Fullerenes

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General Rule for the Stabilization of Fullerene Cages Encapsulating Trimetallic Nitride Templates**

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Fullerenes containing a trimetallic nitride template (TNT) within the cage are a particularly interesting class of endohedral metallofullerenes. Not only are the cage properties modified by the presence of the incarcerated group but, almost uniquely among endohedral metallofullerenes, they are quite stable. Furthermore, they can be produced in multimilligram quantities, and these amounts should increase in the future. The electronic effect of the TNT is such that some fullerenes of sizes and symmetry that are otherwise relatively unstable become available for investigation.[1] The general formula of these TNT endohedral metallofullerenes is $A_{3-n}B_nN@C_k$ ($n = 0$–3; A,B = group III, IV, and rare-earth metals; $k = 68$, 78, and 80) with the archetypal examples of: $Sc_3N@C_{80}$,[2,3] $Sc_3N@C_{68}$,[4] and $Sc_3N@C_{78}$.[5] The structures of $Sc_3N@C_{78}$, $Sc_3N@C_{80}$, and $Sc_3N@C_{68}$ are displayed in Figure 1.

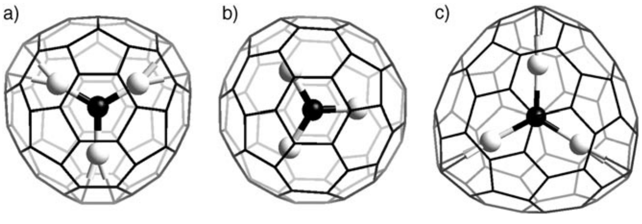

Figure 1. Optimized structures of the archetypal TNT endohedral metallofullerenes: a) D_{3h}-$Sc_3N@C_{78}$, b) C_s-$Sc_3N@C_{80}$ (I_h-C_{80}:**7**), and c) D_3-$Sc_3N@C_{68}$.

Special attention has been paid to lutetium-based TNT endohedral metallofullerenes, $Lu_{3-n}A_nN@C_{80}$ ($n = 0$–2; A = Gd, Ga, and Ho), because they may prove useful as multifunctional contrast agents for X-ray, magnetic resonance imaging, and radiopharmaceuticals.[6] The aim of this research is to use methods based on density functional theory (DFT) to answer the questions: How can the stability of the TNT endohedral metallofullerenes be predicted? Which fullerene cages between C_{60} and C_{84} will be capable of encapsulating TNTs? Aihara and co-workers proposed the bond resonance energy (BRE)[7] to be an indicator of the particular stabilization of free fullerene cages when they encapsulate metal units.[8] However, this method was not a predictive tool because it could not answer whether or not new cages will be capable of encapsulating TNTs.

Up to now, only four carbon cages have been capable of encapsulating TNT units: D_3-C_{68}:**6140**, $D_{3h'}$-C_{78}:**5**, D_{5h}-C_{80}:**6** and I_h-C_{80}:**7**. All these cages, except C_{68}, satisfy the isolated-pentagon rule (IPR). But it is interesting to see that in all cases the empty IPR fullerene isomers isolated so far are different from the carbon cages found in isolable TNT endohedral metallofullerenes. The incorporation of a TNT into the fullerene results in an electron transfer from the metal atoms to the carbon cage, in other words, the formation of a stable ion pair. It should be noted that these fullerene cages are produced only when they are negatively charged by the encapsulated species. Theoretical calculations indicated that the thermodynamic stability of a fullerene molecule depends heavily on the negative charge that resides on it.[9] The bond between the nitride and the cage is markedly defined by the ionic model $Sc_3N^{6+}@C_k^{6-}$ ($k = 68$, 78, and 80).[10] From the geometric point of view, although the free Sc_3N molecule is pyramidal, this fragment has a planar structure inside the fullerene cage. When the Sc_3N unit is

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encapsulated, there is a significant local distortion in the fullerene cage. This distortion results in the outward movement of the carbon atoms closest to the scandium ions, which gives rise to an increase in the tendency of the carbon structure to form a pyramid and an increase in the radius of the fullerene cage.

