErSc}_2\text{N}@C_{80}$,²⁶ and $\text{CeSc}_2\text{N}@C_{80}$.¹⁹ Crystallographic reports on other clusterfullerenes include two studies with the C_{80} (D_{5h} : 31923) cage, $\text{Sc}_3\text{N}@C_{80}$,¹⁰ and $\text{Tb}_3\text{N}@C_{80}$,²³ as well as reports on $\text{Sc}_3\text{N}@C_{68}$,⁶ $\text{Sc}_3\text{N}@C_{78}$,⁷ $\text{Tb}_3\text{N}@C_{84}$,²² $\text{Tb}_3\text{N}@C_{86}$,²³ and $\text{Tb}_3\text{N}@C_{88}$.²³ The cage isomers found for $\text{Tb}_3\text{N}@C_{2n}$ can be assigned to the Gd-, Dy-, and Tm-based clusterfullerenes because their UV-vis spectra are very similar. However, the structures of the clusterfullerenes with other cages ($2n = 76, 82, 90-98$) remain unknown. The available amounts are simply too small to grow diffraction-quality single crystals. ¹³C NMR spectroscopy also requires considerable amounts of the endohedral fullerenes; besides, it provides only the cage symmetry, and hence this information may be ambiguous, especially if it is taken into account that non-IPR isomers may be formed, as documented in recent works.^{6,11,23,27-30} Theoretical studies can aid in the structural determination or at least can narrow down the possible list of isomeric structures to consider them in spectroscopic studies. The early theoretical studies focused on the possible isomerism of endohedral fullerenes,^{31,32} and though they were

limited to only IPR isomers, an important feature of the endohedral fullerenes was revealed: experimentally isolated isomers of empty and endohedral fullerenes are usually different because encapsulated metals or clusters transfer some of their electrons to the carbon cage, and relative stabilities of the fullerene isomers may alter for different charge states.

The electronic structure of nitride clusterfullerenes may be conceived as a result of a 6-fold electron transfer from the cluster to the fullerene. Though the $\text{M}_3\text{N}^{6+}@C_{2n}^{6-}$ ionic model was questioned in recent studies and much smaller net charges of the cluster and the cage as well as strong covalent cluster-cage interactions were established,³³⁻³⁷ the ionic model is still useful for developing stability criteria of nitride clusterfullerenes. The simplest and elegant use of this conjecture to predict the most suitable cage isomers capable of encapsulating nitride cluster was proposed by Campanera et al.³⁸ Assuming the 6-fold electron transfer in nitride clusterfullerenes, the authors have supposed that only those fullerenes with a considerable gap between LUMO + 2 and LUMO + 3 (which become HOMO and LUMO, respectively, in the C_{2n}^{6-} hexaanion and presumably in $\text{M}_3\text{N}@C_{2n}$) may be considered as suitable hosts for nitride clusters. Screening all IPR fullerenes in the $C_{60}-C_{84}$ range, they have found that only C_{60} , C_{78} (D_{3h} : 24109), and C_{80} (I_h : 31924 and D_{5h} : 31923) may be considered as suitable cage isomers. Indeed, besides C_{60} , which appears to be too small to host a Sc_3N cluster, only these and no other IPR cage isomers were found among $\text{Sc}_3\text{N}@C_{2n}$ clusterfullerenes. However, the growing number of non-IPR isomers reported to date, including nitride clusterfullerenes $\text{Sc}_3\text{N}@C_{68}$,⁵ $\text{Sc}_3\text{N}@C_{70}$,¹¹ $\text{Tb}_3\text{N}@C_{84}$,²² and $\text{M}_3\text{N}@C_{78}$ ($\text{M} = \text{Dy}, \text{Tm}$),³⁹ demonstrates that IPR cannot be considered as a firm limitation for the stability of an endohedral fullerene. Thus, a consideration of hundreds and thousands of isomers is required, and therefore the method proposed by Campanera et al.³⁸ cannot be used to distinguish the most suitable cages because many isomers with suitable gaps may be found among those thousands of possible cage isomers. In fact, the argument of the necessity of the large HOMO-LUMO gap is essential for kinetic stability, but it cannot discriminate the isomers with different thermodynamic stabilities.

It is reasonable to conceive that the stability of the cage isomers of endohedral fullerenes should correlate with the stability of the appropriately charged empty cages, the charge being the function of the metal or the cluster composition incorporated.^{1,28,31,32} Thus, we have suggested that the stability of the clusterfullerene isomers should correlate with the stability of the fullerene cages in the hexaanionic state. Screening through the large number of IPR and non-IPR isomers of C_{70} and C_{78} with subsequent DFT calculations, we have proposed the molecular structures of $\text{Sc}_3\text{N}@C_{70}^{11}$ and $\text{M}_3\text{N}@C_{78}$ ($\text{M} = \text{Dy}, \text{Tm}$),³⁹ which both were found to be non-IPR fullerenes, and

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confirmed these findings by the comparison of experimental and DFT predicted spectroscopic data. The study of $M_3N@C_{78}$ also revealed that the cluster size has a strong effect on the carbon cage isomerism, as the IPR isomer D_{3h} : 24109 is more stable for the relatively small Sc_3N cluster in $Sc_3N@C_{78}$, while the lowest energy isomer with Y_3N and the clusters of similar size is based on the non-IPR C_2 : 22010 cage.³⁹ In this work, we apply this methodology for the whole range of carbon cages observed for $M_3N@C_{2n}$ so far (e.g., $C_{68}-C_{98}$) to predict the most possible structures of $M_3N@C_{76}-M_3N@C_{98}$ ($M = Dy, Tm, Tb$). Some of them were isolated but not yet structurally characterized, while others were observed in the mass spectra of the clusterfullerene extracts only but not yet isolated. The data obtained thus for a broad range of cage sizes enabled us to establish general trends in stability of nitride clusterfullerenes.

Computational Details

Semiempirical calculations at the AM1⁴⁰ level were performed using the PC GAMESS package.⁴¹ DFT calculations were performed using a PBE functional⁴² and TZ2P-quality basis set with an SBK-type effective core potential for Sc and Y atoms implemented in the PRIRODA package.^{43,44} The quantum-chemical code employed expansion of the electron density in an auxiliary basis set to accelerate evaluation of the Coulomb and exchange-correlation terms. No symmetry constraints were adopted in the optimization.

Results

Treating the stability criteria of endohedral fullerenes we generally propose that fullerene isomers with three or more fused pentagons cannot be efficiently stabilized by an M_3N cluster and will thus be unstable. Hence, in this work we have considered only IPR isomers or non-IPR isomers with isolated pairs of adjacent pentagons (APPs). The number of such isomers increases from 359 for C_{68} to 16717 for C_{88} . For $C_{90}-C_{98}$ only IPR isomers were considered (the reasons for exclusion of non-IPR isomers are described below). The total amount of isomers of C_{2n} cages studied for each $2n$ and the numbers of the isomers according to a spiral algorithm are listed in Table 1. For all these fullerenes, hexaanion structures were optimized at the AM1 level. Then, the most stable isomers (10 to 20 for each cage size) were optimized at the DFT level to ensure the reliability of AM1-predicted relative energies, and finally $Sc_3N@C_{2n}$ and $Y_3N@C_{2n}$ clusterfullerenes based on the most stable C_{2n}^{6-} isomers were studied by DFT. We have recently shown that the ionic radii of the cluster-forming metal largely determine the cluster-cage interactions as well as the spectroscopic properties of clusterfullerenes. Since the ionic radius of Y (0.90 Å) is close to that of Dy (0.91 Å) and only slightly smaller than that of Tb (0.92 Å) and slightly larger than that of Tm (0.87 Å),⁴⁵ the structures and spectroscopic properties of $Y_3N@C_{2n}$ isomers and those of $M_3N@C_{2n}$ ($M = Tb, Dy, Tm$) clusterfullerenes are assumed to be similar.^{25,39} Thus, the calculated relative energies of $Y_3N@C_{2n}$ isomers are to a great

Table 1. List of C_{2n} Isomers, the Hexaanions of Which Are Studied in This Work^a

C_{2n}	N^b	isomer nos. ^c	N (IPR) ^d	IPR nos. ^e
C_{68}	359	5974–6332	0	—
C_{70}	527	7629–8149	1	D_{5h} : 8149
C_{72}	906	10285–11190	1	D_{6d} : 11190
C_{74}	1296	12951–14246	1	D_{3h} : 14246
C_{76}	2056	17096–19151	2	D_2 : 19150, T_d : 19151
C_{78}	2927	21183–24109	5	24105–24109
C_{80}	4442	27483–31924	7	31918–31924
C_{82}	6091	33628–39718	9	39710–39718
C_{84}	8831	42762–51592	24	51569–51592
C_{86}	11873	51890–63761	19	63743–63761
C_{88}	16717	65022–81738	35	81704–81738
C_{90}			46	99873–99918 ^f
C_{92}			86	126324–126409 ^f
C_{94}			134	153360–153493 ^f
C_{96}			187	191653–191839 ^f
C_{98}			259	230759–231017 ^f

^a The isomers of C_{70}^{6-} and C_{78}^{6-} were studied in refs 11 and 39, respectively. ^b Total number of isomers studied in the hexaanionic state at the AM1 level. ^c The range of their numbers according to spiral algorithm (ref 46). ^d Total number of IPR isomers of C_{2n} for a given $2n$. ^e The range of their numbers according to the spiral algorithm (ref 46). ^f Only IPR isomers are studied for $C_{90}-C_{98}$, and for these fullerenes we use the truncated numbering system which counts only IPR isomers. That is, isomer C_{90} (D_{5h} : 99873) is designated as C_{90} (D_{5h} : 1), isomer C_{90} (C_{2v} : 99874) as C_{90} (C_{2v} : 2), isomer C_{92} (D_2 : 126324) as C_{92} (D_2 : 1), etc.

extent applicable to the lanthanide-based clusterfullerenes, and we consider Y as a model for rare earth metal ions of similar radii.

Relative energies and HOMO–LUMO gaps of the C_{2n}^{6-} and the corresponding $Sc_3N@C_{2n}$ and $Y_3N@C_{2n}$ isomers are listed in Tables 2–4. Whenever the relative energy (denoted also as ΔE) is discussed hereafter for either the empty cages or the clusterfullerenes, it is given versus the energy of the most stable isomer with the same $2n$. Since C_{76} is the smallest fullerene for which $Dy_3N@C_{2n}$ was found in the cluster fullerene extract,²¹ systematic calculations (that is, with consideration of at least 10 lowest energy C_{2n}^{6-} isomers) for smaller fullerenes were performed only for the Sc_3N cluster, while computations of $Y_3N@C_{2n}$ were limited for these cages to the selected isomers, which had the lowest energies for $Sc_3N@C_{2n}$ or could be considered as relatively stable structures based on the cage shape and size. For $C_{76}-C_{88}$, systematic computations were performed for both Sc_3N and Y_3N . Selected $Y_3N@C_{2n}$ and $Sc_3N@C_{2n}$ isomers were considered for $C_{90}-C_{98}$, usually limited to one or a few most stable C_{2n}^{6-} cages with the largest HOMO–LUMO gaps. Whenever M_3N will be used hereafter to designate a trimetallic nitride cluster in the description of the results or in the discussion, it is assumed that these results or observations are valid for both Sc_3N and Y_3N . The ideal symmetry of the cage and its number according to the Fowler spiral numbering scheme⁴⁶ divided by a colon will be used to label carbon cage isomers. With respect to this it should be noted that the symmetry of $M_3N@C_{2n}$ is not necessarily the same as the symmetry of the empty fullerene, and in many cases the former appears to be lower. When the M_3N cluster geometry in the optimized $M_3N@C_{2n}$ structures is discussed, the degree of the cluster pyramidalization is represented by h , the displacement of the nitrogen atom out of the plane formed by the three metal atoms (that is, h is the height of the pyramid formed by the

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Table 2. Relative Energies (ΔE , kJ/mol) and HOMO–LUMO Gaps (gap, eV) of the Most Stable C_{2n}^{6-} and $Sc_3N@C_{2n}$ ($2n = 68, 70, 72, 74$) Isomers as Computed at the DFT Level

