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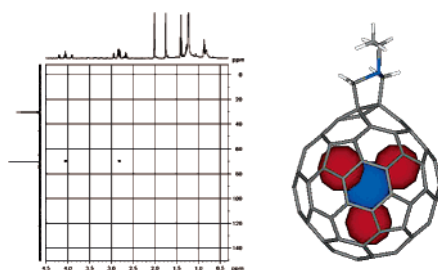
The First Fulleropyrrolidine Derivative of Sc₃N@C₈₀: Pronounced Chemical Shift Differences of the Geminal Protons on the Pyrrolidine Ring

Claudia M. Cardona, Alex Kitaygorodskiy, Angy Ortiz, M. Ángeles Herranz, and Luis Echegoyen*

Department of Chemistry, Clemson University, Clemson, South Carolina 29634

luis@clemson.edu

The first pyrrolidine adduct on Sc₃N@C₈₀ was synthesized and fully characterized. Addition of the *N*-ethylazomethine ylide occurs regioselectively on a [5,6] double bond on the surface of the icosahedral symmetry Sc₃N@C₈₀, exactly in the same position as that described previously for a Diels−Alder adduct of the same compound.[11a,b] This addition pattern results in symmetric pyrrolidine carbons and unsymmetric geminal hydrogens on the pyrrolidine ring, as confirmed by ¹H and ¹³C NMR spectroscopy, especially by HMQC. The shielding environment experienced by these geminal hydrogens differs by 1.26 ppm, indicative of pronounced ring current effects on the surface of this endohedral fullerene. This represents the first fully characterized pyrrolidine adduct on an endohedral metallofullerene.

Introduction

The study of endohedral metallofullerenes is quickly becoming one of the most interesting research areas within the field of carbon-based compounds.[1] Even though mass spectrometric evidence of their existence was already available in the first paper reporting the discovery of Buckminsterfullerene in 1985,[2] there was contro-versy about the location of the metals, since fullerenes with exohedral metals were also observed. It was not until 1991 that Smalley and co-workers unequivocally showed that a lanthanum atom was encapsulated in a C₈₂ fullerene shell,[3] and since then, many analogous species have been isolated.

Many of these fullerenes present some interesting characteristics: they are stable under ambient conditions; their electronic structures differ greatly when compared to those of the parent empty cages; and they have the ability to carry metals with magnetic or radioactive properties. Thus, they have many potential applications in the fields of biomedical and nanomaterial sciences.[4]

Some of these metallofullerenes have unusual structural features, and there is a lot of interest in the stability that the encapsulated moiety confers to the fullerene cage.[5] Dramatic examples include Sc₂@C₆₆ and Sc₃N@C₆₈

* To whom correspondence should be addressed.

(1) (a) Kobayashi, K.; Nagase, S. In *Endofullerenes*: *A New Family of Carbon Clusters*; Akasaka, T., Nagase, S., Eds.; Kluwer Academic Publishers: Dordrecht, The Netherlands, 2002; pp 99−119. (b) Wakahara, T.; Akasaka, T.; Kobayashi, K.; Nagase, S. In *Endofullerenes*: *A New Family of Carbon Clusters*; Akasaka, T., Nagase, S., Eds.; Kluwer Academic Publishers: Dordrecht, The Netherlands, 2002; pp 231−251. (c) Shinohara, H. In *Fullerenes*: *Chemistry*, *Physics*, *and Technology*; Kadish, K. M., Ruoff, R. S., Eds.; John Wiley and Sons: New York, 2000; pp 357−393. (d) Nagase, S.; Kobayashi, K.; Akasaka, T.; Wakahara, T. In *Fullerenes*: *Chemistry*, *Physics*, *and Technology*; Kadish, K. M., Ruoff, R. S., Eds.; John Wiley and Sons: New York, 2000; pp 395−436. (e) Shinohara, H. *Rep. Prog. Phys.* **2000**, *63*, 843−892.

(2) (a) Kroto, H. W.; Heath, J. R.; O'Brien, S. C.; Curl, R. F.; Smalley, R. E. *Nature* **1985**, *318*, 162−163. (b) Heath, J. R.; O'Brien, S. C.; Zhang, Q.; Liu, Y.; Curl, R. F.; Kroto, H. W.; Tittel, F. K.; Smalley, R. E. *J. Am. Chem. Soc.* **1985**, *107*, 7779−7780.