The first ^{13}C NMR spectroscopic analysis of $Sc_3N@C_{80}$ revealed that the Sc_3N moiety rotates freely in the highly symmetric I_h-C_{80}:**7** isomer.[2] Thus, several different orientations of the TNT were found for the slightly different TNT endohedral metallofullerenes of I_h-C_{80}:**7**—$Lu_3N@C_{80}$,[11] $ErSc_2N@C_{80}$,[12] $Sc_3N@C_{80}$,[2] and $Sc_3N@C_{80}$-$C_8H_6(OCH_3)_2$.[13] DFT calculations corroborated that the differences among the most stable isomers are rather small, < 0.10 eV.[10,14] Later, a minor new isomer of $Sc_3N@C_{80}$, which corresponds to the Sc_3N fragment encapsulated by the D_{5h}-C_{80}:**6** isomer, was also isolated and characterized.[3] We focus our study only on the TNT endohedral metallofullerenes of I_h-C_{80}:**7** isomer. Neither of these C_{80} isomers have been isolated as empty fullerenes and are not even the most stable isomers among the seven distinct isomers that satisfy the IPR:[15] D_{5d}-C_{80}:**1**, D_2-C_{80}:**2**, C_{2v}-C_{80}:**3**, D_3-C_{80}:**4**, $C_{2v'}$-C_{80}:**5**, D_{5h}-C_{80}:**6**, and I_h-C_{80}:**7**.[16] Two empty-cage isomers, D_2-C_{80}:**2** and D_{5d}-C_{80}:**1**, have been isolated,[17] and theoretical calculations have shown that the I_h-C_{80}:**7** structure is the less-stable isomer overall.[18] However, electronic-structure calculations showed that the stability of the I_h-C_{80}:**7** isomer increases markedly when six electrons are added to the cage.[19] In the case of $Sc_3N@C_{78}$, the $D_{3h'}$-C_{78}:**5** isomer has not been calculated as the most stable nor has ever been isolated as an empty cage. There are five IPR isomers for the empty C_{78} cage with the following relative stability order: $C_{2v'}$-C_{78}:**3** > C_{2v}-C_{78}:**2** > D_3-C_{78}:**1** > $D_{3h'}$-C_{78}:**5** > D_{3h}-C_{78}:**4**.[20] Unlike in $Sc_3N@C_{80}$, in $Sc_3N@C_{78}$ the metal atoms reside over three pyracylene 6:6 C–C bonds. The fourth fullerene cage, which is capable of incarcerating four atoms, is the non-IPR D_3-C_{68}:**6140**. Other non-IPR structures have also been investigated for $Ca@C_{72}$,[21,22] $La_2@C_{72}$,[23] $Ca@C_{74}$,[21] $Sc_2@C_{74}$,[21,24] and $Sc_2@C_{66}$.[25] It is interesting to note that the only known violations of the IPR rule occur in endohedral metallofullerenes. For the C_{68} stoichiometry, the carbon surface of which consists solely of pentagons and hexagons, there are 6332 possible isomers. Nevertheless, the detailed structural characterization of $Sc_3N@C_{68}$ showed that the carbon cage is the 6140 isomer.[4] Although the cage radius of D_3-C_{68}:**6140** is not only considerably smaller but also distorted, the TNT guest can be encapsulated in a plane in which scandium atoms are directly connected to 5:5 ring junctions.[26]

Formally, a total of six electrons go from the highest occupied nitride orbitals to the lowest unoccupied cage orbitals. This formal electron transfer is accompanied by a large binding energy for the encapsulation process. These were calculated to be -173, -224, and -268 kcal mol^{-1} for $Sc_3N@C_k$ when $k = 68$, 78, and 80, respectively.[10] The $D_{3h'}$-C_{78}:**5** isomer has a closed-shell ground state with three low unoccupied orbitals of symmetries a_2' (-5.15 eV) and e' (-4.88 eV) that are π-antibonding orbitals basically centered in the set of pyracylene 6:6 C–C bond type. These unoccupied orbitals can receive six electrons from the three highest occupied orbitals of the TNT, which are very high in energy: a_1' (-4.44 eV) and e'(-3.51 eV), see Figure 2. For the I_h-C_{80}:**7** isomer, previous theoretical calculations have shown that it has the open-shell configuration $(t_{1g}+h_u)^{16}(g_g)^2(a_g+h_g)^0$. Moreover, I_h-C_{80}:**7** may deform to lower symmetries by Jahn–Teller distortion.[27] It represents an electronic configuration with only two electrons in four low-lying degenerate orbitals, -5.55 eV, which can easily accept six electrons. As a consequence of this electron-charge transfer, the resulting endohedral has a closed-shell configuration. D_3-C_{68}:**6140** has a closed-shell ground state with a HOMO–LUMO gap of 0.52 eV and with three low unoccupied orbitals of symmetries e' (-5.38 eV) and a_1 (-4.79 eV), which can easily accept six electrons as the other two fullerenes do. Indeed, after the electron-charge transfer, the cage is stabilized as the final endohedral complex has a HOMO–LUMO gap of 1.27 eV. A similar gap was found for the TNT endohedral complexes of $D_{3h'}$-C_{78}:**5** and I_h-C_{80}:**7** with 1.24 and 1.18 eV, respectively. These electronic considerations are the key to rationalizing why only some cages can encapsulate TNTs.