C_{2n}	cage isomer	APPs	C_{2n}^{6-}		$Sc_3N@C_{2n}$		C_{2n}	cage isomer	APPs	C_{2n}^{6-}		$Sc_3N@C_{2n}$	
			ΔE	gap	ΔE	gap				ΔE	gap		
C_{68}	D_3 : 6140	3	0.0	1.20	0.0	1.28	C_{70}	C_{2v} : 7854	3	0.0	1.24	0.0	1.29
C_{68}	C_{2v} : 6073	2	8.8	0.65	246.0	0.53	C_{70}	C_2 : 7957	2	17.6	0.93	140.0	0.91
C_{68}	C_1 : 6102	3	47.7	0.98	95.6	0.94	C_{70}	C_1 : 7852	3	41.8	0.75	21.6	0.83
C_{68}	C_2 : 6118	3	54.5	0.71	71.4	0.77	C_{70}	D_{5h} : 8149	0	42.9	0.50	163.7	0.53
C_{68}	C_2 : 6146	2	62.8	0.58	191.7	0.62	C_{70}	C_s : 7960	2	48.6	0.96	179.0	1.00
C_{68}	C_s : 6072	3	81.3	0.68	205.9	0.74	C_{70}	C_1 : 7886	3	54.7	0.84	39.2	0.91
C_{68}	C_s : 6089	3	73.6	1.08	256.9	1.01	C_{70}	C_s : 7922	3	56.1	0.94	68.0	0.85
C_{68}	C_1 : 6138	3	70.1	1.04	87.9	1.03	C_{70}	C_1 : 7887	3	56.8	0.65	43.6	0.65
C_{68}	C_1 : 6116	3	90.5	0.39	123.9	0.48	C_{70}	C_1 : 7851	3	61.8	0.57	28.6	0.61
C_{68}	C_1 : 6039	3	91.0	0.45	200.9	0.53	C_{70}	C_1 : 7849	3	69.4	0.90	35.6	0.88
C_{72}	D_2 : 10611	2	0.0	1.12	54.6	0.89	C_{74}	C_2 : 13295	2	0.0	1.22	18.7	1.04
C_{72}	C_1 : 10610	2	68.7	0.72	34.6	0.75	C_{74}	C_2 : 13333	2	23.2	0.64	51.3	0.73
C_{72}	C_s : 10616	2	71.3	0.53	49.9	0.54	C_{74}	D_{3h} : 14246	0	25.9	0.71	21.3	0.47
C_{72}	C_1 : 10482	3	77.0	1.01	26.7	0.98	C_{74}	C_1 : 13408	2	34.0	1.18	58.5	1.09
C_{72}	C_s : 10528	2	77.3	0.32	0.0	0.39	C_{74}	C_2 : 13290	2	37.7	0.79	51.9	0.73
C_{72}	C_{2v} : 11188	1	79.8	0.61	21.2	0.49	C_{74}	C_2 : 13291	2	54.1	0.87	63.1	0.88
C_{72}	C_1 : 10518	3	99.8	0.82	40.5	0.87	C_{74}	C_2 : 13292	2	69.9	0.94	70.7	0.75
C_{72}	C_1 : 10468	3	100.2	1.12	48.9	1.10	C_{74}	C_1 : 13391	2	70.7	0.84	98.5	0.80
C_{72}	C_1 : 10557	2	101.8	0.73	107.7	0.82	C_{74}	C_3 : 13492	3	71.7	1.10	9.9	1.14
C_{72}	C_2 : 10612	1	104.9	0.54	36.9	0.59	C_{74}	C_{2v} : 14239	2	86.9	0.77	0.0	0.77
C_{72}	C_2 : 10626	2	107.9	0.63	116.6	0.67	C_{74}	C_1 : 13384	2	89.1	0.45	104.4	0.38
C_{72}	C_1 : 10526	3	117.3	0.79	55.6	0.81	C_{74}	C_s : 13336	2	97.8	0.57	50.4	0.57
C_{72}	C_2 : 10693	2	118.8	0.59	53.5	0.60	C_{74}	C_1 : 13479	3	99.3	1.07	38.4	0.99
C_{72}	C_1 : 10688	3	121.6	0.74	56.6	0.77	C_{74}	C_2 : 13961	2	100.9	1.24	132.1	1.05
C_{72}	C_1 : 10469	3	122.2	0.85	70.9	0.78	C_{74}	C_1 : 13771	2	101.3	0.58	57.1	0.62
C_{72}	C_1 : 10774	3	125.8	1.03	40.9	0.95	C_{74}	C_1 : 13549	2	105.2	0.58	49.6	0.55
C_{72}	C_1 : 10615	2	127.9	0.57	66.5	0.63	C_{74}	C_1 : 13410	2	108.6	0.82	74.9	0.91
C_{72}	C_2 : 10554	2	131.7	0.57	148.1	0.58	C_{74}	C_1 : 13393	1	116.4	0.52	65.7	0.50
C_{72}	C_1 : 10849	2	134.1	0.60	132.1	0.59	C_{74}	C_1 : 13334	2	118.1	0.29	72.7	0.30
C_{72}	C_1 : 10538	2	135.4	0.37	51.2	0.36	C_{74}	C_1 : 14049	1	119.5	0.58	47.1	0.53

three metal atoms and the N atom in the vertex). In some cases, especially for IPR isomers, several isomers based on the same carbon cage and different in the position of the cluster are possible. In such cases the data listed in Tables 2–4 correspond to the most stable structures found by optimization of several possible conformations.

$M_3N@C_{68}$. The most stable isomer of C_{68}^{6-} among all studied structures is D_3 : 6140 with three APPs (Table 2). It is almost isoenergetic to the isomer C_{2v} : 6073, which has two APPs ($\Delta E = 8.8$ kJ/mol), while other isomers of C_{68}^{6-} are considerably less stable ($\Delta E = 47.7$ kJ/mol or more). Among the 10 most stable isomers, D_3 : 6140 has the largest HOMO–LUMO gap, 1.20 eV. D_3 : 6140 is also the most stable isomer of $Sc_3N@C_{68}$ (Figure 1); however the stability order of other isomers is significantly different from that of the empty fullerenes. For instance, the relative energy of the $Sc_3N@C_{68}$ isomer based on the C_{2v} : 6073 cage is found to be 246.0 kJ/mol, and this isomer is substantially less stable than many other $Sc_3N@C_{68}$ isomers, though for the empty C_{68}^{6-} this cage is the second among the most stable ones (note also that the isomers C_{2v} : 6073 was also proposed for $Sc_2C_2@C_{68}^{28}$). Such a high relative energy may be explained by the unfavorable location of APPs, so that the cluster, the shape of which follows to some extent the location of APPs, is strongly distorted from equilateral shape, with one of the Sc–N–Sc angles being 163.2°, and two others being equal to 98.4°. Besides, one of the Sc–N bonds in $Sc_3N@C_{68}$ (C_{2v} : 6073) is 1.918 Å, which is much shorter than the optimum Sc–N bond length of ca. 2.05 Å (see Discussion section). The Sc_3N cluster retains almost equilateral shape inside the C_2 : 6118 and C_1 : 6138 cages, while Sc–N distances are 1.98–2.00 Å

(compare to 1.993 Å in D_3 : 6140), and these isomers are the second and the third most stable isomer of $Sc_3N@C_{68}$, with the stability order resembling that of the empty cages. HOMO–LUMO gaps of $Sc_3N@C_{68}$ isomers are almost equal to those of the empty C_{68}^{6-} anions. All other isomers of $Sc_3N@C_{68}$ studied by DFT are at least by 71.4 kJ/mol less stable than the isomer D_3 : 6140. Finally, our theoretical prediction of the highest stability of $Sc_3N@C_{68}$ (D_3 : 6140) agrees well with the results of the single-crystal X-ray study,⁶ which proved experimentally the D_3 : 6140 cage isomer for the isolated $Sc_3N@C_{68}$.

The C_{68} cage appears to be too small for the Y_3N cluster, so that the cluster is forced to be pyramidal ($h = 0.550$ Å) in the DFT-optimized structure of $Y_3N@C_{68}$ (D_3 : 6140). Pyramidalization of the cluster points to the high strain in the structure, which is therefore energetically unfavorable,³⁹ and hence $M_3N@C_{68}$ with a uniform M_3N cluster and an M other than Sc has never been observed experimentally. However, the isolation of the mixed clusterfullerenes $ErSc_2N@C_{68}$ and $Er_2ScN@C_{68}$ was reported by Stevenson et al.⁵

$M_3N@C_{70}$. The study of C_{70}^{6-} and $Sc_3N@C_{70}$ isomers was reported by us recently.¹¹ In brief, the most stable C_{70}^{6-} isomer is C_{2v} : 7854 with three APPs, which is by 43 kJ/mol more stable than C_{70}^{6-} based on the sole IPR isomer of C_{70} , D_{5h} : 8149 (Table 2). The HOMO–LUMO gap of C_{2v} : 7854, 1.24 eV, is the largest among the most stable C_{70}^{6-} isomers, none of which has a gap higher than 1.00 eV. The stability of C_{2v} : 7854 isomer with respect to the IPR cage is further enhanced once the Sc_3N cluster is encapsulated into the fullerene: $Sc_3N@C_{70}$ (C_{2v} : 7854) is 164 kJ/mol more stable than $Sc_3N@C_{70}$ (D_{5h} : 8149). The cluster in $Sc_3N@C_{70}$ (C_{2v} : 7854) is planar and significantly

Table 3. Relative Energies (ΔE , kJ/mol) and HOMO–LUMO Gaps (gap, eV) of the Most Stable C_{2n}^{6-} and $M_3N@C_{2n}$ ($2n = 76, 80, 82, 84, 86, 88; M = Sc, Y$) Isomers as Computed at the DFT Level

C_{2n}	isomer	APPs	C_{2n}^{6-}		$Sc_3N@C_{2n}$		$Y_3N@C_{2n}$		C_{2n}	isomer	APPs	C_{2n}^{6-}		$Sc_3N@C_{2n}$		$Y_3N@C_{2n}$	
			ΔE	gap	ΔE	gap	ΔE	gap				ΔE	gap	ΔE	gap	ΔE	gap
C_{76}	C_s : 17490	2	0.0	1.12	20.0	1.08	0.0	1.24	C_{80}	I_h : 31924	0	0.0	1.83	0.0	1.46	0.0	1.54
C_{76}	C_{2v} : 19138	1	16.8	0.78	41.7	0.80	103.2	0.97	C_{80}	D_{5h} : 31923	0	88.2	1.51	67.0	1.33	70.2	1.40
C_{76}	T_d : 19151	0	20.8	0.14	0.0	0.16	37.7	0.10	C_{80}	C_{2v} : 31922	0	196.7	0.61	166.5	0.67	93.9	0.67
C_{76}	C_1 : 17465	2	53.9	0.89	83.1	0.90	55.4	0.90	C_{80}	C_1 : 31891	1	246.9	0.99	185.1	0.92	149.8	0.97
C_{76}	C_2 : 17765	2	55.8	1.37	116.4	1.13	80.2	1.29	C_{80}	C_1 : 28325	2	262.8	1.36	227.4	1.17	90.0	1.24
C_{76}	C_2 : 17512	2	60.1	1.14	176.6	1.02	71.1	1.15	C_{80}	C_1 : 28319	1	285.6	0.74	239.7	0.84	145.2	0.84
C_{76}	C_2 : 18161	2	64.7	1.12	70.0	1.13	26.1	1.20	C_{80}	C_2 : 29591	2	288.4	1.33	255.4	1.20	110.6	1.41
C_{76}	C_1 : 17588	2	78.7	0.85	81.1	0.75	85.7	0.84	C_{80}	C_1 : 28324	1	295.3	0.47	261.4	0.45	168.5	0.46
C_{76}	C_1 : 17760	2	79.9	1.07	95.7	0.91	83.7	0.98	C_{80}	C_{2v} : 31920	0	301.8	0.58	290.5	0.53	124.5	0.63
C_{76}	C_1 : 17459	1	80.5	0.54	106.2	0.45	149.7	0.54	C_{80}	C_1 : 31876	1	300.0	0.50	232.1	0.47	144.2	0.46
C_{82}	C_{2v} : 39718	0	0.0	0.79	0.0	0.83	29.6	0.84	C_{84}	D_2 : 51589	0	0.0	0.80	13.8	0.80	33.2	0.90
C_{82}	C_{2v} : 39705	1	30.1	1.32	17.7	1.20	0.0	1.32	C_{84}	C_s : 51365	1	1.8	1.34	0.0	1.10	0.0	1.34
C_{82}	C_{3v} : 39717	0	48.9	0.22	58.1	0.21	119.1	0.19	C_{84}	D_{2d} : 51591	0	29.7	0.77	18.0	0.75	48.8	0.82
C_{82}	C_s : 39715	0	54.0	0.54	41.2	0.55	51.0	0.50	C_{84}	C_s : 51578	0	36.9	0.65	43.4	0.67	49.3	0.66
C_{82}	C_s : 39663	1	61.2	1.42	49.8	1.03	32.6	1.51	C_{84}	C_s : 51583	0	37.9	0.89	43.5	0.76	60.7	0.82
C_{82}	C_2 : 39714	0	87.4	0.84	89.5	0.61	54.4	0.64	C_{84}	D_2 : 51590	0	38.5	0.59	39.0	0.70	77.3	0.68
C_{82}	C_s : 39704	1	111.1	0.83	94.2	0.79	103.2	0.87	C_{84}	C_{2v} : 51575	0	48.6	0.64	31.8	0.68	73.4	0.70
C_{82}	C_s : 36652	2	118.1	1.25	146.7	0.94	65.1	1.26	C_{84}	C_2 : 50322	1	55.5	1.37	83.1	0.83	68.1	1.23
C_{82}	C_1 : 39656	1	139.0	0.67	147.8	0.56	104.2	0.65	C_{84}	C_1 : 51350	1	59.3	1.16	70.8	0.90	63.0	1.13
C_{82}	C_s : 39713	0	132.1	0.58	118.8	0.49	104.0	0.50	C_{84}	C_s : 51425	1	63.1	0.99	57.0	0.91	58.9	1.01
C_{86}	D_3 : 63761	0	0.0	1.51	12.2	1.13	3.7	1.47	C_{88}	D_2 : 81738	0	0.0	0.97	0.0	0.81	0.0	0.99
C_{86}	C_{2v} : 63751	0	35.7	0.44	28.6	0.53	0.0	0.56	C_{88}	C_s : 81735	0	70.6	0.61	64.5	0.49	55.5	0.74
C_{86}	C_s : 63757	0	56.0	0.68	0.0	0.63	26.1	0.66	C_{88}	C_s : 81734	0	78.6	0.85	60.9	0.53	77.4	0.88
C_{86}	C_1 : 58832	1	71.5	0.87	45.8	0.80	40.8	0.89	C_{88}	C_1 : 81733	0	89.2	0.59	58.0	0.66	91.3	0.62
C_{86}	C_1 : 63755	0	72.6	0.67	33.5	0.68	34.6	0.69	C_{88}	C_1 : 81729	0	89.9	0.36	63.3	0.53	86.9	0.38
C_{86}	C_1 : 63291	1	79.6	1.06	51.3	0.75	54.9	1.05	C_{88}	C_1 : 80982	1	96.8	1.13	57.2	0.93	78.3	1.18
C_{86}	C_2 : 63339	1	94.6	0.92	48.0	0.72	56.2	0.86	C_{88}	C_2 : 81731	0	96.9	0.67	86.1	0.63	86.9	0.76
C_{86}	C_2 : 63229	1	98.3	1.27	87.9	0.97	69.5	1.34	C_{88}	C_1 : 69747	1	101.5	0.97	80.1	0.78	75.5	0.97
C_{86}	C_2 : 63756	0	103.8	0.45	44.9	0.43	84.5	0.42	C_{88}	C_s : 81712	0	103.4	0.51	43.2	0.54	76.1	0.53
C_{86}	C_s : 63750	0	106.7	0.19	80.6	0.30	87.7	0.23	C_{88}	C_1 : 70333	1	105.9	0.85	105.0	0.41	79.3	0.82