(3) Chai, Y.; Guo, T.; Jin, C.; Haufler, R. E.; Chibante, L. P. F.; Fure, J.; Wang, L.; Alford, M.; Smalley, R. E. *J. Phys. Chem.* **1991**, *95*, 7564−7568.

species,[6] both of which have been isolated and whose fullerene cages do not obey the isolated pentagon rule (IPR). Other examples involve the constitutional isomers of C_{80}.[7] There are seven possible structural isomers satisfying the IPR, yet only the most stable empty cages with D_2 and D_{5d} symmetry have been isolated.[8] In contrast, the two least stable empty isomers with I_h and D_{5h} symmetries are the ones that predominate overwhelmingly when they are filled with metallic nitride clusters in the C_{80} cages.[9]

Over the past 15 years, research on metallofullerenes has advanced slowly due to the limited quantities of isolated material. This fact has restricted in-depth investigations of their properties and synthesis of their exohedral derivatives. Functionalization of the exterior of the cage is necessary to make these materials more useful in future applications and to fine-tune their electronic and physical properties. As of today, there are only a very few examples of derivatized endohedral metallofullerenes that have been isolated and fully characterized. In most cases, studies seem to indicate that metallofullerenes are very reactive toward organic functionalization, giving rise to multiple adducts or regioisomers of the monoadduct.[4a,10] Surprisingly, remarkable selectivity for specific regioisomeric mono-
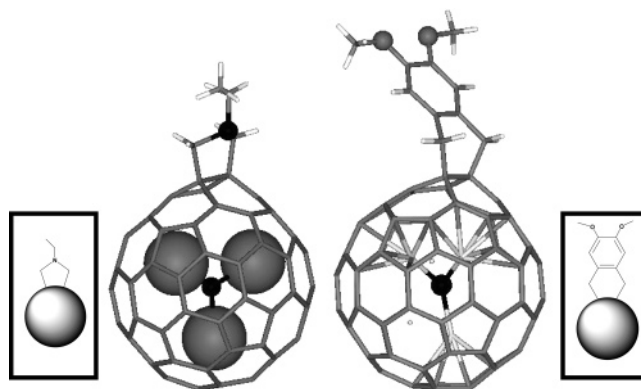
FIGURE 1. DS viewer representation of the *N*-ethyl endohedral fulleropyrrolidine of Sc₃N@C₈₀ (left) and the crystal structure of its Diels−Alder derivative (right); coordinates were downloaded from the original source.[11b] The location of the Sc₃N cluster in the fulleropyrrolidine adduct is only shown as an illustration.

adducts has been observed in two cases.[11] In one of these cases, Dorn and co-workers reported NMR and X-ray crystal data of a Diels−Alder monoadduct of Sc₃N@C₈₀, which is, to our knowledge, the only completely characterized derivative of this endohedral metallofullerene.[11a,b]

Here we report the 1,3-dipolar cycloaddition reaction of an azomethine ylide onto Sc₃N@C₈₀ to yield a pyrrolidine monoadduct.[12] The cycloaddition also seems to occur selectively at a corannulene-type site (a double bond at a [5,6] ring junction abutted by two hexagons) of the icosahedral C_{80} cage, as in the Diels−Alder case (Figure 1). A rather dramatic shielding effect of the methylene protons of the pyrrolidine moiety was observed, in contrast to the Diels−Alder case.

Results and Discussion

Dorn and co-workers first reported the family of encapsulated metallic nitride clusters inside fullerenes.[13] Their trimetallic nitride template (TNT) method to produce endohedral metallofullerenes has afforded macroscopic quantities of materials such as Sc₃N@C₈₀, with yields that exceed those of the abundant empty-cage C_{84}. The latter is the third most abundant fullerene, next to C_{60} and C_{70}, produced under normal conditions.[14] Their TNT method has resulted in the preparation of many other members of this interesting family of compounds.[15]

Isolation of Sc₃N@C₈₀ in macroscopic quantities has facilitated the study of its electronic structure,[15e,16] and all studies suggest a formal transfer of six electrons from

(4) (a) Tóth, É.; Bolskar, R. D.; Borel, A.; González, G.; Helm, L.; Merbach, A. E.; Shitaraman, B.; Wilson, L. J. *J. Am. Chem. Soc.* **2005**, *127*, 799−805. (b) Wilson, L. J.; Cagle, D. W.; Thrash, T. P.; Kennel, S. J.; Mirzadeh, S.; Alford, J. M.; Ehrhardt, G. J. *Coor. Chem. Rev.* **1999**, *190*−*192*, 199−207. (c) Cagle, D. W.; Kennel, S. J.; Mirzadeh, S.; Alford, J. M.; Wilson, L. J. *Proc. Natl. Acad. Sci. U.S.A.* **1999**, *96*, 5182−5187. (d) Thrash, T. P.; Cagle, D. W.; Alford, J. M.; Wright, K.; Ehrhardt, G. J.; Mirzadeh, S.; Wilson, L. J. *Chem. Phys. Lett.* **1999**, *308*, 329−336. (e) Bethune, D. S. *Physica B* **2002**, *323*, 90−96. (f) Bethune, D. S.; Johnson, R. D.; Salem, J. R.; de Vries, M. S.; Yannori, C. S. *Nature* **1993**, *366*, 123−128.

(5) Aihara, J. *J. Phys. Chem. A* **2002**, *106*, 11371−11374.

