

Fullerene Carbon Resonance Assignments through ^{15}N – ^{13}C Coupling Constants and Location of the sp^3 Carbon Atoms of $(\text{C}_{59}\text{N})_2$

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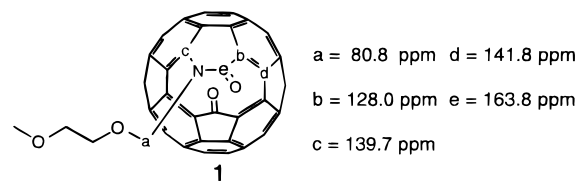
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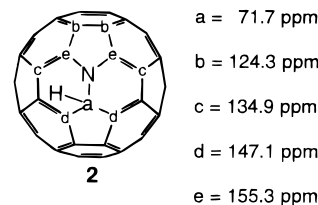
While C_{60} shows a single line at 143 ppm in its ^{13}C NMR spectrum and is a magnetically deshielding moiety,^{1,2} a detailed assignment to all carbon atom resonances in a modified fullerene, which could have up to 60 resonances, is very difficult.^{1,2} With the advent of azafullerene,³ the carbon atoms in positions α and β to the nitrogen, as well as those linking the cage to other substituents, are potentially assignable using ^{13}C – ^{15}N coupling.^{4–6} If this experiment were successful, then assignment of carbons α to cage sp^3 carbons in any modified fullerene should be possible by extrapolation. Here we report that such a characterization is indeed possible for molecules C_{59}HN (**2**), $(\text{C}_{59}\text{N})_2$ (**3**), and the recently synthesized⁷ C_{59} – $(\text{CHPh}_2)\text{N}$ (**4**).

The ^{15}N -labeled compounds were synthesized as described previously,^{3,7–9} but from 50%-labeled (2-methoxyethoxy)methyl azide (MEM- N_3). The ^{15}N -labeled precursor compounds MEM- N_3 and [60]N-MEM azafulleroid have a splitting pattern similar to that of the previously reported ^{15}N -labeled SEM analogs.⁴ Note that because labeled MEM- N_3 has only 50% of the label at the terminus, the nitrogen-coupled carbons appear as a three-line pattern (fortuitously 1:2:1) in the ^{15}N -coupled ^{13}C NMR spectra, due to the sum of a doublet at half-intensity corresponding to ^{15}N -coupled carbons and a singlet corresponding to the unlabeled material.¹⁰ The nitrogen-coupled carbon NMR spectrum of the labeled ketolactam **1** revealed five carbons coupled to nitrogen at 80.8, 128.1, 139.7, 141.8, and 163.8 ppm as shown for structure **1**.¹¹

The labeled ketolactam was then converted to both C_{59}HN and $(\text{C}_{59}\text{N})_2$. The former heterofullerene showed five carbons

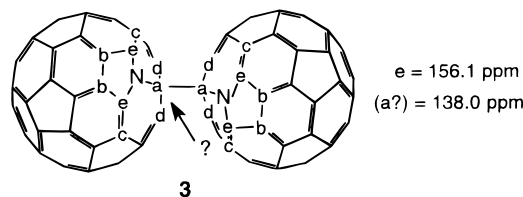


coupled to nitrogen at 71.7, 124.3, 134.9, 147.1, and 155.3 ppm. Assignment of the sp^3 α carbon at 71.7 ppm ($^1J_{\text{C-N}} = 3.5$ Hz) and the sp^2 α carbon at 155.3 ppm ($^1J_{\text{C-N}} = 12.1$ Hz) was straightforward. Low-intensity resonances at 124.3, 134.9, and 147.1 must therefore be a result of β -coupling, where the carbon resonance at 134.9 ppm is modified most by the ^{15}N -coupling. The resonance at 147.1 ppm was shown to also be β -coupled to the proton⁹ as depicted in **2**. This leaves the resonance at



124.3 and 134.9 ppm assignable to “b” or “c”. If resonance arguments apply to spin–spin coupling, then the unusual bond **localization** *sui generis* to fullerene bonding (hexagons are cyclohexatrienes and pentagons are 5-radialenes) demands that “c” be assigned to the 134.9 ppm resonance. This would also explain why “b” and “d”, two carbons which are not in direct conjugation with the nitrogen, show very minor coupling.¹²

Armed with this information, we examined the ^{15}N -coupled ^{13}C NMR spectrum of the dimer to finally locate the interdimer carbon. Only one carbon resonance was found that split at 156 ppm ($^1J_{\text{C-N}} = 11.6$ Hz), one was found that broadened at 138 ppm, and two were found that broadened to a lesser extent at 125.1 and 148.8 ppm. In structure **3**, we show the assignment of one out of the two possible α sites to “e” as well as the uncertainty in assignment of the crucial α carbon “a”.