Table 4. Relative Energies (ΔE , kJ/mol) and HOMO–LUMO Gaps (gap, eV) of the Most Stable C_{2n}^{6-} and $Y_3N@C_{2n}$ ($2n = 90-98$) Isomers as Computed at the DFT Level

C_{2n}	cage	isomer	C_{2n}^{6-}		C_{2n}	cage	isomer	C_{2n}^{6-}		C_{2n}	cage	isomer	C_{2n}^{6-}		C_{2n}	cage	isomer	C_{2n}^{6-}	
			ΔE	gap				ΔE	gap				ΔE	gap				ΔE	gap
C_{90}	C_2 : 43	0.0	0.83	C_{92}	D_3 : 85	0.0	0.63	C_{94}	C_2 : 121	0.0	1.18	C_{96}	D_2 : 186	0.0	1.06	C_{98}	C_2 : 166	0.0	1.02
C_{90}	C_2 : 44	13.5	0.81	C_{92}	C_1 : 66	22.3	0.81	C_{94}	C_2 : 117	19.2	0.71	C_{96}	C_2 : 158	28.0	0.87	C_{98}	C_1 : 247	16.1	0.99
C_{90}	C_1 : 21	39.2	0.67	C_{92}	T : 86	24.2	1.47	C_{94}	C_2 : 126	36.4	0.92	C_{96}	D_{6d} : 187	54.2	1.50	C_{98}	C_2 : 252	29.8	0.97
C_{90}	C_2 : 42	39.8	0.77	C_{92}	C_2 : 65	28.6	1.06	C_{94}	C_2 : 130	44.1	0.85	C_{96}	C_2 : 157	64.3	0.62	C_{98}	C_2 : 174	41.9	0.87
C_{90}	C_2 : 41	42.2	0.31	C_{92}	C_2 : 64	39.7	0.56	C_{94}	C_1 : 132	50.4	0.47	C_{96}	C_1 : 101	65.2	0.86	C_{98}	C_1 : 175	42.1	0.65
C_{90}	C_2 : 45	83.0	0.46	C_{92}	C_2 : 77	43.7	0.88	C_{94}	C_1 : 129	46.6	0.84	C_{96}	C_2 : 167	65.8	0.91	C_{98}	C_1 : 168	43.3	0.64
C_{90}	C_2 : 10	92.8	0.19	C_{92}	C_2 : 36	50.5	0.58	C_{94}	C_1 : 115	47.3	0.59	C_{96}	C_1 : 159	67.6	0.84	C_{98}	C_2 : 221	47.9	0.57
C_{90}	C_2 : 23	81.3	0.50	C_{92}	C_1 : 44	51.5	0.69	C_{94}	C_1 : 125	49.7	0.62	C_{96}	D_2 : 183	68.1	0.75	C_{98}	C_2 : 246	48.5	0.81
C_{90}	C_2 : 40	79.0	0.27	C_{92}	C_2 : 61	56.5	0.89	C_{94}	C_1 : 54	46.7	0.41	C_{96}	C_1 : 160	80.1	0.46	C_{98}	C_{2v} : 167	48.6	0.56
C_{90}	C_s : 35	105.5	0.45	C_{92}	C_s : 16	61.2	0.35	C_{94}	C_1 : 119	57.2	0.72	C_{96}	C_2 : 55	94.7	0.64	C_{98}	C_1 : 161	51.8	0.86
$Y_3N@C_{2n}$																			
C_{90}	C_2 : 43	8.0	0.64	C_{92}	D_3 : 85	0.0	0.82	C_{94}	C_2 : 121	0.0	1.03	C_{96}	D_2 : 186	0.0	0.97	C_{98}	C_2 : 166	0.0	0.98
C_{90}	C_2 : 44	0.0	0.97	C_{92}	T : 86	60.3	1.34	C_{94}	C_2 : 126	28.6	0.87	C_{96}	C_2 : 158	26.5	0.89	C_{98}	C_1 : 247	33.4	0.73
				C_{92}	C_1 : 66	40.0	0.76					C_{96}	D_{6d} : 187	87.6	1.07	C_{98}	C_2 : 252	27.7	0.81
				C_{92}	C_2 : 65	68.0	0.93												

distorted from an equilateral shape ($Sc-N-Sc$ angles are 150.0° and 105.0° ; see Figure 1). However, these are still the lowest energy isomers, as in all other low-energy C_{70}^{6-} cages either a stronger distortion of the cluster is observed or one of the APPs remains uncoordinated. Finally, the DFT-computed HOMO–LUMO gap and the IR spectra of $Sc_3N@C_{70}$ (C_{2v} : 7854) matched those of the experimentally isolated $Sc_3N@C_{70}$, thus justifying the assignment of the latter to the C_{2v} : 7854 cage isomer.¹¹ Similar to $Y_3N@C_{68}$, the Y_3N cluster is still too large for this cage size, and in $Y_3N@C_{70}$ (C_{2v} : 7854) the cluster is predicted to be pyramidal ($h = 0.340 \text{ \AA}$).

$M_3N@C_{72}$. The isomer D_2 : 10611 with two APPs is found to be the lowest energy isomer of C_{72}^{6-} , while the other

structures are less stable by at least 69 kJ/mol (Table 2). Specifically, the only IPR isomer of C_{72} , D_{6d} : 11190, is 226.2 kJ/mol less stable in the hexaanionic state than D_2 : 10611. The HOMO–LUMO gap of D_2 : 10611, 1.12 eV, is among the largest gaps for the 20 lowest energy isomers of C_{72}^{6-} , and only three other isomers in this set have their HOMO–LUMO gaps higher than 1 eV: C_1 : 10482 (1.01 eV), C_1 : 10468 (1.12 eV), and C_1 : 10774 (1.03 eV).

The stability order of the $Sc_3N@C_{72}$ isomers is drastically different from that of the empty C_{72}^{6-} hexaanions. The most stable isomer has the C_s : 10528 cage and a HOMO–LUMO gap of 0.39 eV. The second and the third most stable isomers are C_{2v} : 11188 ($\Delta E = 21.2$ kJ/mol, gap 0.49 eV) and C_1 : 10482

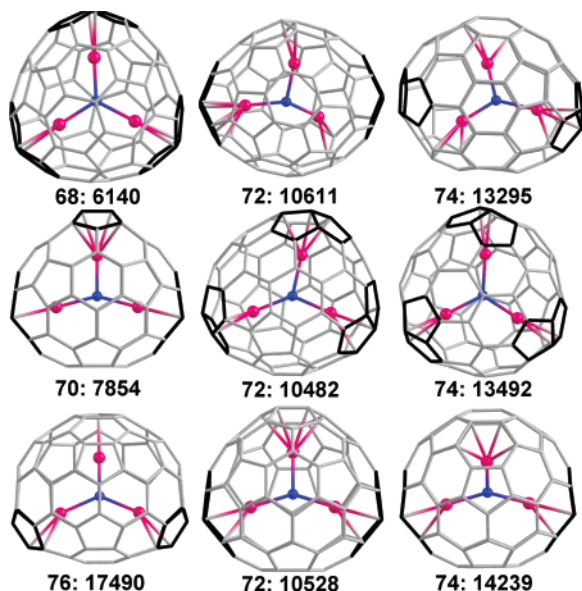


Figure 1. Molecular structures of selected $\text{Sc}_3\text{N}@C_{2n}$ isomers with $2n = 68-76$ (C - gray, N - blue, Sc - pink, APPs are highlighted in black). Sc–C distances shorter than 2.350 Å are shown as bonds.

($\Delta E = 26.7$ kJ/mol, gap 0.98 eV), while the structure with the D_2 : 10611 cage is by 54.6 kJ/mol less stable than the C_s : 10528 isomer and has a gap of 0.89 eV, which is by 0.23 eV smaller than the gap predicted for the same isomer of C_{72}^{6-} . The reason for these changes in the relative stability of the $\text{Sc}_3\text{N}@C_{72}$ isomers becomes obvious when the location of APPs on the cage is analyzed for each structure (Figure 1). The isomer D_2 : 10611 has an elongated shape, and two APPs are located at the poles of the fullerene. Hence, there is no way for Sc_3N to coordinate the two APPs at once, unless the cluster is severely distorted from the equilateral shape, and in the optimized structure of $\text{Sc}_3\text{N}@C_{72}$ (D_2 : 10611) one of the APPs remains uncoordinated. On the contrary, the location of APPs in C_s : 10528, C_{2v} : 11188, and C_1 : 10482 isomers is more favorable for their efficient stabilization by the coordination to Sc atoms. However, even in these most stable isomers the cluster geometry is still significantly distorted from the symmetric configuration. In C_{2v} : 11188 and C_1 : 10482 isomers the cluster is forced to be pyramidal (displacements of nitrogen atom out of the Sc_3 plane are 0.155 and 0.208 Å, respectively); moreover, the cluster is significantly distorted from C_3 symmetry inside C_1 : 10482, two of the Sc–N–Sc angles being 100.8° and 132.5°. The cluster is almost planar ($h = 0.022$ Å) in the C_s : 10528 isomer, but distortion from the equilateral shape is even stronger: one Sc–N–Sc angle is 144.8°, while two others are 107.6°.

For $\text{Y}_3\text{N}@C_{72}$ we have studied the C_s : 10528 isomer because of its highest stability for $\text{Sc}_3\text{N}@C_{72}$ and the C_1 : 10482 and C_1 : 10468 isomers because of the relatively high HOMO–LUMO gaps of these cages in C_{72}^{6-} as well as in $\text{Sc}_3\text{N}@C_{72}$. The stability order is different from that predicted for $\text{Sc}_3\text{N}@C_{72}$. $\text{Y}_3\text{N}@C_{72}$ (C_1 : 10482) is the most stable isomer among the three studied structures. In the C_1 : 10482 and C_s : 10528 isomers the Y_3N cluster is pyramidal ($h = 0.446$ and 0.325 Å, respectively). In $\text{Y}_3\text{N}@C_{72}$ (C_1 : 10468) the cluster is close to planarity ($h = 0.053$ Å) but is severely distorted from the threefold symmetry with two Y–N–Y angles having abnormal values (140.1° and 99.1°). These structural and energetic reasons

clearly indicate why it was not possible to isolate a C_{72} nitride cluster structure in our extended experimental studies.

$\text{M}_3\text{N}@C_{74}$. The correlation between the relative stabilities of $\text{Sc}_3\text{N}@C_{74}$ and C_{74}^{6-} isomers resembles the situation described above for the C_{72} cage (Table 2). The most stable isomer of C_{74}^{6-} , C_2 : 13295, has two APPs which are located almost on the opposite poles of the fullerene. As a result, the encapsulated cluster cannot efficiently stabilize two APPs, leaving one of them uncoordinated (Figure 1). The relative energy of $\text{Sc}_3\text{N}@C_{74}$ (C_2 : 13295) is 18.7 kJ/mol, while the most stable isomer of $\text{Sc}_3\text{N}@C_{74}$ is based on the C_{2v} : 14239 cage (Figure 1), which in the C_{74}^{6-} state is by 87 kJ/mol less stable than C_{74}^{6-} (C_2 : 13295). In $\text{Sc}_3\text{N}@C_{74}$ (C_{2v} : 14239), which obeys C_s symmetry, the cluster is slightly pyramidal ($h = 0.151$ Å) and significantly distorted from the threefold symmetry: one of Sc–N–Sc angles is 146.2°, and two others are 105.9°.

The second most stable isomer of $\text{Sc}_3\text{N}@C_{74}$, C_3 : 13492 (Figure 1), is also based on the relatively unstable cage ($\Delta E = 71.7$ kJ/mol for C_{74}^{6-}). This isomer has three APPs and the largest HOMO–LUMO gap (1.10 eV in C_{74}^{6-} , 1.14 eV in $\text{Sc}_3\text{N}@C_{74}$) among 20 of the most stable cages. The APPs are located around the equator of the cage and closer to one of the poles. The cluster follows the C_3 symmetry of the cage, while the Sc atoms of the Sc_3N cluster are coordinated to APPs and the cluster is pyramidal ($h = 0.329$ Å). Computations of $\text{Y}_3\text{N}@C_{74}$ isomers were performed only for C_2 : 13295, C_3 : 13492, and C_{2v} : 14239 cages. Their relative stability is significantly altered compared to $\text{Sc}_3\text{N}@C_{74}$ isomers: the most stable $\text{Y}_3\text{N}@C_{74}$ isomer is based on the C_3 : 13492 cage, while C_2 : 13295 and C_{2v} : 14239 isomers are 52.1 and 86.8 kJ/mol less stable. The cluster is pyramidal in all optimized $\text{Y}_3\text{N}@C_{74}$ molecules, $h = 0.568$, 0.088, and 0.573 Å in C_3 : 13492, C_2 : 13295, and C_{2v} : 14239 isomers, respectively, and in the latter two isomers it is also significantly distorted similar to the distortion of the Sc_3N cluster in the corresponding $\text{Sc}_3\text{N}@C_{74}$ structures described above. These findings support the fact that an isolation of a stable C_{74} nitride cluster fullerene was not successful up until now.

$\text{M}_3\text{N}@C_{76}$. C_{76} has two IPR isomers. In the hexaanionic form one of them, T_d : 19151, is the third most stable isomer with the relative energy of 20.8 kJ/mol, but it has a very low HOMO–LUMO gap (0.14 eV). Another IPR isomer, D_2 : 19150, has a gap of 0.75 eV and is by 101.0 kJ/mol less stable than the most stable structure, the non-IPR isomer C_s : 17490 with two APPs and an HOMO–LUMO gap of 1.12 eV (Table 3). Significantly, seven structures from the list of ten most stable C_{76}^{6-} isomers have two APPs, two isomers have only one APP, and there are no stable isomers with three APPs.

