Endohedral Fullerenes

DOI: 10.1002/anie.200603281

Violating the Isolated Pentagon Rule (IPR): The Endohedral Non-IPR C_{70} Cage of $Sc_3N@C_{70}$**

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Endohedral fullerenes are a form of fullerenes in which atoms, ions, or clusters are trapped in their interior.[1–5] They exhibit a variety of new structural, magnetic, and electronic properties that are important for potential applications in electronics and medicine.[1–7] Numerous endohedral fullerenes with various encaged species and various forms of the carbon cage have been isolated recently. The latter exhibits a large variety of cavity sizes ranging from C_{60} to C_{100}.[1–12] There have even been cages reported that do not obey the isolated pentagon rule (IPR). These non-IPR cages include $Sc_2@C_{66}$,[8] $Sc_3N@C_{68}$,[9,11c] $Sc_2C_2@C_{68}$,[13] and $La_2@C_{72}$.[14] C_{70} fullerenes are a peculiar species because up to now only noble-gas atoms (He, Ne, Ar, Kr, Xe),[15] N,[16] and P[16a] have been encapsulated inside the C_{70} cage. The metal atoms that typically form endohedral fullerenes with other cages[1–12] have not yet been entrapped in C_{70}. Besides $Sc_3N@C_{68}$, the trimetallic nitride endohedral fullerenes (cluster fullerenes) exhibit a large variety of cage sizes;[3,5,11,12] however, a $M_3N@C_{70}$ species is missing.

Herein we report the synthesis of the first endohedral cluster fullerene of C_{70}, namely, $Sc_3N@C_{70}$, by the "reactive gas atmosphere" method and its isolation by two-step HPLC. We present the first spectroscopic studies of $Sc_3N@C_{70}$ as well as the elucidation of its structure by a combination of experimental methods and DFT computations. These results show that this fullerene cage does not follow the IPR as the first example of this for C_{70}.

$Sc_3N@C_{70}$ was produced along with several known $Sc_3N@C_{2n}$ ($2n = 68$, 78, 80) cluster fullerenes according to the "reactive gas atmosphere" method[3,5,11c,12a] and was isolated by two-step HPLC (see the Supporting Information). In the first-step HPLC, $Sc_3N@C_{70}$ was eluted on Buckyprep column together with C_{84}, which was subsequently removed in the second-step HPLC on a Buckyclutcher column (see the Supporting Information). HPLC and MS analysis showed the purity of the isolated $Sc_3N@C_{70}$ ($t_R = 21.5$ min, m/z 989) to be higher than or equal to 99%, (Figure 1), which was crucial for the further spectroscopic characterization. The good agreement of the measured isotope distribution of $Sc_3N@C_{70}$ with the calculated one confirms the proposed composition (inset of Figure 1b). The yield of $Sc_3N@C_{70}$ is only 1.8% of that of $Sc_3N@C_{68}$ (see the Supporting Information).