(6) (a) Wang, C.-R.; Kai, T.; Tomiyama, T.; Yoshida, T.; Kobayashi, Y.; Nishibori, E.; Takata, M.; Sakata, M.; Shinohara, H. *Nature* **2000**, *408*, 426−427. (b) Stevenson, S.; Fowler, P. W.; Heine, T.; Duchamps, J. C.; Rice, G.; Glass, T.; Harich, K.; Hajdull, E.; Bible, R.; Dorn, H. C. *Nature* **2000**, *408*, 427−428. (c) Olmstead, M. M.; Lee, T. M.; Duchamp, J. C.; Stevenson, S.; Marciu, D.; Dorn, H. C.; Balch, A. L. *Angew. Chem., Int. Ed.* **2003**, *42*, 900−903.

(7) (a) Furche, F.; Ahlrichs, R. *J. Chem. Phys.* **2001**, *114*, 10362−10367. (b) Ma, J.; Jiang, J.; Yuan, R.-K. *Z. Phys. D* **1997**, *42*, 289−292. (c) Fujita, M.; Kurita, N.; Nakao, K. *Synth. Met.* **1995**, *70*, 1509−1510. (d) Nakao, K.; Kurita, N.; Fujita, M. *Phys. Rev. B* **1994**, *49*, 11415−11420. (e) Klin, D. J.; Seitz, W. A.; Schmalz, T. G. *Nature* **1986**, *323*, 703−706.

(8) Hennrich, F. H.; Michel, R. H.; Fisher, A.; Richard-Schneider, S.; Gilb, S.; Kappes, M. M.; Fuchs, D.; Bürk, M.; Kobayashi, K.; Nagase, S. *Angew. Chem., Int. Ed. Engl.* **1996**, *35*, 1732−1734. (b) Wang, C.-R.; Sugai, T.; Kai, T.; Tomiyama, T.; Shinohara, H. *Chem. Commun.* **2000**, 557−558.

(9) (a) Yeretzian, C.; Hansen, K.; Alvarez, M. M.; Min, K. S.; Gillan, E. G.; Holczer, K.; Kaner, R. B.; Whetten, R. L. *Chem. Phys. Lett.* **1992**, *196*, 337−342. (b) Cao, B.; Hasegawa, M.; Okada, K.; Tomiyama, T.; Okazaki, T.; Suenaga, K.; Shinohara, H. *J. Am. Chem. Soc.* **2001**, *123*, 9679−9680. (c) Duchamp, J. C.; Demortier, A.; Fletcher, K. R.; Dorn, D.; Iezzi, E. B.; Glass, T.; Dorn, H. C. *Chem. Phys. Lett.* **2003**, *375*, 655−659. (d) Krause, M.; Dunsch, L. *Chem. Phys. Chem.* **2004**, *5*, 1445−1449.

(10) (a) Akasaka, T.; Kato, T.; Kobayashi, K.; Nagase, S.; Yamamoto, K.; Funasaka, H.; Takahashi, T. *Nature* **1995**, *374*, 600−601. (b) Cao, B.; Wakahara, T.; Maeda, Y.; Han, A.; Akasaka, T.; Kato, T.; Kobayashi, K.; Nagase, S. *Chem. Eur. J.* **2004**, *10*, 716−720. (c) Akasaka, T.; Nagase, S.; Kobayashi, K.; Suzuki, T.; Kato, T.; Kikuchi, K.; Achiba, Y.; Yamamoto, K.; Funasaka, H.; Takahashi, T. *Angew. Chem., Int. Ed. Engl.* **1995**, *34*, 2139−2141. (d) Kobayashi, K.; Nagase, S.; Maeda, Y.; Wakahara, T.; Akasaka, T. *Chem. Phys. Lett.* **2003**, *374*, 562−566. (e) Iezzi, E. B.; Cromer, F.; Stevenson, P.; Dorn, H. C. *Synth. Met.* **2002**, *128*, 289−291. (f) Bolskar, R. D.; Benedetto, A. F.; Husebo, L. O.; Price, R. E.; Jackson, E. F.; Wallace, S.; Wilson, L. J.; Alford, J. M. *J. Am. Chem. Soc.* **2003**, *125*, 5471−5478. (g) Lu, X.; He, X.; Feng, L.; Shi, Z.; Gu, Z. *Tetrahedron* **2004**, *60*, 3713−3716.

(11) (a) Iezzi, E. B.; Duchamp, J. C.; Harich, K.; Glass, T. E.; Lee, H. M.; Olmstead, M. M.; Balch, A. L.; Dorn, H. C. *J. Am. Chem. Soc.* **2002**, *124*, 524−525. (b) Lee, H. M.; Olmstead, M. M.; Iezzi, E.; Duchamp, J. C.; Dorn, H. C.; Balch, A. L. *J. Am. Chem. Soc.* **2002**, *124*, 3494−3495. (c) Maeda, Y.; Matsunaga, Y.; Wakahara, T.; Takahashi, S.; Tsuchiya, T.; Ishitsuka, M. O.; Hasegawa, T.; Akasaka, T.; Liu, M. T. H.; Kokura, K.; Horn, E.; Yoza, K.; Kato, T.; Okubo, S.; Kobayashi, K.; Nagase, S.; Yamamoto, K. *J. Am. Chem. Soc.* **2004**, *126*, 6858−6859.