When Sc_3N is encapsulated inside C_{76} , DFT predicts the most stable isomer to be the T_d : 19151 cage, but this isomer has a small gap (0.16 eV) as in the case of the empty hexaanion C_{76}^{6-} . The second most stable isomer of $\text{Sc}_3\text{N}@C_{76}$ has the C_s : 17490 cage (Figure 1) and an HOMO–LUMO gap of 1.08 eV. Hence this structure might be a suitable candidate for the stable $\text{Sc}_3\text{N}@C_{76}$ clusterfullerene. The cluster inside this cage is planar, although it is distorted from a 3-fold symmetry (Sc–N–Sc angles are 133.3° and 113.1°). These distortions are not as strong as those in the lowest energy isomers of $\text{Sc}_3\text{N}@C_{72}$ and $\text{Sc}_3\text{N}@C_{74}$ clusterfullerenes discussed above. The interesting feature of the cluster geometry in $\text{Sc}_3\text{N}@C_{76}$ (C_s : 17490) is

that two of the Sc–N bonds are rather long (2.113 Å, which may be compared to 2.034 Å in $Sc_3N@C_{80}$ discussed below), while the third bond is very short (1.984 Å, which is much shorter than 1.993 Å in $Sc_3N@C_{68}$ and comparable to one of the Sc–N bonds in $Sc_3N@C_{70}$, 1.987 Å, which is the shortest Sc–N bond predicted by DFT for experimentally isolated Sc_3N clusterfullerenes).

The increase of the cluster size by replacing Sc_3N to Y_3N results in significant changes in the relative stability of different cage isomers. The most stable isomer of $Y_3N@C_{76}$ is C_5 : 17490, while T_{4i} : 19151 is less stable by 37.7 kJ/mol. The reason for such a change in stability may be explained by the different size and shape of the cavity inside the cage, which can be occupied by the cluster. The cage of the T_{4i} : 19151 isomer appears to be too small for the Y_3N cluster, and the latter is significantly pyramidalized ($h = 0.639$ Å). On the contrary, the C_5 : 17490 cage is more suitable for this cluster size, and the degree of the cluster pyramidalization is much lower ($h = 0.255$ Å). For the same reason the isomer C_5 : 18161, being rather unstable as in the case of C_{76}^{6-} and $Sc_3N@C_{76}$ ($\Delta E = 64.7$ and 70.0 kJ/mol, respectively), becomes the second most stable isomer for $Y_3N@C_{76}$ ($\Delta E = 26.1$ kJ/mol). The cage of the C_5 : 18161 isomer has such a size and shape that the encapsulated Y_3N cluster remains planar.

Experimentally $M_3N@C_{76}$ has not been isolated for any homogenous M_3N cluster. $Dy_3N@C_{76}$ was observed by mass spectrometry in the crude product of the synthesis of $Dy_3N@C_{2n}$ clusterfullerenes,²¹ but its amount was not sufficient yet for an isolation of this compound and for its spectroscopic characterization. Results of this work show that this clusterfullerene most probably has the C_5 : 17490 cage isomer. The asymmetric cluster configuration in this structure seems to be favorable for the formation of the mixed $Sc_xM_{3-x}N@C_{76}$ clusterfullerenes.

$M_3N@C_{78}$. The study of C_{78}^{6-} and $M_3N@C_{78}$ ($M = Sc, Y, La, Lu$) isomers was reported by us recently.³⁹ In brief, the most stable C_{78}^{6-} isomer is IPR D_{3h} : 24109 (gap 1.21 eV), which is followed by the non-IPR isomer C_2 : 22010 ($\Delta E = 59.1$ kJ/mol, gap 1.60 eV) with two APPs. The relative stability order found for C_{78}^{6-} was preserved for the $Sc_3N@C_{78}$ isomers in agreement with experimental isolation of $Sc_3N@C_{78}$ with the IPR D_{3h} : 24109 cage.⁷ However, with the larger Y_3N cluster inside, the C_2 : 22010 cage (Figure 2) becomes the most stable one, being by 83.6 kJ/mol lower in energy than the D_{3h} : 24109 isomer. When switching from Sc_3N to Y_3N , a dramatic change in the stability of the cage isomers can be explained by an unsuitable size of the D_{3h} : 24109 cage, which forces the encapsulated Y_3N cluster to be pyramidal ($h = 0.554$ Å). On the contrary, the Y_3N cluster has enough space to be planar inside the C_2 : 22010 isomer. For the same reason, two other non-IPR isomers of $Y_3N@C_{78}$, C_1 : 21975 ($\Delta E = 65.1$ kJ/mol, gap 1.21 eV) and C_1 : 22646 ($\Delta E = 67.5$ kJ/mol, gap 1.26 eV), are also more stable than the D_{3h} : 24109 isomer of $Y_3N@C_{78}$.

Experimental spectroscopic studies of the recently isolated $Tm_3N@C_{78}$ ¹³ and the major isomer of $Dy_3N@C_{78}$ ³⁹ have shown that their carbon cages are different from that of $Sc_3N@C_{78}$. DFT-computed vibrational spectrum of $Y_3N@C_{78}$ (C_2 : 22010) showed perfect agreement to the experimental spectra of $Dy_3N@C_{78}$ and $Tm_3N@C_{78}$ hence proving the assignment of

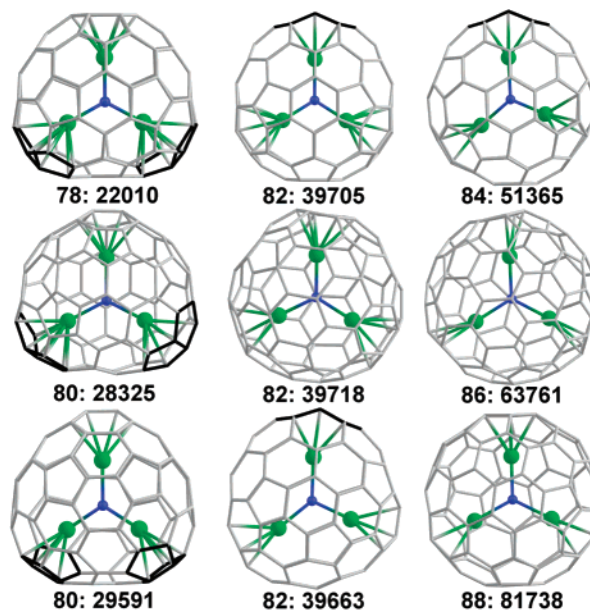


Figure 2. Molecular structures of selected $Y_3N@C_{2n}$ isomers with $2n = 78-86$ (C - gray, N - blue, Y - green, APPs are highlighted in black). Y–C distances shorter than 2.550 Å are shown as bonds.

the cage structure of these clusterfullerenes to the C_2 : 22010 cage in agreement with the DFT-predicted higher stability of the latter.³⁹

$M_3N@C_{80}$. The three lowest energy isomers of C_{80}^{6-} are IPR structures: the most stable one, I_h : 31924, is 88.2 kJ/mol more stable than D_{5h} : 31923, which in due turn is by 108.5 kJ/mol more stable than the following C_{2v} : 31922 isomer (Table 3). The fourth isomer, the non-IPR C_1 : 31891 with one APP, is by 247 kJ/mol less stable than I_h : 31924. Besides a remarkable stability, the two first isomers also have a large HOMO–LUMO gap (1.83 and 1.51 eV, respectively) and can therefore be regarded as suitable cages for the formation of nitride clusterfullerenes. Indeed, $M_3N@C_{80}$ based on I_h : 31924 and D_{5h} : 31923 cages (also referred in the literature as isomers I and II) are the most abundant clusterfullerenes for any M.

The order of isomer stability for $Sc_3N@C_{80}$ follows that for C_{80}^{6-} , albeit the energy difference between the three first structures and the others are smaller than those for empty cages. The difference between $Sc_3N@C_{80}$ (I_h : 31924) and $Sc_3N@C_{80}$ (D_{5h} : 31924) is 67.0 kJ/mol, and the C_1 : 31922 isomer is by 166.5 kJ/mol less stable than I_h : 31924 (*versus* 246.9 kJ/mol for empty C_{80}^{6-}). For $Y_3N@C_{80}$ the energy gap between IPR and non-IPR structures is further diminished. The isomers I_h : 31924 and D_{5h} : 31924 are still the most stable ones, but the third most stable isomer is C_1 : 28325 (Figure 2), which has two APPs and a gap of 1.24 eV. While this isomer is less stable than I_h : 31924 by 262.8 and 227.4 kJ/mol for C_{80}^{6-} and $Sc_3N@C_{80}$, respectively, for $Y_3N@C_{80}$ its relative energy is only 90.0 kJ/mol, being slightly lower than that for the IPR C_{2v} : 31922 (the third isomer in stability order for C_{80}^{6-} and $Sc_3N@C_{80}$). In agreement with the results of these calculations, only two isomers are known for $Sc_3N@C_{80}$, but for $Dy_3N@C_{80}$ Yang et al.¹⁵ have recently reported the isolation of the third isomer, albeit in a much smaller yield. It was found that the onset in the absorption spectrum of $Dy_3N@C_{80}$ (III) is at 1.31 eV, close to that of $Dy_3N@C_{80}$ (II), and based on the

results of our calculations the non-IPR C_1 : 28325 or C_2 : 29591 cage isomers (Figure 2) are energetically favored for $Dy_3N@C_{80}$ (III).

A significant stabilization of the other cage isomers with respect to I_h : 31924 and D_{5h} : 31923 cages for $Y_3N@C_{80}$ may be understood if the cage and the cluster size are analyzed. The difference between the isomers is most apparent when Y–N distances are compared, namely, 2.060 Å in I_h : 31924 (the cluster has C_3 symmetry in this isomer), 2.104/2.148/2.153 Å in C_1 : 28325, and 2.111/2.146/2.146 Å in C_2 : 29591. It appears that the cluster is constrained in I_h : 31924 and has more space in the other isomers, which results in a lengthening of the Y–N bonds by 0.04–0.09 Å in C_1 : 28325 or C_2 : 29591 isomers of $Y_3N@C_{80}$ compared to I_h : 31924. Noteworthy, Y_3N is slightly pyramidal in the pyrrolidine adduct of $Y_3N@C_{80}$,⁴⁷ and Dy_3N , which has a similar size to Y_3N , is the largest M_3N cluster known to be nearly planar inside C_{80} (I_h : 31924).²⁵ Hence, it may be expected that the strain caused by the insufficient inner size of the cage for the M_3N cluster is rather high for the I_h : 31924 cage, and the larger Tb_3N and Gd_3N clusters are forced to be pyramidal in $M_3N@C_{80}$ (I_h : 31924) as shown by single-crystal X-ray diffraction studies.^{17,23}

$M_3N@C_{82}$. Among the ten most stable isomers of C_{82}^{6-} , five obey the IPR, including the most stable C_{2v} : 39718 isomer (Table 3). However, only non-IPR isomers have HOMO–LUMO gaps above 1 eV, namely C_{2v} : 39705 ($\Delta E = 30.1$ kJ/mol, gap 1.32 eV), C_s : 39663 ($\Delta E = 61.2$ kJ/mol, gap 1.42 eV), and C_2 : 36652 ($\Delta E = 118.1$ kJ/mol, gap 1.25 eV). The stability order of these isomers found for C_{82}^{6-} is mostly preserved for $Sc_3N@C_{82}$; however the C_{2v} : 39705 isomer is stabilized relative to the C_{2v} : 39718 cage ($\Delta E = 17.7$ kJ/mol versus 30.1 kJ/mol for the C_{82}^{6-}). The HOMO–LUMO gaps of the C_s : 39663 and C_2 : 36652 isomers of $Sc_3N@C_{82}$ are significantly smaller than those in C_{82}^{6-} which probably points to the less effective cluster–cage interactions than those in $Sc_3N@C_{82}$ (C_{2v} : 39705) or in the smaller cages described above, in which the gaps of $Sc_3N@C_{2n}$ are usually similar to those of C_{2n}^{6-} . Thus, for $Sc_3N@C_{82}$, if isolated at all, the C_{2v} : 39705 isomer may be suggested as the most probable structure based on its thermodynamic stability and large HOMO–LUMO gap.

The stability order of $Y_3N@C_{82}$ isomers is significantly altered compared to $Sc_3N@C_{82}$ or C_{82}^{6-} . The most stable isomer of $Y_3N@C_{82}$ is C_{2v} : 39705 (gap 1.32 eV), followed by C_{2v} : 39718 ($\Delta E = 29.6$ kJ/mol, gap 0.84 eV) and the almost isoenergetic C_s : 39663 ($\Delta E = 32.6$ kJ/mol, gap 1.51 eV) (Figure 2). Note that contrary to $Sc_3N@C_{82}$, the band gaps of the C_s : 39663 and C_2 : 36652 isomers of $Y_3N@C_{82}$ are similar to those for C_{82}^{6-} . The analysis of the DFT optimized molecular structures of these isomers in comparison to their $Sc_3N@C_{82}$ analogues has shown that in the latter the Sc_3N cluster is displaced toward one side of the cage, while Y_3N is in a center position inside the fullerene. As a result, Sc and Y atoms are coordinated to different fragments of the cage, which apparently results in a different efficiency of the cluster–cage interactions.

$M_3N@C_{82}$ ($M = Tm$ and Dy) were isolated experimentally,^{13,21} and their UV–vis absorption spectra are shown to be very similar pointing to the identical cage structures of these clusterfullerenes. However, structural studies of these com-

pounds have not been reported yet. Both compounds have large optical gaps, exceeding 1.3 eV. Based on the results of this work, the isomers C_{2v} : 39705 and C_s : 39663 can be proposed as the most probable cage structures because of their high thermodynamic stability and the large HOMO–LUMO gap. Further spectroscopic or structural studies are required to favor one of these structures.

$M_3N@C_{84}$. The list of ten most stable isomers of C_{84}^{6-} includes six IPR isomers and four isomers with one APP (Table 3). As in the case of C_{82}^{6-} , the non-IPR isomers have higher HOMO–LUMO gaps; specifically, only the non-IPR isomers have HOMO–LUMO gaps higher than 1 eV, while the HOMO–LUMO gaps for IPR structures do not exceed 0.8 eV. The two most stable isomers, IPR D_2 : 51589 and non-IPR C_s : 51365 (Figure 2), are essentially isoenergetic; however the much higher HOMO–LUMO gap of the non-IPR cage (1.34 eV versus 0.80 eV for IPR isomer) makes it a preferable candidate for the both thermodynamically and kinetically stable $M_3N@C_{84}$. For the $Sc_3N@C_{84}$ and $Y_3N@C_{84}$ series, this isomer is the most stable one, and its stabilization relative to the D_2 : 51589 isomer in the $C_{84}^{6-}-Sc_3N@C_{84}-Y_3N@C_{84}$ sequence can be pointed out (Table 3). The HOMO–LUMO gaps of the C_s : 51365 and the non-IPR C_1 : 51350 and C_2 : 50322 isomers of $Sc_3N@C_{84}$ are significantly smaller than those in the corresponding C_{84}^{6-} or $Y_3N@C_{84}$ isomers. The analysis of their DFT optimized structures shows that, similar to the case of $M_3N@C_{82}$ discussed above, these fullerenes are too large for a Sc_3N cluster, and the latter has to be displaced to one of the parts of the fullerene cages to establish an interaction with the cage. On the contrary, the Y_3N cluster resides in the center of the $Y_3N@C_{84}$ cages, and hence the bonding sites for Sc are different from those of Y.