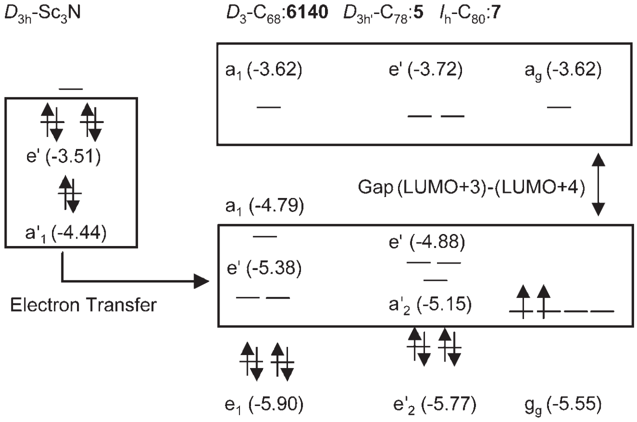

Figure 2. Representation of the ionic bond between the trimetallic nitride template (TNT) and the fullerene cages D_3-C_{68}:**6140**, $D_{3h'}$-C_{78}:**5**, and I_h-C_{80}:**7**. There is a formal transfer of six electrons from the three highest occupied orbitals of the TNT unit to the three lowest unoccupied orbitals of the fullerene cages. Consequently, the $M_3N@C_k$ ($k = 68$, 78, and 80) complexes are described as $Sc_3N^{6+}@C_k^{6-}$ with a relatively large HOMO–LUMO gap nearly equal to the (LUMO + 3)–(LUMO + 4) found in the free cages: The (LUMO + 3)–(LUMO + 4) rule.

On the one hand, the three cages studied here—D_3-C_{68}:**6140**, $D_{3h'}$-C_{78}:**5**, and I_h-C_{80}:**7**—have three very low-lying LUMOs accompanied with a large energy separation between the LUMO + 3 and LUMO + 4 (see Figure 2). On the other hand, the TNT has three HOMOs that are relatively high in energy. Consequently, the cage orbitals can easily accommodate six electrons that stem from the three destabilized orbitals. Moreover, the electronic structure of the empty fullerenes suggests that it acquires, presumably, a considerable HOMO–LUMO gap after a transfer of six electrons, thus giving stability to the final complex. The final HOMO–LUMO gap of the TNT endohedral metallofullerenes can be estimated from the gap between LUMO + 3 and LUMO + 4 of the free cages. The calculated and estimated values are 1.27/1.17 eV for $Sc_3N@C_{68}$, 1.24/1.16 eV for $Sc_3N@C_{78}$, and 1.18/1.93 eV for $Sc_3N@C_{80}$. The main conclusion that can be drawn from this observation is that we can predict HOMO–LUMO gaps by simply checking the molecular-orbital energies of the free fullerene cage. In principle, only the free isomers with a large (LUMO + 3)–(LUMO + 4) gap will be predisposed to encapsulate TNTs. To check whether this statement can be generalized, we calculated (LUMO + 3)–(LUMO + 4) gaps for all the IPR isomers from C_{60} to C_{84}. There are 51 IPR isomers: 1 of C_{60}, C_{70}, C_{72}, and C_{74}; 2 of C_{76}; 5 of C_{78}; 7 of C_{80}; 9 of C_{82}; 24 for C_{84}.[16] The result is quite surprising and conclusive: the (LUMO + 3)–(LUMO + 4) gap for all IPR cages is smaller than 1 eV, except for C_{60}, $D_{3h'}$-C_{78}:**5**, D_{5h}-C_{80}:**6**, and I_h-C_{80}:**7** isomers, see Figure 3. C_{60} can be rejected because its cavity measured through the cage radius, 3.551 Å, is not big enough to encapsulate a four-atom unit. In the rest of fullerene cages the cavity is not a limitation for the encapsulation. Apart from the well-known TNT endohedral metallofullerenes we have encapsulated Sc_3N into D_{3h}-C_{78}:**4** and C_s-C_{84}:**3** isomers as a test case to corroborate our predictions. D_{3h}-C_{78}:**4** isomer is the least-stable isomer among all IPR C_{78} isomers and is 0.99 eV less stable than the $D_{3h'}$-C_{78}:**5** isomer. The cage seems to be suitable for the TNT encapsulation as the scandium atoms can be also oriented to the reactive 6:6 C–C bonds as occurs in $D_{3h'}$-C_{78}:**5**. However, the electronic configuration of the free cage does not seem to be favorable for the encapsulation due to a small (LUMO + 3)–(LUMO + 4) gap of 0.66 eV, which, according to the rule, prevents the maximum stabilization required for the formation. The final TNT endohedral complex of D_{3h}-C_{78}:**4** is 4.89 eV less stable than the TNT encapsulation inside $D_{3h'}$-C_{78}:**5**. Up to now, none of the C_{84} isomers has encapsulated TNTs although from the geometric point of view these cages have a big enough cavity. However, no C_{84} isomer has a (LUMO + 3)–(LUMO + 4) gap larger than 1 eV. For instance, C_s-C_{84}:**3** isomer has a (LUMO + 3)–(LUMO + 4) of 0.53 eV, which is a good prediction of the final HOMO–LUMO gap for the $Sc_3N@C_{84}$ complex, 0.48 eV.