(12) Maggini, M.; Scorrano, G.; Prato, M. *J. Am. Chem. Soc.* **1993**, *115*, 9798−9799.

(13) Stevenson, S.; Rice, G.; Glass, T.; Harich, K.; Cromer, F.; Jordan, M. R.; Craft, J.; Hadju, E.; Bible, R.; Olmstead, M. M.; Maltra, K.; Fisher, A. J.; Balch, A. L.; Dorn, H. C. *Nature* **1999**, *401*, 55−57.

(14) Krätschmer, W.; Lamb, L. D.; Fostiropoulus, K.; Huffman, D. R. *Nature* **1990**, *347*, 354−358.
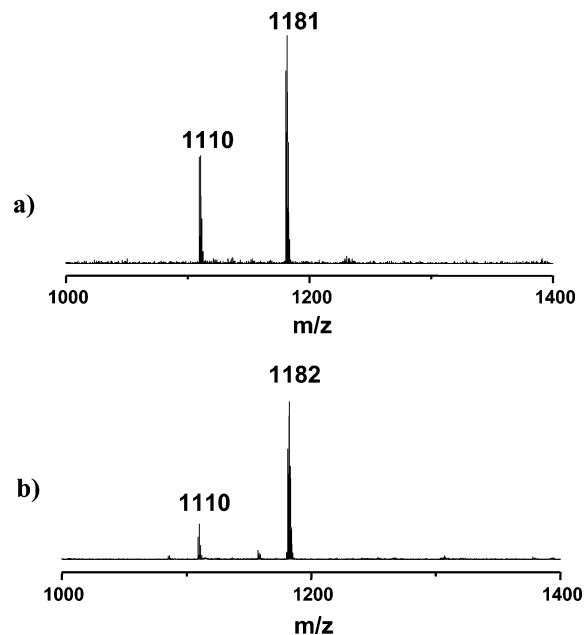
the Sc_3N moiety to the fullerene cage. In fact, an experimental report using photoemission and X-ray absorption spectroscopy determined an effective transfer of 6.3 electrons,[16c] and molecular orbital calculations predict that the HOMO is essentially a fullerene-based orbital while the Sc_3N fragment represents the LUMO of this endohedral metallofullerene.[16b] This electronic transfer from the encapsulated cluster to the fullerene cage is a common feature in endohedral metallofullerenes. A negative surface charge brings into question the reactivity of the carbon sphere and thus the feasibility of performing chemical derivatizations, such as dipolar addition reactions of azomethine ylides. Interestingly, azomethine ylides have been successfully added to the carbon cages of $La@C_{82}$ and $Ga@C_{82}$ metallofullerenes very recently. However, these reactions have resulted in mono- and multiadducts, but no specifics have been reported concerning the symmetry of the products and/or the sites of reaction.[10b,g] Thus characterization of these interesting derivatives remains a rather unexplored field in the area of endohedral fullerenes.

To our knowledge, there has only been one other report in a patent application of a pyrrolidine derivative of $Sc_3N@C_{80}$.[17] In this patent application, the authors indicated that refluxing for 24 h in o-dichlorobenzene (180 °C) was required for the synthesis of this derivative, and no characterization details were provided.

In our hands, $Sc_3N@C_{80}$ proved to be very reactive, and the pyrrolidine monoadduct was isolated in reasonable yields after 15 min of reaction at 120 °C from a solution of $Sc_3N@C_{80}$ (purified by HPLC) with an excess of N-ethyl glycine and paraformaldehyde in o-dichlorobenzene. We also carried out this reaction with ¹³C-enriched (99%) paraformaldehyde to investigate the site of reaction and the symmetry of the product. This reaction gave rise to a derivative that was ¹³C-labeled at one of the methylene carbons of the pyrrolidine ring, as depicted in Scheme 1.

The main product of the reaction was purified by column chromatography (SiO_2) and identified as the pyrrolidine monoadduct by MALDI-TOF MS (Figure 2), with the molecular ion at m/z 1181 (at m/z 1182 when ¹³C-enriched paraformaldehyde was employed). The mass spectrum also showed the parent metallofullerene, $Sc_3N@C_{80}$, at m/z 1110, from the fragmentation of the adduct after laser desorption ionization.