Experimentally $M_3N@C_{84}$ was isolated for $M = Tm$,¹³ Dy ,²¹ and Tb .²² For $Tb_3N@C_{84}$ and $Dy_3N@C_{84}$ the second, less abundant isomer was also isolated in small amounts. The results of this work are in perfect agreement with X-ray crystallographic studies of the major isomer of $Tb_3N@C_{84}$, which is shown to have a C_s : 51365 cage.²² Reliable spectroscopic and/or structural data are not available yet for the minor isomer of $M_3N@C_{84}$, but our results show that it might be based on the IPR D_2 : 51589 cage (and in this case it should have a rather small band gap and a low kinetic stability) or on one of the C_s : 51425, C_1 : 51350, or C_2 : 50322 isomers, which are almost isoenergetic and have band gaps of 1.01, 1.13, and 1.23 eV, respectively.

$M_3N@C_{86}$. The most stable isomer of C_{86}^{6-} , D_3 : 63761, obeys the IPR and has the largest HOMO–LUMO gap, 1.51 eV, among the 10 lowest energy isomers of C_{86}^{6-} . As in the case of C_{84}^{6-} , the list of the most stable structures includes six IPR and four non-IPR isomers, all of the latter with one APP (Table 3). For $Sc_3N@C_{86}$, the isomer D_3 : 63761 is by 12.2 kJ/mol less stable than C_s : 63757, and it has a smaller HOMO–LUMO gap than the empty C_{86}^{6-} for the same reason as discussed above for $Sc_3N@C_{82}$ and $Sc_3N@C_{84}$ isomers. For $Y_3N@C_{86}$, the isomer D_3 : 63761 (Figure 2) is also the second most stable one, while the isomer C_{2v} : 63751 is by 3.7 kJ/mol lower in energy. However, the latter has a small HOMO–LUMO gap (0.56 eV), and hence it is expected to be kinetically unstable. On the contrary, the isomer $Y_3N@C_{86}$ (D_3 : 63761) has a gap of 1.47 eV and should thus be both thermodynamically and kinetically stable. This finding agrees well with X-ray

(47) Echegoyen, L.; Chancellor, J.; Cardona, C. M.; Elliott, B.; Rivera, J.; Olmstead, M. M.; Balch, A. L. *Chem. Commun.* **2006**, 2653–2655.

crystallographic studies of $Tb_3N@C_{86}$, which was proved to have a D_3 : 63761 cage.²³ The same cage structure may be suggested for $Tm_3N@C_{86}$ ¹³ and $Dy_3N@C_{86}$.²¹

$M_3N@C_{88}$. The most stable isomer of C_{88}^{6-} , the IPR D_2 : 81738 cage, is separated from all other structures by a gap of 70.6 kJ/mol (Table 3). Hence, this isomer appears to be the most stable for $Sc_3N@C_{88}$ and $Y_3N@C_{88}$ (Figure 2). The most stable non-IPR cage, C_1 : 80982, is by 96.8, 57.2, and 78.3 kJ/mol less stable for C_{88}^{6-} , $Sc_3N@C_{88}$, and $Y_3N@C_{88}$, respectively. The HOMO–LUMO gap of 0.99 eV calculated for $Y_3N@C_{88}$ (D_2 : 81738) suggests that this clusterfullerene might be kinetically stable. The thermodynamic and kinetic stability predicted for $Y_3N@C_{88}$ (D_2 : 81738) agrees well with the result of X-ray crystallographic studies of $Tb_3N@C_{88}$, which is shown to have the D_2 : 81738 cage isomer.²³

$M_3N@C_{2n}$ ($2n = 90-98$). The studies of the $C_{82}^{6-}-C_{88}^{6-}$ isomers have shown that the relative stability of non-IPR isomers diminishes in comparison to the IPR structures with the increase of the cage size. This is manifested in the decrease of the number of non-IPR isomers present in the list of the 10 most stable isomers and also in the increase of the relative energy of the most stable non-IPR isomers with respect to the most stable IPR isomers (see Discussion section below). We suggest that this trend is valid for the larger fullerenes as well, and hence calculations of the $C_{90}^{6-}-C_{98}^{6-}$ fullerenes were performed only for IPR cages (Table 4). Besides, computations for $Y_3N@C_{2n}$ ($2n = 90-98$) isomers were limited to the cages with the highest stability and/or the largest HOMO–LUMO gap. Calculations for $Sc_3N@C_{2n}$ ($2n = 90-98$) have no practical purposes as these clusterfullerenes have never been observed experimentally, and besides, the results for the C_{2n} ($2n \geq 82$) show that Sc_3N cannot effectively interact with larger cages. However, for the sake of comparison and discussion of the general trends (see below), we performed DFT optimizations for the $Sc_3N@C_{2n}$ isomers corresponding to the most stable $Y_3N@C_{2n}$ structures.

The two lowest energy isomers of C_{90}^{6-} , C_2 : 43 and C_2 : 44, have the largest HOMO–LUMO gaps (0.83 and 0.81 eV, respectively) among the 10 most stable isomers and are shown to be almost isoenergetic (C_2 : 44 is less stable by 13.5 kJ/mol). For $Y_3N@C_{90}$, the isomer C_2 : 44 (Figure 3) is 8.0 kJ/mol more stable and, more importantly, has a considerably larger HOMO–LUMO gap than the C_2 : 43 isomer (0.97 eV *versus* 0.64 eV, respectively). Hence, C_2 : 44 is suggested as the most probable cage isomer for the experimentally observed $Dy_3N@C_{90}$.²¹

The most stable isomer of C_{92}^{6-} is D_3 : 85, but this structure has a rather small HOMO–LUMO gap (0.63 eV), and the three following higher energy isomers with higher HOMO–LUMO gaps, C_1 : 66 ($\Delta E = 22.3$ kJ/mol, gap 0.81 eV), T : 86 ($\Delta E = 24.2$ kJ/mol, gap 1.47 eV), and C_2 : 65 ($\Delta E = 28.6$ kJ/mol, gap 1.06 eV) may be also suggested as probable hosts for M_3N clusters. For $Y_3N@C_{92}$, the isomer D_3 : 85 (Figure 3) is significantly stabilized compared to the other structures, being at least by 60 kJ/mol lower in energy than the others. Hence, the D_3 : 85 cage can be suggested for the experimentally observed $Dy_3N@C_{92}$,²¹ but the other isomers (C_1 : 66, C_2 : 65, and especially T : 86) cannot be excluded because of the small HOMO–LUMO gap of D_3 : 85, which may result in its low kinetic stability.

The most stable isomer of C_{94}^{6-} is C_2 : 121, and this structure also has the largest HOMO–LUMO gap (1.18 eV) among the

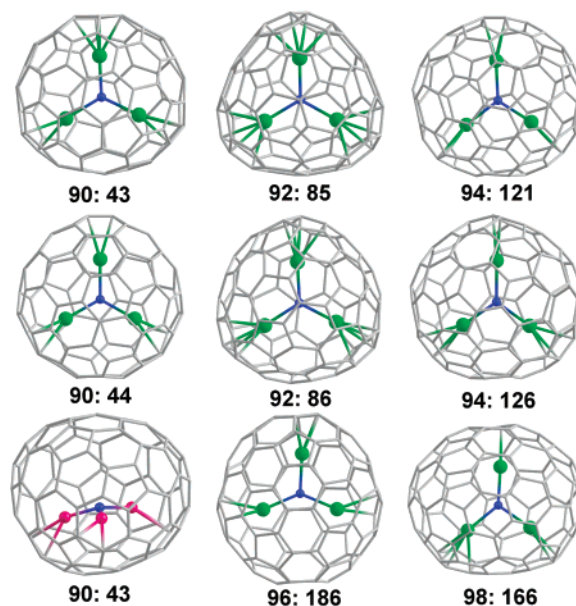


Figure 3. Molecular structures of selected $Y_3N@C_{2n}$ isomers with $2n = 90-98$ (C - gray, N - blue, Sc - pink, Y - green). $Sc_3N@C_{90}$ (C_2 : 43) is also shown for comparison. Y–C distances shorter than 2.580 Å and Sc–C distances shorter than 2.350 Å are shown as bonds.

10 lowest energy isomers. Calculations for $Y_3N@C_{94}$ were performed only for this structure and for the C_2 : 126 isomer, which is the third most stable isomer ($\Delta E = 36.4$ kJ/mol) and has a comparably large HOMO–LUMO gap (0.93 eV). $Y_3N@C_{94}$ (C_2 : 121) (Figure 3) is found to be by 28.6 kJ/mol more stable than the isomer based on the C_2 : 126 cage, and the HOMO–LUMO gap of the former, 1.03 eV, suggests that this structure most probably corresponds to the experimentally observed $Dy_3N@C_{94}$.²¹

The most stable isomer of C_{96}^{6-} is D_2 : 186 (gap 1.06 eV) followed by C_2 : 158 ($\Delta E = 28.0$, gap 0.88 eV) and D_{6d} : 187 ($\Delta E = 54.2$ kJ/mol, gap = 1.50 eV). Only these three structures were further considered for $Y_3N@C_{96}$ as other isomers are less stable and have small HOMO–LUMO gaps (less than 1 eV). It is found that $Y_3N@C_{96}$ (D_2 : 186) (Figure 3) is the lowest energy isomer as in the case of empty cages, and its HOMO–LUMO gap (0.97 eV) is rather close to that of C_{96}^{6-} . The larger gap, 1.07 eV, is predicted for $Y_3N@C_{96}$ (D_{6d} : 187), but this isomer is thermodynamically less stable ($\Delta E = 87.6$ kJ/mol). Moreover, a significant decrease of the gap after encapsulation of the Y_3N cluster points to the ineffective cluster–cage interactions in this cage. Finally, $Y_3N@C_{96}$ (C_2 : 158) is less stable than D_2 : 186 by 26.6 kJ/mol and has a small HOMO–LUMO gap (0.59 eV). Thus, the experimentally observed $Dy_3N@C_{96}$ ²¹ most probably has the D_2 : 186 cage structure.

The lowest energy isomer of C_{98}^{6-} is C_2 : 166, and this structure also has the largest HOMO–LUMO gap among the 10 most stable isomers of C_{98}^{6-} . Thus, calculations for $Y_3N@C_{98}$ isomers were performed for C_2 : 166 (Figure 3) and also for the second and third most stable isomers of C_{98}^{6-} , C_1 : 247 ($\Delta E = 16.1$ kJ/mol, gap 0.99 eV) and C_2 : 252 ($\Delta E = 29.8$ kJ/mol, gap 0.97 eV). The higher energy isomers of C_{98}^{6-} have smaller HOMO–LUMO gaps (less than 0.87 eV) and were not considered for $Y_3N@C_{98}$. The isomer C_2 : 166 is also the most stable for $Y_3N@C_{98}$ and has an HOMO–LUMO gap of 0.98 eV. Cluster–cage interactions in the C_1 : 247 and C_2 : 252 isomers are less effective, which results in their lower thermo-

Table 5. Relative Energies (ΔE , kJ/mol) and HOMO–LUMO Gaps (gap, eV) for Selected $\text{Sc}_2@C_{76}$ Isomers as Computed at the DFT Level

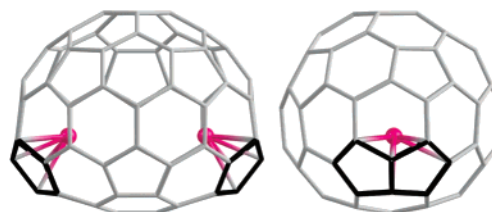
cage isomer	C_{76}^{6-}		$\text{Sc}_2@C_{76}$	
	ΔE	gap	ΔE	gap
C_s : 17490	0.0	1.12	0.0	0.72
C_2 : 17765	55.8	1.37	74.7	0.79
C_2 : 17512	60.1	1.14	51.2	0.91
C_2 : 18161	64.7	1.12	88.6	0.51
D_2 : 19150	101.0	0.75	122.8	0.65

dynamic stability and significant decrease of the HOMO–LUMO gap as compared to the empty cages. Thus, C_2 : 166 is considered to be the most probable cage isomer of $\text{Dy}_3\text{N}@C_{98}$.²¹

Discussion

Correlation of Calculated Values with the Experimental Data and Assignment of New Cages. The methodology adopted in this work, i.e., prescreening of thousands of C_{2n}^{6-} isomers at the AM1 level followed by DFT calculations of the lowest energy cages, enabled us to determine the most stable isomers of $\text{Sc}_3\text{N}@C_{2n}$ and $\text{Y}_3\text{N}@C_{2n}$ in a wide range of cage sizes. More importantly, it appears that the most stable isomers found in this work are those which were confirmed experimentally, at least for $\text{Sc}_3\text{N}@C_{68}$,⁶ $\text{Sc}_3\text{N}@C_{78}$,⁷ $\text{M}_3\text{N}@C_{80}$ (I_h),^{24,25,47} $\text{M}_3\text{N}@C_{80}$ (D_{5h}),^{10,23} $\text{Tb}_3\text{N}@C_{84}$,²² $\text{Tb}_3\text{N}@C_{86}$,²³ and $\text{Tb}_3\text{N}@C_{88}$,²³ characterized by single-crystal X-ray diffraction, and for $\text{Sc}_3\text{N}@C_{70}$ and $\text{M}_3\text{N}@C_{78}$, for which the structures are elucidated based on the DFT calculations and vibrational spectroscopy.^{11,39} If there are two or more isomers of the same composition ($\text{M}_3\text{N}@C_{80}$, $\text{M}_3\text{N}@C_{78}$, $\text{M}_3\text{N}@C_{84}$), the most abundant structures were predicted in this work to be more stable. It should be emphasized that our results are obtained from the first principles, without the use of any preliminary information such as cage symmetry. The only assumption used was that three or more adjacent pentagons in the fullerene cage could be avoided. On the one hand, our findings confirm the reliability of the PBE/TZ2P method for the prediction of the relative stabilities of nitride clusterfullerenes. On the other hand, though the conditions at which fullerenes are formed can hardly be described by a chemical equilibrium, our results demonstrate that the products are preferably formed under thermodynamic stability control. Hence, in the absence of unambiguous structural information on the nitride clusterfullerenes from experimental studies, the determination of the most stable isomers by DFT computations may be considered as a reasonable and reliable alternative to the X-ray crystallographic studies, especially if supported by spectroscopic information such as optical band gap and vibrational spectra. Specifically, results of this work may be used for a tentative structural assignment of those structures, which cannot be characterized by X-ray diffraction at this time.