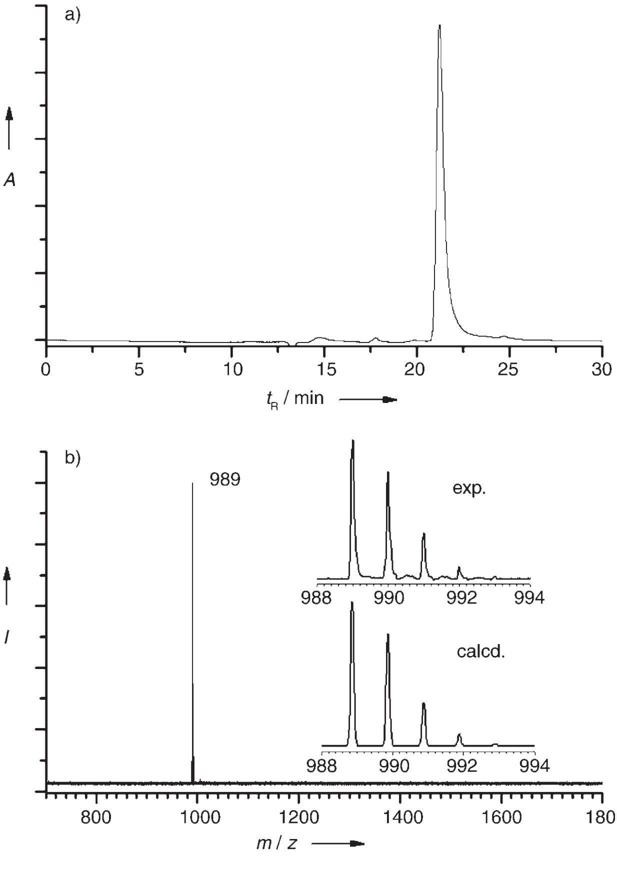

Figure 1. a) Chromatogram of $Sc_3N@C_{70}$ (10×250 mm Buckyclutcher column; flow rate 1.0 mL min^{-1}; injection volume 500 μL; toluene as eluent; 20°C; A: absorbance, t_R: retention time). b) Positive-ion laser desorption time-of-flight (LD-TOF) mass spectrum of $Sc_3N@C_{70}$. The insets show the experimental and calculated isotope distributions of $Sc_3N@C_{70}$.

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[**] We cordially thank K. Leger, S. Schiemenz, F. Ziegs, and H. Zöller for technical assistance as well as Prof. Chunru Wang (Institute of Chemistry, Chinese Academy of Sciences) for the program generating fullerene isomers. S.Y. thanks the Alexander von Humboldt Foundation for financial support. Financial support from the DAAD and the CRDF (grant RUC2-2830-MO-06) and computer time at the Research Computing Center of the Moscow State University for A.P. are gratefully acknowledged.

Supporting information for this article is available on the WWW under http://www.angewandte.org or from the author.

The UV/Vis/NIR spectrum of $Sc_3N@C_{70}$ dissolved in toluene shows a spectral onset of 960 nm (Figure 2), which corresponds to an optical band gap of 1.3 eV[1–12] and indicates that $Sc_3N@C_{70}$ is a stable fullerene. The optical band gap of $Sc_3N@C_{70}$ is larger than those of $Sc_3N@C_{68}$ (1.1 eV) and $Sc_3N@C_{78}$ (1.0 eV) but smaller than those of $Sc_3N@C_{80}$ (I) (1.7 eV) and $Sc_3N@C_{80}$ (II) (1.6 eV).[9,11c,12a,17–19] The electronic absorption spectrum of $Sc_3N@C_{70}$ has less features than that of its neighboring cluster fullerene $Sc_3N@C_{68}$.[11c] The strongest absorption of $Sc_3N@C_{70}$ lies at 696 nm along with several shoulder peaks at 468, 558, 807, and 894 nm (inset of Figure 2), which are in general red-shifted relative to those of $Sc_3N@C_{68}$.[11c] Accordingly, the color of $Sc_3N@C_{70}$ in toluene (green-yellow) is quite different from those of $Sc_3N@C_{68}$ (purple), $Sc_3N@C_{78}$ (dark green), and $Sc_3N@C_{80}$ (I) (orange).

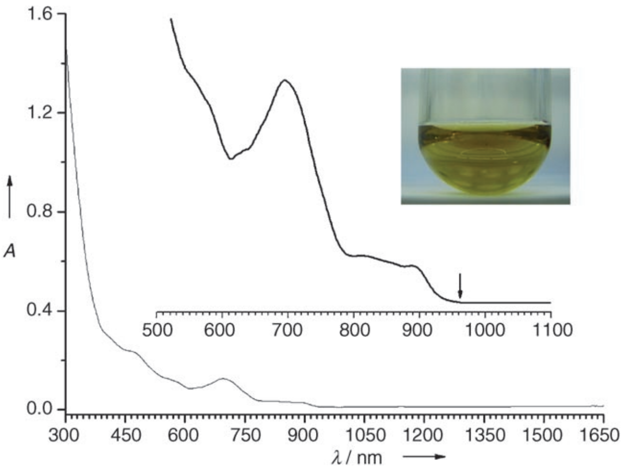

Figure 2. UV/Vis/NIR spectrum of $Sc_3N@C_{70}$ in toluene. The insets show a magnification in the spectral range 500–1100 nm and a photograph of a solution of $Sc_3N@C_{70}$ in toluene. The arrow marks the spectral onset.