The ¹³C NMR of the ¹³C-enriched $Sc_3N@C_{80}$-fulleropyrrolidine exhibits a single signal at 70.09 ppm, indicating

(15) (a) Krause, M.; Wong, J.; Dunsch, L. Chem. Eur. J. 2005, 11, 706−711. (b) Stevenson, S.; Phillips, J. P.; Reid, J. E.; Olmstead, M. M.; Rath, S. P.; Balch, A. L. Chem. Commun. 2004, 2814−2815. (c) Iezzi, E. B.; Duchamp, J. C.; Fletcher, K. R.; Glass, T. E.; Dorn, H. C. Nano Lett. 2002, 2, 1187−1190. (d) Stevenson, S.; Lee, H. M.; Olmstead, M. M.; Kozikowski, C.; Stevenson, P.; Balch, A. L. Chem. Eur. J. 2002, 8, 4528−4535. (e) Krause, M.; Kuzmany, H.; Georgi, P.; Dunsch, L.; Vietze, K.; Seifert, G. J. Chem. Phys. 2001, 115, 6596−6605. (f) Macfarlane, R. M.; Bethune, D. S.; Stevenson, S.; Dorn, H. C. Chem. Phys. Lett. 2001, 343, 229−234. (g) Olmstead, M. M.; de Bettencourt-Dias, A.; Duchamp, J. C.; Stevenson, S.; Dorn, H. C. J. Am. Chem. Soc. 2000, 122, 12220−12226.
(16) (a) Alvarez, L.; Pichler, T.; Georgi, P.; Schwieger, T.; Peisert, H.; Dunsch, L.; Hu, Z.; Knupfer, M.; Fink, J.; Bressler, P.; Mast, M.; Golden, M. S. Phys. Rev. B 2002, 66, 035107-1−035107-7. (b) Campanera, J. M.; Bo, C.; Olmstead, M. M.; Balch, A. L.; Poblet, J. M. J. Phys. Chem. A 2002, 106, 12356−12364. (c) Gluch, K.; Feil, S.; Mattleubner, S.; Echt, O.; Scheier, P.; Märk, T. D. J. Phys. Chem. A 2004, 108, 6990−6995.
(17) Dorn, H. C.; Iezzi, E. B.; Duchamp, J. U.S. Patent Application 20040054151, March 18, 2004.

FIGURE 2. MALDI-MS of the products obtained with (a) unlabeled paraformaldehyde and with (b) ¹³C-labeled paraformaldehyde.

SCHEME 1. Depiction of the 1,3-Dipolar Cycloaddition of the N-Ethyl Azomethine Ylide to $Sc_3N@C_{80}$
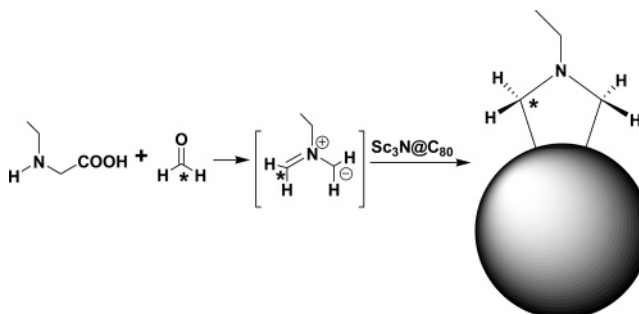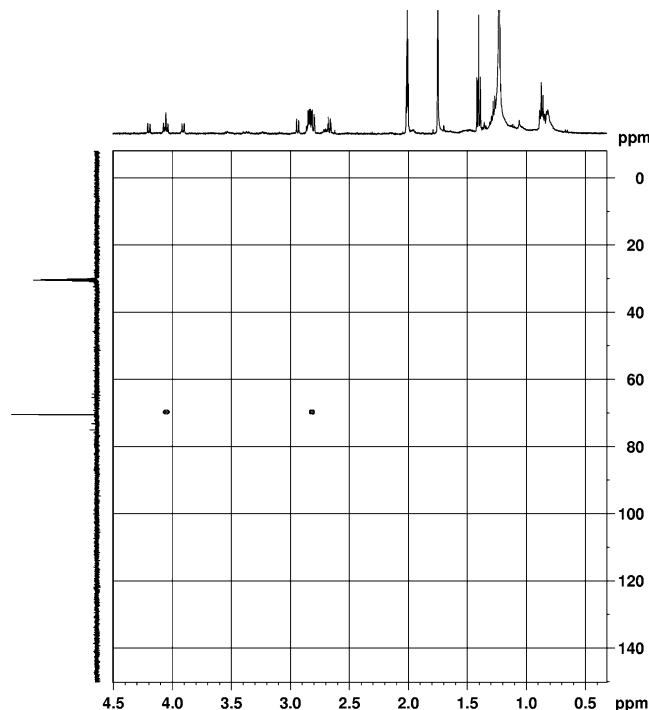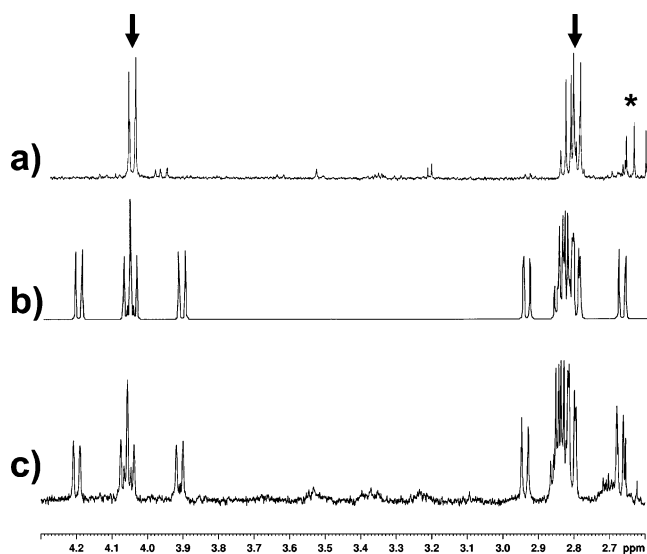