As the calculations are performed under the assumption that the stability of $\text{M}_3\text{N}@C_{2n}$ correlates with that of C_{2n}^{6-} , these results can be used for the assignment of the cage isomers of $\text{M}_2@C_{2n}$ endohedral fullerenes, where M is a trivalent metal. Moreover, even a better correlation between the stability of C_{2n}^{6-} and $\text{M}_2@C_{2n}$ is expected because such a factor like the cage dimensions (see discussion below), which can be definitive for $\text{M}_3\text{N}@C_{2n}$ isomers, cannot play an important role for dimetallofullerenes. For instance, $\text{La}_2@C_{72}$ is known to have

**Figure 4.** Molecular structure of the lowest energy isomer of $\text{Sc}_2@C_{76}$ (C_s : 17490). Adjacent pentagons are highlighted in black; Sc–C distances shorter than 2.350 Å are shown as bonds. DFT-optimized Sc–Sc distance in this structure is 4.876 Å. Hessian calculations confirmed that this structure is the energy minimum (i.e., it has no imaginary frequencies).

D_2 symmetry from the ^{13}C NMR spectra,³⁰ and recently Slanina et al.⁴⁸ performed a series of DFT calculations for isomers of C_{72}^{6-} with D_2 or higher symmetry and found that the most stable isomer is based on cage D_2 : 10611. Our calculations of the C_{72} hexaanions (Table 2), which were not limited to D_2 isomers, also predict this isomer to be the most stable one.

$\text{Sc}_2@C_{76}$ isolated by Wang et al.⁴⁹ was found to have 35 ^{13}C NMR lines, three of which had double intensity. Considering only IPR isomers, it was supposed that the molecule was based on the D_2 : 19150 isomer, and lower symmetry determined by NMR spectroscopy was due to the presence of two isomers with the same carbon cage but different position of Sc atoms. The results of this work show that D_2 : 19150 is unstable in the hexaanionic state, and the formation of $\text{Sc}_2@C_{76}$ based on the C_s : 17490 cage might be expected. Though this isomer should produce a somewhat different ^{13}C NMR pattern (6 single intensity and 35 double intensity peaks), it cannot be excluded by experimental data because of a low signal-to-noise ratio and the coincidence of some peaks. To validate this assignment we have performed calculations for a series of $\text{Sc}_2@C_{76}$ isomers based on C_s : 17490, C_2 : 17765, C_2 : 17765, C_2 : 17512, C_2 : 18161, and D_2 : 19150 cages, chosen from the lowest energy C_{76}^{6-} isomers because of their compatibility with the ^{13}C NMR data. The relative energies are listed in Table 5. $\text{Sc}_2@C_{76}$ (C_s : 17490) (Figure 4) is indeed the lowest energy isomer, being by 50–90 kJ/mol more stable than the other C_2 -symmetric structures, while the D_2 : 19150 isomer is at least by 141 kJ/mol less stable. Interestingly, the band gap of $\text{Sc}_2@C_{76}$ (C_s : 17490) is only 0.72 eV, which is by 0.40 eV smaller than the value of 1.12 eV predicted for $\text{Sc}_3\text{N}@C_{76}$ (C_s : 17490). Smaller band gaps were also observed for $\text{La}_2@C_{78}$ ⁵⁰ (ca 1.00 eV based on the onset value) and $\text{La}_2@C_{80}$ ¹² (1.41 eV) as opposed to $\text{Sc}_3\text{N}@C_{78}$ ³⁴ (1.41 eV) and $\text{Sc}_3\text{N}@C_{80}$ ¹² (1.69 eV), though these endohedral fullerenes are based on the same cage isomers of C_{78} and C_{80} , respectively. The DFT predicted value agrees well with the optical band gap 0.94 eV determined in the experimental absorption spectrum of $\text{Sc}_2@C_{76}$ (note that the method used systematically underestimates band gaps of endohedral fullerenes by ca. 0.2–0.3 eV). Thus, the reassignment of $\text{Sc}_2@C_{76}$ to the non-IPR C_s : 17490 cage is proposed as a result of this work.

Stability of the Cage Isomers on the per-Atomic Basis.

The broad range of the fullerene sizes studied in this work

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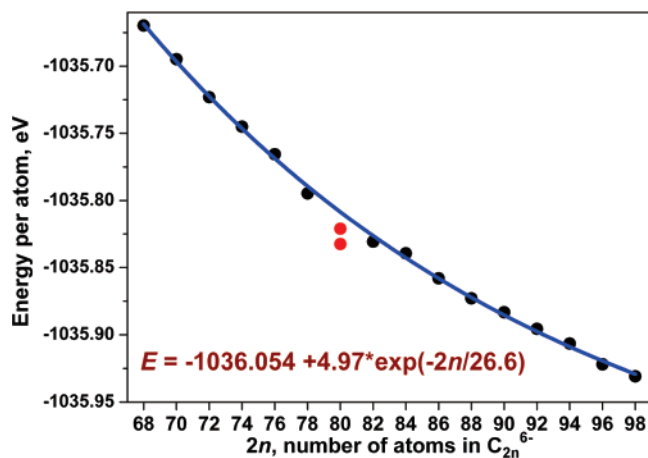


Figure 5. Normalized energies of the most stable C_{2n}^{6-} isomers (black dots) and their fit with the exponential decay function (blue line). Normalized energies for $C_{80}^{6-} I_h$: 31924 and D_{5h} : 31923 isomers are shown as red dots.

enabled us to follow the general trends in their stabilities. To compare the energies of the fullerenes of different sizes, the absolute energies were normalized to the number of atoms in the given fullerene. Figure 5 plots the normalized energies of the most stable C_{2n}^{6-} isomers versus the number of atoms. The smooth decrease of the energy is observed, which can be perfectly fitted by an exponential decay (Figure 5). This trend can be explained by a reinforcing combination of two factors: (i) the decrease of the curvature of the cage with the increase of the cage size, which decreases the strain and hence increases the stability on the per-atomic basis, and (ii) the increase of the cage size decreases the on-site Coulomb repulsions of six surplus electrons in C_{2n}^{6-} . However, deviations of 0.013 and 0.024 eV from the exponential function for $C_{80}^{6-} I_h$: 31924 and $C_{80}^{6-} D_{5h}$: 31923 isomers are obvious; in other words, these isomers are by 98 and 185 kJ/mol more stable than they might be if they were like all other fullerenes (those which obey the smooth decay in the normalized energy). The enhanced stability of the two C_{80}^{6-} isomers explains the increased yield of $M_3N@C_{80}$ compared to all other cage sizes (for instance, $Dy_3N@C_{80} I_h$: 31924 and $Dy_3N@C_{80} D_{5h}$: 31923) constitute ca. 70 and 10 mol %, respectively, of the whole $Dy_3N@C_{2n}$ mixture obtained in the synthesis).²¹ $Sc_3N@C_{72}$ and $Sc_3N@C_{74}$ may be used as an example of the opposite situation: the cages, which correspond to the most stable isomers of these clusterfullerenes, are relatively unstable in the C_{2n}^{6-} form (77.3 and 86.9 kJ/mol, respectively, above the isomers for which the normalized energy lies on the line in Figure 5), and this might be one of the reasons why $Sc_3N@C_{72}$ and $Sc_3N@C_{74}$ are not formed in the arc burning in noticeable amounts.

Thus, not only the isomeric structure of the clusterfullerenes correlates with the DFT-predicted relative stability of the isomers, but also the experimental yields of $M_3N@C_{2n}$ correlate with the stability of C_{2n}^{6-} cage on a per-atomic basis. The cage should be stable enough to favor the formation of the clusterfullerenes, and if its normalized energy is significantly higher than the fitting curve in Figure 5, clusterfullerenes may not be formed at all.

Isolated Pentagon Rule and Cage Size. The specific feature of the $M_3N@C_{2n}$ fullerenes and the C_{2n}^{6-} hexaanions is that the non-IPR isomers can compete in stability with the IPR structures, and in many cases non-IPR fullerenes are even more

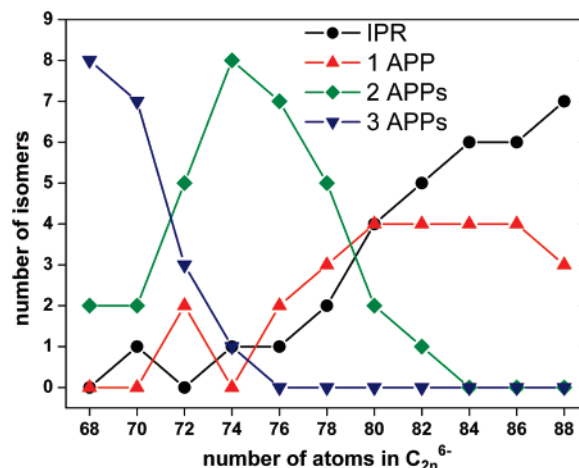


Figure 6. Number of isomers with given number of APPs among the 10 lowest energy C_{2n}^{6-} isomers plotted as a function of $2n$. The total numbers of IPR isomers available for $C_{68}-C_{88}$ are listed in Table 1.

stable than the IPR ones (see Tables 2–4). In fact, a fairly systematic correlation between the relative stability of non-IPR isomers and the cage size can be found. Figure 6 plots the number of IPR isomers and the isomers with one, two, or three APPs among the 10 lowest energy isomers of C_{2n}^{6-} for each cage size *versus* the number of atoms in the fullerene (note, that there are no isomers with four or more APPs among the lowest energy structures for any cage size studied). It is obvious that for small fullerenes (C_{68}, C_{70}) the isomers with three APPs are dominating, but starting from C_{76}^{6-} there are no such isomers among the most stable structures. The isomers with two APPs are dominating for $C_{72}^{6-}-C_{78}^{6-}$, but not for larger cages. Finally, the highest number of isomers with one APP can be found for $C_{80}^{6-}-C_{86}^{6-}$. Significantly, the number of IPR isomers among the lowest energy structures is increasing with the cage size. Moreover, the relative energies of the most stable IPR and non-IPR isomers also follow a similar trend: the non-IPR isomers become less and less stable as the fullerene size increases (see Tables 2–4), and starting from C_{86}^{6-} the non-IPR isomers cannot compete in stability with the IPR ones (this is also true for C_{80}^{6-} , but in this case it happens because of the unusually high stability of I_h : 31924 and D_{5h} : 31923 isomers). Hence, the formation of non-IPR endohedral fullerenes for larger cages is highly unlikely.

It should be noted that the isolated pentagon rule, which disfavors fullerene isomers with edge-sharing pentagons due to an increased local strain for the carbon atoms on the pentagon–pentagon edges, is justified for the uncharged carbon cages with the amount of π -electrons coinciding with the amount of carbon atoms.⁴⁶ The result of the 6-fold electron transfer to the fullerene may be formally conceived as a change of the hybridization state of six carbon atoms from sp^2 to sp^3 (of course, it should not be taken literally because the charge is often delocalized over the cage, but still this assumption appears to be instructive). As the pentagon adjacencies may be stabilized by the change of the hybridization of the carbon atoms in pentagon/pentagon junctions to the $C(sp^3)$ state, which can be exemplified by the isolation of the stable $C_{50}Cl_{10}$ ⁵¹ or $C_{64}H_4$ ⁵²

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non-IPR fullerenes, one may conceive that the 6-fold electron transfer to the fullerene can stabilize up to three APPs. This reasoning agrees with the fact that the C_{2n}^{6-} isomers with more than three APPs were not found among the lowest energy structures. However, the influence of the 6-fold charging of the fullerene should be diminished with the growth of the cage size, and hence its stabilizing role for the pentagon adjacencies is leveled down for larger fullerenes. With the increase of the cage size a more uniform distribution of the pentagon-induced strain over the fullerene is possible, and hence, localization of such a strain in pentagon adjacencies should become more unfavorable than that for the smaller cages.