The FTIR spectrum of $Sc_3N@C_{70}$ (Figure 3 a) exhibits significant differences from those of $Sc_3N@C_{68}$ (D_3), $Sc_3N@C_{78}$ (D_{3h}), $Sc_3N@C_{80}$ (I, I_h), and $Sc_3N@C_{80}$ (II, D_{5h}), which we have previously reported (see the Supporting Information).[3,5,11c,12a,e] The spectrum of $Sc_3N@C_{70}$ exhibits more lines than $Sc_3N@C_{80}$ (I, II),[12a] which suggests a lower cage symmetry of $Sc_3N@C_{70}$. Note that the overall spectral pattern of $Sc_3N@C_{2n}$ cluster fullerenes, which is mostly determined by the tangential and radial cage modes,[3,5,11c,12a,e,20] is highly sensitive to the structure of the fullerene (see the Supporting Information). This high sensitivity to structural differences makes IR spectroscopy a powerful tool for the structural analysis of the cluster fullerenes.[3–5,11,12,20]

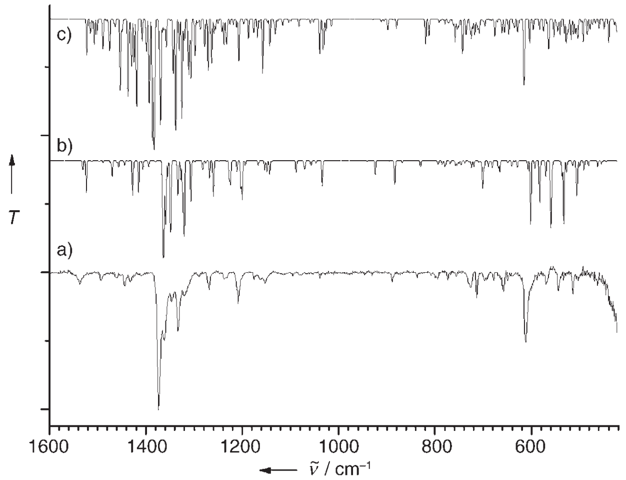

Figure 3. a) Experimental FTIR spectrum of $Sc_3N@C_{70}$. Calculated IR spectra of b) the non-IPR isomer C_{2v}:7854 $Sc_3N@C_{70}$ and c) the IPR-isomer D_{5h}:8149 $Sc_3N@C_{70}$. *T*: transmission.

To elucidate the cage symmetry of $Sc_3N@C_{70}$, the IPR-obeying D_{5h}-symmetric cage (isomer 8149) was considered first and its molecular structure and IR spectrum were calculated at the DFT level. The computed IR spectrum of $Sc_3N@C_{70}$ (D_{5h}:8149) (Figure 3 c) quite clearly does not fit the experimental spectrum. Moreover, the HOMO–LUMO gap of $Sc_3N@C_{70}$ (D_{5h}:8149) calculated by DFT is only 0.53 eV (see the Supporting Information; HOMO: highest occupied molecular orbital, LUMO: lowest unoccupied molecular orbital), which is substantially smaller than the measured value.[21] Thus, for $Sc_3N@C_{70}$ both the HOMO–LUMO gap and the IR spectrum rule out the IPR-obeying D_{5h}-symmetric cage (isomer 8149). Hence, an appropriate non-IPR cage (out of the 8148 non-IPR isomers of C_{70}[22]) must be considered as the cage structure of $Sc_3N@C_{70}$.

The IPR disfavors the formation of fullerene isomers with edge-sharing pentagons because of the increased local strain of the carbon atoms at the shared edges. This rule is valid for uncharged carbon cages in which the number of π electrons equals the number of carbon atoms.[22] The driving force for the formation of Sc_3N-encapsulating cluster fullerenes is the formal transfer of six electrons from the cluster to the LUMO of the fullerene.[11c,12e,23] Thus, up to six carbon atoms in the sixfold-charged cages may formally have sp^3 hybridization, which leads to a violation of the IPR. Encapsulation of a metal or cluster may result in an additional stabilization of formally sp^3-hybridized carbon atoms[8,9,11c,13,14] and thus allow non-IPR cages to be stable, as has been already demonstrated for four non-IPR cages.[24] Hence, it is reasonable to assume that the cage hosting the Sc_3N cluster should have no more than three pairs of edge-sharing pentagons, which should be located on the cage in such a way that their coordination to the Sc atoms of the cluster is possible.

According to the above criteria, 116 isomers with three or less pairs of adjacent pentagons can be considered to be preferable among 8148 non-IPR isomers of C_{70} (see the Supporting Information). We performed DFT optimization of the hexaanions of all these isomers.[25] The largest HOMO–LUMO gap (1.24 eV) and the highest stability was found for the sixfold-charged state of the isomer C_{2v}:7854, which is about 43 kJ mol^{-1} lower in energy than D_{5h}:8149.[26] C_{2v}:7854 is the only isomer among the 116 isomers that has a HOMO–LUMO gap above 1 eV (see the Supporting Information).