that both methylene carbons of the five-membered ring are equivalent. This suggests that there is a plane of symmetry through the metallofullerene monoadduct similar to that observed for the Diels−Alder derivative of $Sc_3N@C_{80}$.[11a] A Heteronuclear Multiple Quantum Coherence (HMQC) experiment also corroborated the presence of a plane of symmetry through the pyrrolidine derivative by showing that two types of geminal protons are attached to equivalent carbons (Figure 3). All of these data indicate that the 1,3-dipolar cycloaddition occurred at the same [5,6] double bond of the I_h isomer as in the Diels−Alder case.

Dorn et al. reported that the methylene protons of the Diels−Alder six-membered-ring adduct were not equivalent, and their resonances appeared at 3.41 and 3.57 ppm.[11a] For the pyrrolidine adduct described here, the geminal protons of the methylenes in the five-membered ring are also nonequivalent, but these exhibit a much more dramatic chemical shift difference ($\Delta\delta = 1.26$ ppm). As Figure 4a shows, these geminal resonances appear as doublets centered at δ 2.81 ($^2J = 9.9$ Hz) and 4.07 ($^2J = 9.9$ Hz).[18] The ¹H NMR of the ¹³C-enriched pyrrolidine derivative showed an interesting splitting pattern with

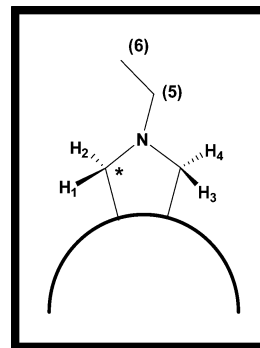**FIGURE 3.** HMQC spectrum of ¹³C-labeled Sc₃N@C₈₀ fulleropyrrolidine.

FIGURE 4. Comparison of the ¹H NMR spectra (Bruker 500 MHz) of the pyrrolidine products obtained from (a) unlabeled paraformaldehyde, (c) ¹³C-labeled paraformaldehyde, and (b) a simulation of spectrum c. The arrows indicate the geminal proton resonances. The asterisk indicates an impurity.

$^1J_{CH}$ of 134 and 145 Hz for the upfield and downfield geminal protons, respectively (Figure 4c). Simulation of the coupling pattern (Table 1, Figure 4b) indicates a different vicinal spin−spin coupling ($^3J_{CH}$ = 9 and 2.4 Hz) between the ¹³C atom and the geminal protons on the

(18) Since the value of $\nu_o\delta/^2J$ = 64 for the geminal protons of the pyrrolidine ring, the AX spin system notation was used and the chemical shifts were measured directly from the observed line frequencies (Günther, H. In *NMR Spectroscopy: Basic Principles, concepts, and applications in chemistry*, 2nd ed.; John Wiley& Sons: Chichester, UK 1995).

TABLE 1. *J* Couplings Employed in the Simulation of the ¹³C-Labeled ¹H NMR Spectrum Shown in Figure 4b (*g*-NMR V3.6)[a]

nucleus	group no.	δ (ppm)	J(Hz) 1	2	3	4	5	6
¹H	1	4.06						
	2	2.81	9.20					
	3	4.07	0.50	0.50				
	4	2.81	0.50	0.50	9.20			
	5	2.84	0.50	0.50	0.50	0.50		
	6	1.39	0.00	0.00	0.00	0.00	7.20	
¹³C	*	70.0	145.0	134.0	9.00	2.40	4.50	0.00

[a] The correlation between the geminal protons was clearly observed in the COSY spectrum of the fulleropyrrolidine (Supporting Information).

other carbon of the pyrrolidine ring. Different dihedral angles between these atoms in the conformation of the 5-membered ring may be the cause. The simulation also revealed a negligible, if at all, coupling between the two methylene groups of the pyrrolidine moiety, and between these methylenes and the methylene of the *N*-ethyl group. There is also a long-range effect on the resonances of the *N*-ethyl methylene group (δ 2.84 ppm, ^3J = 4.5 Hz) from the ¹³C-carbon of the pyrrolidine ring.

The large Δδ of these fulleropyrrolidine geminal hydrogens indicates that there is a pronounced deshielding/shielding effect on these protons, which may be caused by paramagnetic/diamagnetic ring currents on the surface of the cage, by an endohedral trimetallic nitride effect, or by a combination of the two.