Stability of IPR Isomers. The exclusive stability of the I_h : 31924 and D_{5h} : 31923 isomers of C_{80}^{6-} discussed above may be understood recalling their hexagon indices, defined by Raghavachari⁵³ to quantify the distribution of pentagon-induced curvature in IPR fullerenes. According to the definition, the neighbor index of each hexagon is the number of hexagons to which it is adjacent, and every fullerene isomer can be characterized by a set of indices $(h_0, h_1, h_2, h_3, h_4, h_5, h_6)$, where h_k is the number of hexagons with neighbor index k . As each hexagon in the IPR isomer is adjacent to at least three other hexagons, h_0, h_1 , and h_2 are equal to 0 for all IPR isomers, and the combination of only four indices (h_3, h_4, h_5, h_6) may be used as a signature of hexagon adjacencies in a given fullerene isomer.^{46,53} According to Raghavachari,⁵³ the indices of all hexagons should be as close to each other as possible to minimize the steric strain. Hence, the lowest strain is expected for those structures, in which all indices are equal, and for the range of cage sizes studied in the work, C_{68} – C_{98} , this condition is fulfilled only for C_{80} (I_h : 31924) and C_{80} (D_{5h} : 31923), the index combination of which is (0, 30, 0, 0).⁴⁶ Thus, the exceptional stability of these C_{80}^{6-} isomers may be explained by the favorable distribution of the pentagons, which leads to the least steric strain. More complex conditions had to be derived for other IPR fullerenes, namely, (h_3, h_4, h_5, h_6) indices should be $(80 - 2n, 3n - 90, 0, 0)$ for C_{2n} with $2n \leq 80$ and $(0, 70 - n, 2n - 80, 0)$ for C_{2n} with $2n \geq 80$.⁴⁶ For the IPR isomers of C_{76} – C_{88} these conditions are satisfied for C_{76} (T_d : 19151), C_{78} (D_{3h} : 24109), C_{82} (C_{2v} : 39718), C_{84} (D_2 : 51589), C_{84} (D_2 : 51590), C_{84} (D_{2d} : 51591), C_{86} (D_3 : 63761), and C_{88} (D_2 : 81738). This list perfectly corresponds to the lowest energy IPR isomers of C_{76}^{6-} – C_{88}^{6-} found in this work. For larger cages these conditions are less instructive, because many of the IPR isomers satisfy them, but one can still notice that the lowest energy isomers of C_{90}^{6-} – C_{98}^{6-} also have the optimum distribution of pentagons. Interestingly, it appears that the relative energies of the IPR C_{2n}^{6-} isomers follow the rationalization of the stability based on the steric strain much better than the relative energies of uncharged fullerenes. DFT calculations predict that, by violation of the above specified conditions, the most stable uncharged IPR isomers are D_2 : 19150 for C_{76} ,⁵⁴ D_{5d} : 31918 for C_{80} ,^{54,55} C_2 : 39712 for C_{82} ,^{54,56} C_2 : 63759 for C_{86} ,⁵⁴ and C_s : 17 for C_{88} .⁵⁷

Structural Relationships between the Fullerenes. Analysis of the cage structures of the lowest energy $M_3N@C_{2n}$ isomers

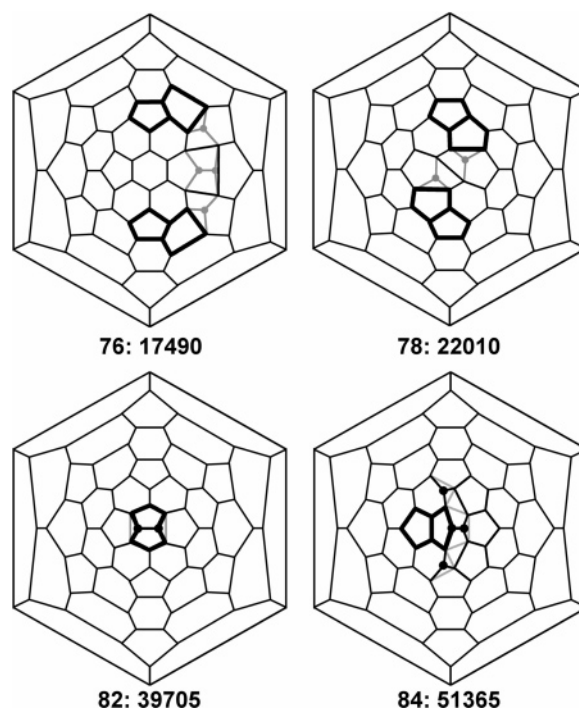


Figure 7. Schlegel diagrams of C_{76} (C_s : 17490), C_{78} (C_s : 22010), C_{82} (C_{2v} : 39705), and C_{84} (C_s : 51365) showing the relationships of these structures to C_{80} (I_h : 31924). The atoms and bonds in C_{80} , which should be removed, are shown as gray circles and lines, respectively. The atoms, which should be added to C_{80} to obtain C_{82} and C_{84} , are shown as black circles. APPs are shown in thick black lines.

revealed that many of them have common structural motifs, and we could find two groups of interrelated structures. The first group consists of the C_{70} (C_{2v} : 7854), C_{72} (C_s : 10528), and C_{74} (C_{2v} : 14239) cages, all corresponding to the most stable $Sc_3N@C_{2n}$ isomers. The structure of C_{72} (C_s : 10528) can be envisaged as a result of addition of two carbon atoms to C_{70} (C_{2v} : 7854) near to one of its APPs with small structural rearrangements of the whole structure (see Figure S1 in the Supporting Information). Likewise, C_{74} (C_{2v} : 14239) can be obtained after the addition of two carbon atoms to C_{72} (C_s : 10528) near to the place where the atoms were added to C_{70} (C_{2v} : 7854) to form C_{72} (C_s : 10528). Thus, the major part of the cage is the same for all three structures.

The second group comprises C_{76} (C_s : 17490), C_{78} (C_s : 22010), C_{82} (C_{2v} : 39705), and C_{84} (C_s : 51365). These cages correspond to the lowest energy isomers of $Y_3N@C_{2n}$, and all of them are structurally related to C_{80} (I_h : 31924). Figure 7 shows Schlegel diagrams of these cages demonstrating how they can be obtained by removal or addition of certain atoms and bonds in C_{80} (I_h : 31924). For instance, C_{82} (C_{2v} : 39705) can be obtained from C_{80} (I_h : 31924) by insertion of a C_2 unit into the center of a hexagon. In general, it can be seen that aside from the local transformations, all these cages share the common motif of C_{80} (I_h : 31924). Finally, C_{82} (C_s : 39663), which is also considered as a possible structure for $M_3N@C_{82}$, is closely related to C_{84} (C_s : 51365) and can be obtained from the latter by the removal of two carbon atoms with subsequent pairwise Stone–Wales transformation (see Figure S2a). On the other hand, this cage can be obtained from the C_{78} (D_{3h} : 24109) by the insertion of four carbon atoms in the local fragment of the latter (Figure S2b).

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The structural relationships between the cage isomers, especially in the second group, demonstrate that the high stability of these particular cage isomers is not accidental. We have already pointed out that the exceptional stability of C_{80}^{6-} (I_h : 31924) can be explained by the optimum distribution of the pentagons, which minimizes the strain of the cage. Certainly, this factor remains important for other fullerenes, even though they may be non-IPR, and in this regard the high stability of the cages retaining a significant part of the C_{80} (I_h : 31924) cage is not surprising. Moreover, the exceptional stability of C_{80}^{6-} (I_h : 31924) on the per-atomic basis appears to be one of the reasons why non-IPR isomers retaining a significant part of its structure can compete in stability with IPR isomers.

Cluster–Cage Interactions. The data in Tables 2–4 demonstrate that though the cage stability is very important in determining the structures of clusterfullerenes, the trends in the relative energies of $M_3N@C_{2n}$ isomers cannot be explained by this factor alone. Obviously, the cage should provide a suitable geometry for the enclosed cluster; that is, there should be enough inner space in the cage for the latter. The most striking example of the influence of this factor is the case of $M_3N@C_{78}$, in which an insufficient cage size of the D_{3h} : 24109 isomer for the Y_3N cluster and the clusters of similar size in the formation of different cage isomers of $Sc_3N@C_{78}$ and $M_3N@C_{78}$ ($M = Dy, Tm$) clusterfullerenes.³⁹ Besides, if the fullerene has APPs, they should be located in such a way that their coordination by Sc atoms of the cluster is possible without a significant distortion of the latter. When this condition is not fulfilled for the lowest energy C_{2n}^{6-} isomers, the $M_3N@C_{2n}$ isomers of these cages are destabilized and the most stable isomers of the clusterfullerenes are based on the relatively unstable cages. As a result, such clusterfullerenes might be absent in the products of the arc-discharge synthesis, as can be exemplified by $Sc_3N@C_{72}$ and $Sc_3N@C_{74}$, for which the lowest energy isomers of C_{2n}^{6-} have an unfavorable arrangement of APPs.

To quantify the influence of the cage geometry on the cluster–cage interaction we have analyzed the cluster binding energy (BE) in the series of $M_3N@C_{2n}$ clusterfullerenes, which are listed in Table S1 (Supporting Information). The binding energy of the cluster may be defined as the energy change in the reaction $M_3N + C_{2n} = M_3N@C_{2n}$, which will be further referred to as BE-1. Table S1 (Supporting Information) lists BE-1 values computed in this work for a series of $Sc_3N@C_{2n}$ and $Y_3N@C_{2n}$ clusterfullerenes.

Earlier, BE-1 values for experimentally isolated $Sc_3N@C_{2n}$ clusterfullerenes were reported to be -12.07 eV for $Sc_3N@C_{68}$ at the B3LYP/6-31G* level;⁵⁸ -9.73 and -9.62 eV for $Sc_3N@C_{78}$ at the BP/TZP^{33,59} and B3LYP/6-31G* levels,⁵⁸ respectively; -10.72 and -11.60 eV for $Sc_3N@C_{80}$ at the BL3YP/BLYP/6-31G*⁶⁰ and BP/TZP levels,³³ respectively. The values computed in this work, -12.50 , -10.51 , and -12.48 eV for $Sc_3N@C_{68}$ (D_3 : 6140), $Sc_3N@C_{78}$ (D_{3h} : 24109), and $Sc_3N@C_{80}$ (I_h : 31934), respectively, are by 0.5 – 0.8 eV larger, but the same trend in the values is observed (almost

identical values for $Sc_3N@C_{68}$ and $Sc_3N@C_{80}$ and smaller BE-1 value for $Sc_3N@C_{78}$). The values predicted for $Sc_3N@C_{70}$ (C_{2v} : 7854), -12.43 eV, and $Sc_3N@C_{80}$ (D_{5h} : 31923), -12.38 eV, are also close to the BE-1 values of $Sc_3N@C_{68}$ and $Sc_3N@C_{80}$ (I_h : 31924). In fact, the values for four of the five experimentally isolated $Sc_3N@C_{2n}$ clusterfullerenes are the highest among the whole series of $Sc_3N@C_{2n}$ molecules studied theoretically in this work.

The BE-1 values for $Y_3N@C_{2n}$ with small cages ($2n < 78$) are all below 10 eV (Table S1). The largest value, -11.32 eV, is predicted for $Y_3N@C_{84}$ (C_s : 51365), which has the same cage isomer as that of the experimentally isolated $Tb_3N@C_{84}$. Comparably large BE-1 values are also predicted for $Y_3N@C_{2n}$ with other experimentally observed cage isomers: -10.82 eV for $Y_3N@C_{78}$ (C_2 : 22010), -10.38 eV for $Y_3N@C_{80}$ (I_h : 31924), -10.25 eV for $Y_3N@C_{80}$ (D_{5h} : 31923), -10.37 eV for $Y_3N@C_{88}$ (D_2 : 81738). Finally, similar values are also predicted for some of the structures suggested in this study for the clusterfullerenes, which are not yet structurally characterized: -10.98 eV for $Y_3N@C_{82}$ (C_{2v} : 39705), -10.35 eV in $Y_3N@C_{82}$ (C_s : 39663), -10.90 eV for $Y_3N@C_{92}$ (D_3 : 85). Note that the largest BE-1 values for $Y_3N@C_{2n}$ are systematically smaller than the largest values for $Sc_3N@C_{2n}$.

Though experimentally isolated $M_3N@C_{2n}$ structures usually have large BE-1 values, some of them do not: the opposite examples are $Sc_3N@C_{78}$ (D_{3h} : 24109) and $Y_3N@C_{86}$ (D_3 : 63761). On the other hand, some of the nonisolated compounds are also expected to have a large BE-1 (see Table S1). Hence, BE-1 values may be misleading in some cases and appear to be not very instructive for the goal of this study. Since the relative stability of the empty fullerene isomers is strongly affected by the charge, BE-1 values are determined not only by the effect of the cage geometry and cluster–cage interaction but also by the relative stabilities of the cages in the neutral state. For instance, a BE-1 for the non-IPR C_2 : 22010 isomer of $Sc_3N@C_{78}$ is higher than that of the IPR D_{3h} : 24109 isomer because the non-IPR isomer is substantially less stable in the neutral form (by 234.0 kJ/mol), rather than because this non-IPR isomer is more suitable for the encapsulation of the Sc_3N cluster. Likewise, the small BE-1 value for $Sc_3N@C_{78}$ in comparison to all other Sc_3N -based clusterfullerenes can be explained by the fact that D_{3h} : 24109 is the only stable cage in the uncharged form (it is predicted to be the second lowest energy IPR isomer of C_{78} ⁵⁴), while other cages found in $Sc_3N@C_{2n}$ are unstable in the uncharged form. To focus presumably on the effect of the cage geometry and the cluster–cage bond formation on the BE, we have also computed the energy changes in the reaction $M_3N^{6+} + C_{2n}^{6-} = M_3N@C_{2n}$. The values computed this way (named BE-2 hereafter) should be less sensitive to the relative stability of the empty cages because the hexaanion is used as the starting state of the fullerene.⁶¹ However, the drawback of this scheme is that the energy in this case is dominated by the large classical Coulomb term. For instance, 125.3 eV are released by placing the $6+$ point charge into the center of the $6-$ charged sphere with a radius of 4.138 Å (i.e., the radius of DFT-optimized I_h : 31924

(58) Park, S. S.; Liu, D.; Hagelberg, F. *J. Phys. Chem. A* **2005**, *109* (39), 8865–8873.

(59) The basis set used in ref 33 comprised triple- ζ + polarization for C and N atoms and complex basis set for Sc (frozen core for 1s and 2sp shells, double- ζ for 3s and 3p electrons, triple- ζ for nd and $(n + 1)s$ electrons, and single Slater orbital for $(n + 1)p$ electrons).

(60) Kobayashi, K.; Sano, Y.; Nagase, S. *J. Comput. Chem.* **2001**, *22* (13), 1353–1358.

(61) We could not find the bonded state for Sc_3N^{6+} and Y_3N^{6+} clusters at the PBE/TZ2P level of theory, and hence point energies were used for M_3N^{6+} calculated with the cluster geometries taken from $M_3N@C_{80}$ (I_h : 31924).