Encapsulation of the Sc_3N cluster results in an additional stabilization of the C_{2v}:7854 cage. According to DFT calculations, $Sc_3N@C_{70}$ (C_{2v}:7854) (Figure 4) is 164 kJ mol^{-1} more stable than $Sc_3N@C_{70}$ (D_{5h}:8149). The calculated HOMO–LUMO gap of $Sc_3N@C_{70}$ (C_{2v}:7854) is 1.29 eV, which is almost

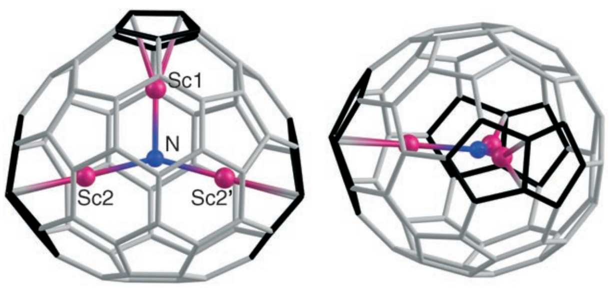

Figure 4. DFT-optimized structure of $Sc_3N@C_{70}$ (C_{2v}:7854). The three pairs of the adjacent pentagons are highlighted in black.

the same as that of the hexaanion of empty C_{70}. The arrangement of the adjacent pentagons gives the Sc_3N cluster C_{2v} symmetry, and it is thus significantly distorted from an equilateral-triangle configuration. The Sc1-N-Sc2 and Sc2-N-Sc2′ angles of the DFT-optimized structure are 105° and 150°, respectively, whereas the Sc1–N and Sc2–N bond lengths are 1.987 and 2.060 Å, respectively (see also the Supporting Information).

The DFT-simulated IR spectrum of $Sc_3N@C_{70}$ (C_{2v}:7854) is compared with the experimental spectrum in Figure 3. Unlike for $Sc_3N@C_{70}$ (D_{5h}:8149), the computed spectrum of $Sc_3N@C_{70}$ (C_{2v}:7854) (Figure 3b) agrees perfectly with the experimental spectrum (Figure 3a) in the ranges of both the tangential and the radial cage modes (see the Supporting Information).[27] Therefore, on the basis of both the analysis of the HOMO–LUMO gap and the IR spectrum, the cage structure of $Sc_3N@C_{70}$ is assigned as the C_{2v}:7854 isomer.

In summary, we have synthesized $Sc_3N@C_{70}$, the first non-IPR cage of C_{70} hosting a cluster. $Sc_3N@C_{70}$ is a stable fullerene with a large band gap of 1.3 eV. The FTIR spectrum in combination with DFT calculations confirm the assignment of the non-IPR isomer C_{2v}:7854 as the cage structure of $Sc_3N@C_{70}$. Thus, besides $Sc_3N@C_{68}$, $Sc_3N@C_{70}$ provides a further example of stabilization of non-IPR cages by encapsulation of an asymmetrical Sc_3N cluster, which differs from all other reported symmetrical Sc_3N-based cluster fullerenes. With $Sc_3N@C_{70}$ representing the fifth member of the non-IPR endohedral fullerene family, this study provides new insight into non-IPR features of endohedral fullerenes.

Experimental Section

The general procedures for the synthesis of $Sc_3N@C_{70}$ by a modified Krätschmer–Huffman DC-arc discharging method with the addition of NH_3 (20 mbar) have been described elsewhere.[3,5,11,12] Separation of the cluster fullerenes was performed by two-step HPLC (Hewlett–Packard 1100) with toluene as the eluent. In the first step, a linear combination of two analytical Buckyprep columns (4.6 × 250 mm; Nacalai Tesque) was applied. The second isolation step was performed on a semipreparative Buckyclutcher column (10 × 250 mm; Regis, USA). A UV detector set to 320 nm was used for detection of the fullerene. The purity of the isolated products was checked by HPLC on the same Buckyclutcher column, followed by LD-TOF MS analysis (Biflex III, Bruker) running in both positive- and negative-ion modes. Sample preparation and experimental details for UV/Vis/NIR and FTIR spectroscopic measurements were described previously.[3,5,11,12]

DFT computations were performed with the PRIRODA package[28] employing the PBE density functional[29] and the implemented TZ2P-quality basis set with effective-core potential for Sc atoms.[30]

Received: August 10, 2006
Revised: October 15, 2006

Keywords: endohedral fullerenes · isolated pentagon rule · nitride clusters · quantum chemical calculations · vibrational spectroscopy