Several examples of ring-current effects on fullerenes have been reported before. Wudl and co-workers observed an extreme ring-current effect on the chemical shifts of methano adducts directly attached to C₆₀.[19] The NMR spectrum of the geminal protons of the C₆₀-dihydrofulleroid derivative showed two doublet signals with a Δδ of 3.48 ppm. Wilson et al. have also observed such ring-current effects on pyrrolidine derivatives of C₇₀.[20] While an *N*-methyl fulleropyrrolidine adduct on C₆₀ exhibits symmetric carbons and symmetric geminal hydrogens (singlet resonance at 4.38 ppm),[12] three isomeric monoadducts are isolated for the reaction with C₇₀. One of these structures, the 7,8-isomer, exhibits an ¹H NMR spectrum that closely resembles the splitting pattern of the endohedral metallofulleropyrrolidine reported here.[18] This C₇₀ pyrrolidine monoadduct (Figure 5) has two equivalent

(19) (a) Suzuki, T.; Li, Q.; Khemani, K. C.; Wudl, F. *J. Am. Chem. Soc.* **1992**, *114*, 7301−7302. (b) Prato, M.; Suzuki, T.; Wudl, F.; Lucchini, V.; Maggini, M. *J. Am. Chem. Soc.* **1993**, *115*, 7876−7877.
(20) Wilson, S. R.; Lu, Q. *J. Org. Chem.* **1995**, *60*, 6496−6498.
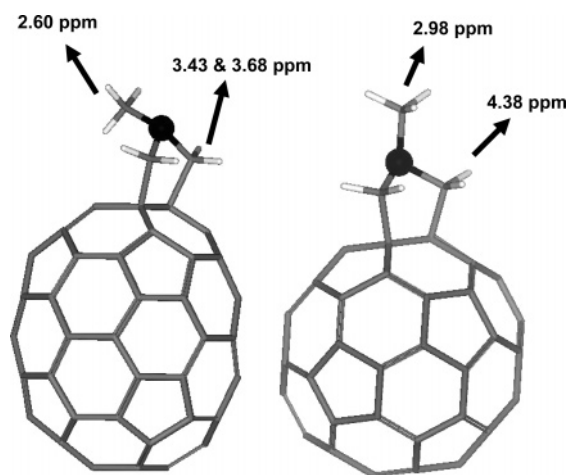
FIGURE 5. ^{1}H NMR resonances of the methylene protons and the *N*-methyl group on the 7,8-isomer of the C_{70} pyrrolidine adduct on the left, and on the C_{60} fulleropyrrolidine derivative on the right.
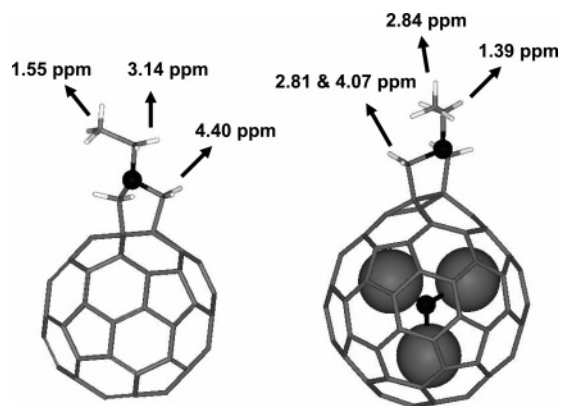
FIGURE 6. ^{1}H NMR resonances of the *N*-ethyl fulleropyrrolidine derivatives of C_{60} (left) and $Sc_3N@C_{80}$ (right).

methylene carbons each with two nonequivalent geminal hydrogens at δ 3.43 (J = 15.0 Hz) and 3.68 (J = 15.0 Hz). This NMR evidence indicates that the product has a plane of symmetry that bisects the pyrrolidine ring perpendicularly, but no such symmetry is observed for the environments in the front and back of the ring. This further confirms that addition to $Sc_3N@C_{80}$ occurred at the same bond as the Diels−Alder reaction occurred on the icosahedral cage. However, the degree of deshielding/shielding is much larger for the $Sc_3N@C_{80}$ pyrrolidine ($\Delta\delta$ of 1.26 ppm) when compared to the $\Delta\delta$ of 0.25 ppm observed for the 7,8-pyrrolidine adduct on C_{70}. Wilson also ascribed the shielding effect on the *N*-methyl group of the pyrrolidine derivative of C_{70} (2.60 ppm for the 7,8-isomer) to ring currents localized on the surface of the fullerene cage.[20] For comparison, the *N*-methyl protons of a fulleropyrrolidine on C_{60} appear at 2.98 ppm (Figure 5).[12]

Similarly, comparison of the *N*-ethyl ^{1}H NMR resonances of a C_{60} fulleropyrrolidine derivative with those of the *N*-ethyl group of the $Sc_3N@C_{80}$ derivative shows significant shielding for the latter. As Figure 6 depicts, the proton resonances of the ethyl group of the C_{60} derivative appear at δ 1.55 (t, 3H, CH_3, J = 7.3 Hz) and

3.14 ppm (q, 2H, CH_2, J = 7.3 Hz),[21] while those of the $Sc_3N@C_{80}$ pyrrolidine derivative are significantly shielded at 1.39 (t, 3H, CH_3, J = 7.2 Hz) and 2.84 ppm (q, 2H, CH_2, J = 7.2 Hz).