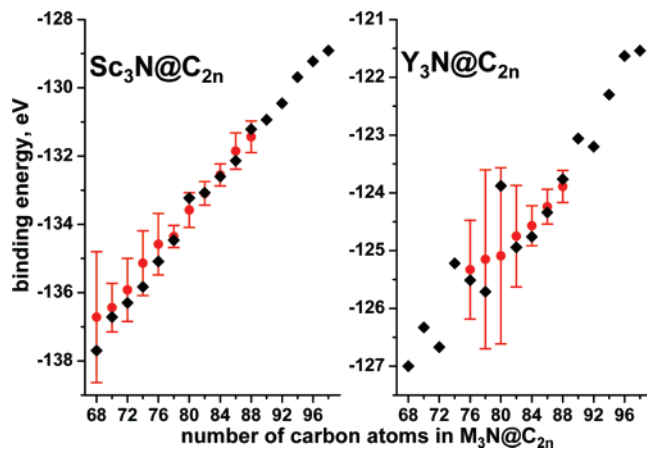


Figure 8. BE-2 values for the lowest energy isomers of $\text{Sc}_3\text{N}@C_{2n}$ and $\text{Y}_3\text{N}@C_{2n}$ (black squares) and mean BE-2 values for 10 lowest energy isomers together with 95% probability confidence interval (red dots and “error” bars) plotted as the function of the number of atoms in the fullerenes.

isomer of C_{80}^{6-}),⁶² which is close to 123.9 and 133.2 eV, DFT-computed BE-2 values computed for $\text{Y}_3\text{N}@C_{80}$ (I_h : 31924) and $\text{Sc}_3\text{N}@C_{80}$ (I_h : 31924), respectively. Moreover, as the electrostatic potential inside the charged sphere scales with the sphere radius as R^{-1} , one may expect that the absolute BE-2 values should decrease smoothly with the increase of cage size.

BE-2 values for all studied compounds are listed in Table S2 (Supporting Information). Figure 8 plots the BE-2 values for the most stable $\text{M}_3\text{N}@C_{2n}$ isomers for each $2n$, and also the average values for a set of 10 isomer with the lowest energy C_{2n}^{6-} cages together with a 95% confidence interval *versus* the cage size.

It is shown that, for the same cage isomer, the binding energies for Y_3N are by 9–10 eV smaller than those for Sc_3N . The reason for this is not clear yet, but in fact it correlates with the lower yields of Y_3N and lanthanide-based clusterfullerenes compared to $\text{Sc}_3\text{N}@C_{2n}$. The BE-2 becomes systematically smaller with the increase of cage size, which can be explained by the classical Coulomb interaction as discussed above. When the 95% probability confidence interval may be estimated (for a set of data with 10 points it is defined as 2.31 times the standard deviation), its magnitude varies considerably with cage size. For $\text{Sc}_3\text{N}@C_{2n}$, the magnitude is the largest for the smallest cage, $2n = 68$, then it decreases to a cage size of $2n = 76$, and remains almost the same for the larger cages. For $\text{Y}_3\text{N}@C_{2n}$, the largest magnitudes are found for C_{78} and C_{80} , while, for larger cages, the interval decreases rapidly, remaining almost constant for C_{86} and C_{88} . Thus, it appears that for large cage sizes the range of BE-2 values is rather small, which means that for these cages the differences in their shape and dimensions are relatively unimportant for the cluster. On the contrary, this factor is very important for smaller cages. For Sc_3N , the shape of the cage is one of the definitive factors up to $\text{Sc}_3\text{N}@C_{76}$, while for the larger Y_3N cluster it is important up to C_{82} . Significantly, besides the size of the cage and the cluster, for $\text{Sc}_3\text{N}@C_{2n}$ clusterfullerenes with smaller cages the location of APPs is also very important because most of the cage isomers in the C_{68} – C_{76} cage sizes have two to three APPs. It is obvious from the data presented above that the coordination of the metal

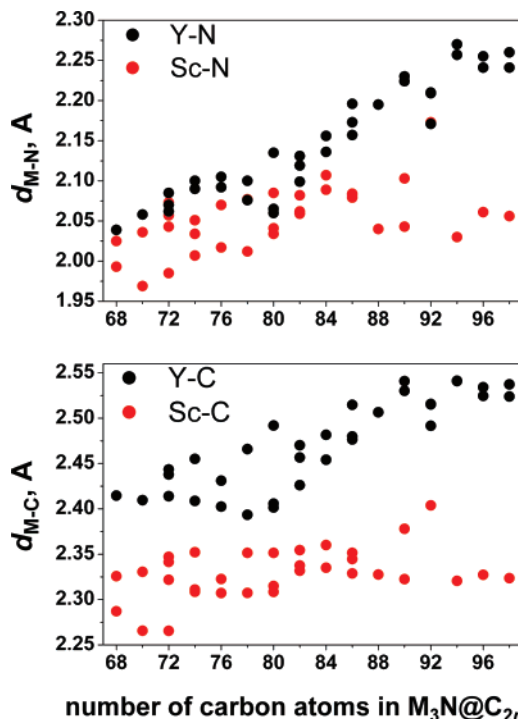


Figure 9. Averaged Sc–N, Y–N, Sc–C and Y–C distances in selected $\text{Sc}_3\text{N}@C_{2n}$ and $\text{Y}_3\text{N}@C_{2n}$ isomers listed in Table S1 (the isomers from Tables 4 are also added for $\text{Y}_3\text{N}@C_{2n}$, $2n = 90$ – 98) plotted as a function of the cage size.

atoms to APPs is important for stabilization of the latter, and hence only the cages for which the topology allows coordination of *all* APPs can lead to the stable $\text{Sc}_3\text{N}@C_{2n}$ isomers. This factor is less important for $\text{Y}_3\text{N}@C_{2n}$ clusterfullerenes because the size of the Y_3N cluster is simply too large to fit the cages smaller than C_{76} , while larger cages have a smaller number of APPs.

Interestingly, BE-2 values for the most stable $\text{M}_3\text{N}@C_{2n}$ isomers are usually lower than or close to the average value for a set of 10 isomers, with the exception of $\text{M}_3\text{N}@C_{80}$. It is obvious that for $\text{Y}_3\text{N}@C_{80}$ (I_h : 31924) the encapsulation of the cluster is substantially less favorable than that for most of the other C_{80} isomers, because the Y_3N cluster is already too large for this almost spherical cage (similar conclusion was also reported by Gan et al.⁶³). It is the only exclusive stability of the cage which makes $\text{Y}_3\text{N}@C_{80}$ (I_h : 31924) the lowest energy isomer.

Optimum M–N and M–C Distances. To study the influence of the cage size and shape on the cluster geometry and metal–carbon distances, average Sc–N, Y–N, Sc–C, and Y–C interatomic distances in selected isomers of $\text{Sc}_3\text{N}@C_{2n}$ and $\text{Y}_3\text{N}@C_{2n}$ were studied (for Sc–C and Y–C, nine shortest M–C bonds were averaged). Figure 9 plots these distances versus the cage size of the isomers of $\text{Sc}_3\text{N}@C_{2n}$ and $\text{Y}_3\text{N}@C_{2n}$ listed in Table S1. Though the values for different isomers of the given cage size are significantly scattered, it is still possible to figure out that the longest Sc–N bond distances do not exceed 2.10 Å, and this maximum value does not depend on the cage size. On the contrary, the Y–N distances increase systematically with the cage size up to C_{90} , while for larger cages the saturation of the bond lengths around 2.25 Å is found. In a similar fashion, averaged Sc–C bonds for $\text{Sc}_3\text{N}@C_{74}$ – $\text{Sc}_3\text{N}@C_{98}$ stay in the

(62) Classical Coulomb energy is determined as q_1q_2/R^{-1} , where q_1 and q_2 are charges of the particle and sphere, and R is the radius of the sphere.

(63) Gan, L.-H.; Yuan, R. *ChemPhysChem* **2006**, *7* (6), 1306–1310.

narrow range 2.30–2.35 Å, while Y–C distances show a tendency to increase up to ca. 2.50–2.55 Å in $Y_3N@C_{90}$, and these values are preserved for large cages. The only exclusion from these rules is $M_3N@C_{92}$ (D_3 : 85) with M being both Sc and Y, as Sc–N and Sc–C distances are much longer than those in all other $Sc_3N@C_{2n}$ molecules, while Y–N and Y–C distances are, on the contrary, shorter than those in other $Y_3N@C_{2n}$ molecules of similar cage size.

To understand why $M_3N@C_{92}$ (D_3 : 85) shows different geometry parameters from all other clusterfullerenes we have analyzed the nature of bonding between the cluster and the cage in this and other clusterfullerenes. Interestingly, in $M_3N@C_{92}$ (D_3 : 85) the metal atoms are coordinated to pyracelene units, and analysis of spatial distribution of MOs shows that some of them are largely localized on the pyracelene units and have large metal–carbon bonding contributions. Similar MOs were found in $Sc_3N@C_{78}$ (D_{3h} : 24109), in which Sc atoms are also bonded to the pyracelene units.^{33,34} On the contrary, in most other clusterfullerenes it is difficult to point to the MOs with considerable metal–cage bonding contribution; instead, metal–cage covalent interactions are distributed over many MOs (see ref 37 for detailed discussion of this phenomenon). Thus, in $Sc_3N@C_{78}$ (D_{3h} : 24109) and $M_3N@C_{92}$ (D_3 : 85) the metal–cage interactions are better described by a “classical” covalent bonding while for a majority of other clusterfullerenes the “back-donation” scheme has to be applied as proposed by Liu et al.³⁷

Based on Figure 9, it can be concluded that the optimal Sc–N and Sc–C distances in $Sc_3N@C_{2n}$ are ca. 2.05 and 2.30–2.35 Å, respectively. For small cage sizes, these parameters cannot be realized because there is not enough space for the cluster, and hence the cluster is strained by the carbon cage. The optimum geometry for Sc_3N is realized in $Sc_3N@C_{80}$, and this is one of the reasons, besides stability of the cage alone, for the high yield of $Sc_3N@C_{80}$. For $Sc_3N@C_{80}$ the optimum distances are reached if the cluster resides in the center of the cage, while for larger cages the Sc_3N cluster has to be displaced to one of the cage sides to preserve the optimum Sc–N and Sc–C bond lengths (Figure 3). Apparently, displacement of the cluster from the cage center results in a less effective cluster–cage interaction as was already discussed above, and the $Sc_3N@C_{2n}$ clusterfullerenes with the cage size of C_{82} and larger are not formed in detectable amounts. For $Y_3N@C_{2n}$, the optimum Y–N and Y–C distances may be estimated as 2.25 and 2.50–2.55 Å, respectively. These values are reached for the cage sizes of C_{90} – C_{98} , and $Dy_3N@C_{2n}$ clusterfullerenes up to these cage sizes are observed.²¹ In the larger cages displacement of the M_3N cluster from the cage center can be expected, and it is one of the reasons why nitride clusterfullerenes with larger cage sizes are not formed.

Conclusions

Systematic quantum-chemical calculations of the hexaanions of empty fullerene cages, C_{2n}^{6-} , within a broad isomeric and compositional range ($2n = 68-98$, more than 16 000 isomers were considered for some of the compositions), followed by calculations of the $M_3N@C_{2n}$ ($M = Sc, Y$) clusterfullerenes based on the most stable cages resulted in the finding of the most stable $M_3N@C_{2n}$ isomers for a broad range of fullerene cage sizes. We have found that the most stable isomers always correspond to the structurally characterized clusterfullerenes,

which enabled us to predict the cage structures for some $M_3N@C_{2n}$ compounds, whose structures are not yet experimentally described. The relative stability of the clusterfullerene isomers was found to be a function of both the relative stability of the 6-fold charged cage isomers and of the cage size and dimensional parameters. Moreover, the overall yield of the clusterfullerenes was shown to correlate well with the cage stabilities considered on the per atomic basis, and the exceptional stability of C_{80}^{6-} (I_h : 31924) and C_{80}^{6-} (D_{5h} : 31923) fullerenes was found to be the reason for the high yield of the clusterfullerenes based on these cages, in spite of the unfavorable encapsulation energy for larger clusters. Moreover, the relative stability of the hexaanions of IPR isomers was found to correlate well with their hexagonal indices, while it is not generally true for uncharged fullerenes, and the exceptional stability of two most stable C_{80} isomers was explained by the optimum distribution of pentagons on their surface minimizing the steric strain. In addition, the structures of the most stable non-IPR isomers of C_{76} (C_s : 17490), C_{78} (C_2 : 22010), C_{82} (C_{2v} : 39705), and C_{84} (C_s : 51365) were found to be closely related to the C_{80} (I_h : 31924) cage, which explains why these particular non-IPR isomers have the lowest energy. The binding energy of the cluster is analyzed as the function of the cage size, and it is found that for large cages the factors related to the cage size and geometry become relatively unimportant. Finally, the study of the evolution of the cluster size and the metal–carbon distances with the increase of the cage size show that the optimum Sc–N and Sc–C distances for the $Sc_3N@C_{2n}$ family are reached at $2n = 80$, and further increase of the cage size is not favorable for the clusterfullerene formation. On the contrary, the optimum parameters for the Y_3N cluster are reached in C_{90} – C_{98} cages, justifying the formation of larger cages than those in the $Sc_3N@C_{2n}$ family.

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Note added in proof: Recently the first nitride clusterfullerene with C_{76} cage, $DySc_2N@C_{76}$, was isolated and characterized in our group (Yang, S.; Popov, A. A.; Dunsch, L. *Small* **2007**, submitted). In accordance with the results of this work, the cage structure of $DySc_2N@C_{76}$ was assigned to the C_s : 17490 isomer. Exclusive formation of the clusterfullerene with the mixed $DySc_2N$ cluster and much lower yield of $Sc_3N@C_{76}$ and $Dy_3N@C_{76}$ also agree with the structural peculiarities of $M_3N@C_{76}$ (C_s : 17490) discussed above.

Supporting Information Available: DFT-optimized Cartesian coordinates of the molecules listed in Tables 2–4, BE-1 and BE-2 values, and the figures showing structural relationships (i) among C_{70} (C_{2v} : 8504), C_{72} (C_s : 10528) and C_{74} (C_{2v} : 14239) fullerenes and (ii) among C_{82} (C_s : 39663), C_{78} (D_{3h} : 24109), and C_{84} (C_s : 51365) fullerenes. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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