[1] L. Dunsch, S. Yang, *Electrochem. Soc. Interface* **2006**, *15*, 34–39.
[2] a) H. Shinohara, *Rep. Prog. Phys.* **2000**, *63*, 843–892; b) *Endofullerenes: A New Family of Carbon Clusters* (Eds.: T. Akasaka, S. Nagase), Kluwer, Dordrecht, **2002**.
[3] L. Dunsch, M. Krause, J. Noack, P. Georgi, *J. Phys. Chem. Solids* **2004**, *65*, 309–315.
[4] S. F. Yang, L. Dunsch, *Angew. Chem.* **2006**, *118*, 1321–1324; *Angew. Chem. Int. Ed.* **2006**, *45*, 1299–1302.
[5] For a review, see: L. Dunsch, S. Yang, *Small*, submitted.
[6] S. H. Yang, *Trends Chem. Phys.* **2001**, *9*, 31–43.
[7] S. F. Yang, L. Z. Fan, S. H. Yang, *J. Phys. Chem. B* **2004**, *108*, 4394–4404.
[8] C. R. Wang, T. Kai, T. Tomiyama, T. Yoshida, Y. Kobayashi, E. Nishibori, M. Takata, M. Sakata, H. Shinohara, *Nature* **2000**, *408*, 426–427.
[9] S. Stevenson, P. W. Fowler, T. Heine, J. C. Duchamp, G. Rice, T. Glass, K. Harich, E. Hajdu, R. Bible, H. C. Dorn, *Nature* **2000**, *408*, 427–428.
[10] C. R. Wang, T. Kai, T. Tomiyama, T. Yoshida, Y. Kobayashi, E. Nishibori, M. Takata, M. Sakata, H. Shinohara, *Angew. Chem.* **2001**, *113*, 411–413; *Angew. Chem. Int. Ed.* **2001**, *40*, 397–399.
[11] a) S. F. Yang, L. Dunsch, *J. Phys. Chem. B* **2005**, *109*, 12320–12328; b) S. F. Yang, L. Dunsch, *Chem. Eur. J.* **2006**, *12*, 413–419; c) S. F. Yang, M. Kalbac, A. Popov, L. Dunsch, *Chem. Eur. J.* **2006**, *12*, 7856–7862; d) S. F. Yang, M. Kalbac, A. Popov, L. Dunsch, *ChemPhysChem* **2006**, *7*, 1990–1995.
[12] a) M. Krause, L. Dunsch, *ChemPhysChem* **2004**, *5*, 1445–1449; b) M. Krause, J. Wong, L. Dunsch, *Chem. Eur. J.* **2005**, *11*, 706–711; c) M. Krause, L. Dunsch, *Angew. Chem.* **2005**, *117*, 1581–1584; *Angew. Chem. Int. Ed.* **2005**, *44*, 1557–1560; d) M. Krause, X. Liu, J. Wong, T. Pichler, M. Knupfer, L. Dunsch, *J. Phys. Chem. A* **2005**, *109*, 7088–7093; e) M. Krause, A. Popov, L. Dunsch, *ChemPhysChem* **2006**, *7*, 1734–1740.
[13] Z. Q. Shi, X. Wu, C. R. Wang, X. Lu, H. Shinohara, *Angew. Chem.* **2006**, *118*, 2161–2165; *Angew. Chem. Int. Ed.* **2006**, *45*, 2107–2111.
[14] a) H. Kato, A. Taninaka, T. Sugai, H. Shinohara, *J. Am. Chem. Soc.* **2003**, *125*, 7782–7783; b) C. M. Beavers; T. Zuo, J. C. Duchamp, K. Harich, H. C. Dorn, M. M. Olmstead, A. L. Balch, *J. Am. Chem. Soc.* **2006**, *128*, 11352–11353.
[15] a) M. Saunders, H. A. Jimenezvaquez, R. J. Cross, S. Mroczkowski, D. I. Freedberg, F. A. L. Anet, *Nature* **1994**, *367*, 256–258; b) M. Saunders, H. A. Jimenezvaquez, R. J. Cross, S. Mroczkowski, M. L. Cross, D. E. Giblin, R. J. Poreda, *J. Am. Chem. Soc.* **1994**, *116*, 2193–2194.
[16] a) E. Dietel, A. Hirsch, B. Pietzak, M. Waiblinger, K. Lips, A. Weidinger, A. Gruss, K. P. Dinse, *J. Am. Chem. Soc.* **1999**, *121*, 2432–2437; b) K. Lips, M. Waiblinger, B. Pietzak, A. Weidinger, *Mol. Mater.* **2000**, *13*, 217–224.
[17] S. Stevenson, G. Rice, T. Glass, K. Harich, F. Cromer, M. R. Jordan, J. Craft, E. Hajdu, R. Bible, M. M. Olmstead, K. Maitra, A. J. Fisher, A. L. Balch, H. C. Dorn, *Nature* **1999**, *401*, 55–57.