Interestingly, both the Diels−Alder and the pyrrolidine monoadducts of $Sc_3N@C_{80}$ yield products derived only from the icosahedral C_{80} isomer. There is no evidence for the presence of a D_{5h} $Sc_3N@C_{80}$ adduct product.[9c,d] Since the ylide addition reaction was performed on fullerene samples known to contain substantial quantities of $Sc_3N@C_{78}$ as well (see the Supporting Information), it is important to note that no products derived from this compound were isolated.

As stated earlier, the shielding/deshielding effects observed for the methylene resonances of the pyrrolidine adduct on $Sc_3N@C_{80}$ may also originate or have contributions from the encapsulated trimetallic nitride moiety. However, computational studies seem to indicate that long time-scale experiments, such as ^{13}C NMR, can only detect the cage symmetry, and distortions of the endohedral Sc_3N are averaged out over time by its motion.[22] Nonetheless, modification of the cage by an adduct may distort the geometry of the trapped cluster, and provoke a change of its motion or even fix its position within the cage. Attributing this shielding effect to the trimetallic moiety can only be corroborated by preparing other fulleropyrrolidine derivatives with different trimetallic nitride groups inside, provided that the addends are attached to the same site on the cage. We are in the process of conducting such experiments and examining the electronic properties of all the compounds by electrochemical and EPR methods.

Conclusions

Conditions were found for the efficient 1,3-dipolar cycloaddition reaction of *N*-ethylazomethine ylide to $Sc_3N@C_{80}$ to form a monoadduct derivative. The reaction was very selective and only one regioisomer product of the I_h constitutional isomer of $Sc_3N@C_{80}$ was isolated, even when the reaction was conducted in the presence of $Sc_3N@C_{78}$ (and presumably D_{5h} $Sc_3N@C_{80}$). The reaction occurred with high efficiency in a matter of minutes. As far as we know, this is the first report of a well-characterized pyrrolidine adduct on an endohedral metallofullerene. It exhibited very interesting shielding/deshielding effects of the geminal pyrrolidine hydrogens, presumably due to surface ring currents on the C_{80} cage.

Experimental Section

All solvents employed (HPLC grade) and other reagents were commercially available, and used without further purification. The ^{13}C-labeled paraformaldehyde was obtained from Cambridge Isotope (99% enriched). Luna Innovations graciously supplied the $Sc_3N@C_{80}$ to us. This raw material was purified by HPLC (Buckyclutcher column, 25 cm × 10 mm, Regis Chemical Company), using toluene as the mobile phase (see the Supporting Information). In a typical reaction, an excess of *N*-ethyl glycine (25-fold) and paraformaldehyde (125-fold) were added to 4.6 mg of $Sc_3N@C_{80}$ in 10 mL of *o*-

(21) Wang, G.-W.; Zhang, T.-H.; Hao, E.-H.; Jiao, L.-J.; Murata, Y.; Komatsu, K. *Tetrahedron* **2003**, *59*, 55−60.
(22) Heine, T.; Vietze, K.; Seifet, G. *Magn. Reson. Chem.* **2004**, *42*, S199−S201.

dichlorobenzene. The mixture was heated to 120 °C under argon. The progress of the reaction was followed by TLC and usually took no longer than 15 min. The reaction mixture was then purified by column chromatography (SiO_2, CS_2) and 2.6 mg of the fulleropyrrolidine monoadduct was obtained (73% yield, based on recovered unreacted material). MALDI-MS (1,8,9-trihydroxyanthracene): m/z 1181, 1110. All chemical shifts are reported in ppm referenced to TMS, except where noted. ^{1}H NMR (500 MHz, CS_2, acetone-d_6): δ 1.39 (t, 3H, J = 7.2 Hz), 2.84 (q, CH_2, 2H, J = 7.2 Hz), 2.81 (d, CH, 2H, J = 9.9 Hz), 4.07 (d, CH, 2H, J = 9.9 Hz). ^{13}C NMR (125 MHz, CS_2, acetone-d_6, referenced to deuterated solvent): δ 70.09 (CH). Unfortunately, we could not obtain an HPLC trace of the pyrrolidine derivative with our instrumentation. *g*-NMR for Machintosh v3.6 (Cherwell Scientific Publishing Limited) was employed to do the ^{1}H NMR simulations.

Supporting Information Available: COSY spectra of both the ^{13}C-labeled and unlabeled *N*-ethyl fulleropyrrolidine of Sc₃N@C₈₀; HPLC traces of raw Sc₃N@C₈₀ material as supplied from Luna Innovations and after purification by HPLC. This material is available free of charge via the Internet at http://pubs.acs.org.

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