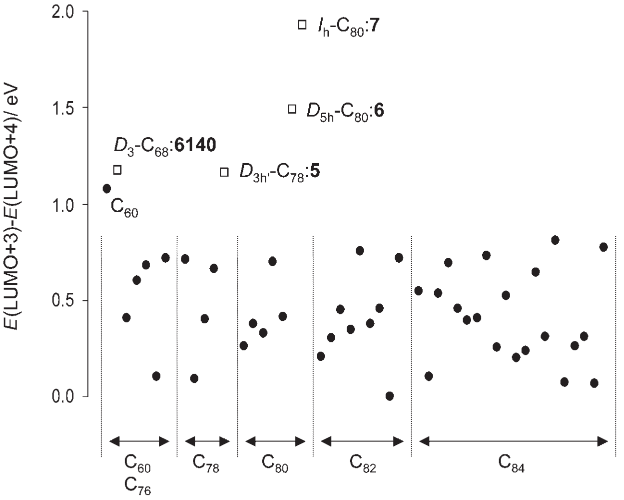

Figure 3. The (LUMO + 3)–(LUMO + 4) gap for all IPR isomers from C_{60} to C_{84} and also the non-IPR D_3-C_{68}:**6140**. Only isomers with the gap larger than 1 eV have been capable of encapsulating TNT units.

In summary, we propose an easy way of determining which fullerene cages will be capable of encapsulating TNTs based on the electronic structure of the free fullerene cages. All TNT endohedral metallofullerenes are formed by the encapsulation of a metallic nitride template inside one of the following cages: D_3-C_{68}:**6140**; $D_{3h'}$-C_{78}:**5**; D_{5h}-C_{80}:**6**; I_h-C_{80}:**7**. None of these cages has ever been isolated or detected experimentally. $Sc_3N@C_k$ ($k = 68$, 78, 80) complexes may be formally described by the ionic model $Sc_3N^{6+}@C_k^{6-}$. A total of six electrons formally transfer from the three highest occupied TNT orbitals to three low-lying unoccupied cage orbitals. The resulting endohedral complex has a relatively large HOMO–LUMO gap, which gives it stability. We have shown that the final HOMO–LUMO gap of these TNT endohedral metallofullerenes can be estimated from the (LUMO + 3)–(LUMO + 4) gap found in the free cages, which corresponds to the hypothetical anion when six additional electrons are added to the free cage, C_k^{6-}. The search for large (LUMO + 3)–(LUMO + 4) gaps (> 1 eV) in the 51 IPR fullerene isomers from C_{60} to C_{84} revealed that only C_{60}, D_{3h}-C_{78}:**5**, D_{5h}-C_{80}:**6**, and I_h-C_{80}:**7** provide a suitable electronic structure for encapsulating the TNTs. From the geometrical point of view, C_{60} is the only fullerene cage limited by having a cavity too small to encapsulate a four-atom unit. Furthermore, on principle we can predict that no other IPR fullerene cages between C_{60} and C_{84} will be capable of encapsulating a TNT. At least, they will not be as stable as the TNT complexes already known now. The non-IPR D_3-C_{68}:**6140** cage also obeys the (LUMO + 3)–(LUMO + 4) rule. Therefore, the search for new fullerene cages that encapsulate TNTs must be focused on non-IPR fullerenes only.

Experimental Section

Methods: The calculations were carried out by using DFT methodology with the ADF2000 program.[28] The local-density approximation (LDA) characterized by the electron-gas exchange together with the Vosko–Wilk–Nusair (VWN) parameterization[29] for correlation were used. Gradients were corrected by means of the Becke[30] and Perdew[31] non-local corrections to the exchange and correlation energy, respectively. First-order Pauli scalar relativistic corrections were added in variation to the total energy for all systems. Triple-ζ polarization Slater basis sets were employed to describe the valence electrons of C, Sc, and N atoms.[32] The geometries of all fullerene cages have been extracted from the Fullerene Structure Library constructed by Mitsuho Yoshida.[33] Single-point calculations were used for all empty cages except for the free cages D_3-C_{68}:**6140**, $D_{3h'}$-C_{78}:**5**, I_h-C_{80}:**7**, and the TNT endohedral complexes, which were fully optimized.

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