[18] L. Dunsch, P. Georgi, M. Krause, C. R. Wang, *Synth. Met.* **2003**, *135*, 761–762.

[19] M. M. Olmstead, A. Bettencourt-Dias, J. C. Duchamp, S. Stevenson, D. Marciu, H. C. Dorn, A. L. Balch, *Angew. Chem.* **2001**, *113*, 1263–1265; *Angew. Chem. Int. Ed.* **2001**, *40*, 1223–1225.

[20] M. Krause, H. Kuzmany, P. Georgi, L. Dunsch, K. Vietze, G. Seifert, *J. Chem. Phys.* **2001**, *115*, 6596–6605.

[21] It is well known that DFT calculations systematically underestimate the HOMO–LUMO gap; however, the code that we used underestimated the energy gaps of $Sc_3N@C_{68}$ and $Sc_3N@C_{78}$ by only 0.2 eV (see references [11c,12e]). If the underestimation for $Sc_3N@C_{70}$ is comparable or even higher (up to 0.5 eV), the predicted HOMO–LUMO gap would still be less than 1 eV and therefore much smaller than the measured value (1.3 eV).

[22] As the number of non-IPR isomers of C_{70} (8148, see P. W. Fowler, D. E. Manolopoulos, *An Atlas of Fullerenes*, Clarendon Press, Oxford, **1995**) is very high, it was necessary to establish some criteria to exclude those non-IPR cages that are highly strained and unfavorable, and consequently to reduce the set of probable structures.

[23] J. M. Campanera, C. Bo, J. M. Poblet, *Angew. Chem.* **2005**, *117*, 7396–7399; *Angew. Chem. Int. Ed.* **2005**, *44*, 7230–7233.

[24] These include $Sc_2@C_{66}$, $Sc_3N@C_{68}$, $Sc_2C_2@C_{68}$, and $La_2@C_{72}$. In all these cases the pairs of adjacent pentagons are coordinated to the endohedral metal atoms.

[25] Since in trimetallic nitride cluster fullerenes six electrons of the cluster are formally transferred to the carbon cage, the analysis of the relative energies and HOMO–LUMO gaps in hexaanions (rather than in the neutrally charged isomers) is reasonable (see also references [11c,12e,22]).

[26] The neutral form of the C_{2v}:7854 isomer of C_{70} is 369 $kJ\,mol^{-1}$ less stable than the IPR isomer of C_{70} (D_{5h}:8149).

[27] Similarly good agreements of the DFT-simulated IR spectra with the measured ones were observed for $Sc_3N@C_{68}$ (D_3) and $Sc_3N@C_{78}$ (D_{3h}). The systematic underestimation of the computed frequencies of these latter compounds was already documented (see references [11c,12e]) to be around 10 cm^{-1}. Thus, the code used for DFT calculations is reliable and the assignment of the cage structure by this method is confirmed.

[28] D. N. Laikov, *Chem. Phys. Lett.* **1997**, *281*, 151–156.

[29] J. P. Perdew, K. Burke, M. Ernzerhof, *Phys. Rev. Lett.* **1996**, *77*, 3865–3868.

[30] **Note added in proof** (December 14, 2006): recently, two new non-IPR endohedral fullerenes were reported. a) $Tb_3N@C_{84}$: C. M. Beavers, T. Zuo, J. C. Duchamp, K. Harich, H. C. Dorn, M. M. Olmstead, A. L. Balch, *J. Am. Chem. Soc.* **2006**, *128*, 11352–11353; b) $La@C_{72}$: T. Wakahara, H. Nikawa, T. Kikuchi, T. Nakahodo, G. M. A. Rahman, T. Tsuchiya, Y. Maeda, T. Akasaka, K. Yoza, E. Horn, K. Yamamoto, N. Mizorogi, Z. Slanina, S. Nagase, *J. Am. Chem. Soc.* **2006**, *128*, 14228–14229..