It is possible that, as is well known in fullerene chemistry, when a fullerene is a substituent, it has a strong deshielding effect.^{1,2} If C_{59}N has the same magnetic properties as C_{60} , in $(\text{C}_{59}\text{N})_2$, each half of the molecule acts as a deshielding group on the other; also, the interball bonding carbons “a” are pressed against the opposite ball’s nitrogen atom’s lone pair, which causes further deshielding. An additional complication is that the “a” carbons are α to their own ball’s nitrogen but β to the adjacent ball’s nitrogen. This could cause further splitting and/or broadening of the signal corresponding to the α carbon “a”. Quantum calculations at the LDF (local density functional) level reveal that the hybridization of “a” is between sp^2 and sp^3 ; the C–H coupling constant in **2** also supports this theory,^{9,13} and allows for the possible assignment of “a” at 138 ppm.¹⁴ However, we were still concerned about the magnitude of

(12) On the other hand, if σ -delocalization (hyperconjugation) were an important mechanism for spin–spin coupling, then these assignments could be reversed. Theoretical calculations also suggest this reverse assignment: Bühl, M.; Curioni, A.; Andreoni, W. Preprint, February 1997. We thank Dr. Andreoni for private communication prior to publication.

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(1) Hawkins, J. M.; Loren, S.; Meyer, A.; Nunlist, R. *J. Am. Chem. Soc.* **1991**, *113*, 7770–7771.

(2) Hawkins, J. M.; Meyer, A.; Lewis, T. A.; Bunz, U.; Nunlist, R.; Ball, G. E.; Ebbesen, T. W.; Tanigaki, K. *J. Am. Chem. Soc.* **1992**, *114*, 7954–7955.

(3) Hummelen, J. C.; Knight, B.; Pavlovich, J.; González, R.; Wudl, F. *Science* **1995**, *269*, 1554–1555. For C_{59}N in the gas phase see: Averdung, J.; Luftmann, H.; Schlachter, I.; Mattay, J. *Tetrahedron* **1995**, *51*, 6977–6982. Lamparth, I.; Nuber, B.; Schick, A.; Skiebe, T.; Grosser, T.; Hirsch, A. *Angew. Chem., Int. Ed. Engl.* **1995**, *34*, 2257–2258. Another condensed phase approach was recently disclosed: Nuber, B.; Hirsch, A. *J. Chem. Soc., Chem. Commun.* **1996**, 1421–1422.

(4) Prato, M.; Chan Li, Q.; Wudl, F.; Lucchini, V. *J. Am. Chem. Soc.* **1993**, *115*, 1148–1150.

(5) Schick, G.; Grosser, T.; Hirsch, A. *J. Chem. Soc., Chem. Commun.* **1995**, 2289–2290.

(6) Schick, G.; Hirsch, A.; Mauser, H.; Clark, T. *Chem. Eur. J.* **1996**, *2*, 935–943.

(7) Bellavia-Lund, C.; González, R.; Hummelen, J. C.; Hicks, R. G.; Sastre, A.; Wudl, F. *J. Am. Chem. Soc.* **1997**, *119*, 2946–2947.

(8) Hummelen, J. C.; Prato, M.; Wudl, F. *J. Am. Chem. Soc.* **1995**, *117*, 7003–7004.

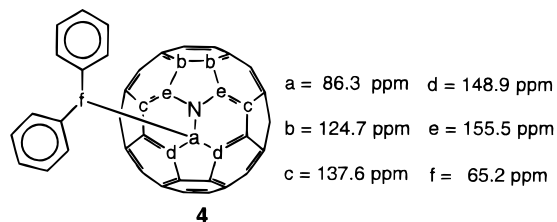
(9) Keshavarz-K, M.; González, R.; Hicks, R.; Srdanov, G.; Srdanov, V.; Collins, T.; Hummelen, J. C.; Bellavia-Lund, C.; Pavlovich, J.; Wudl, F.; Holczer, K. *Nature* **1996**, *383*, 147–150.

(10) Note that, in the sp^3 region, the singlet and doublet overlap to give a two line pattern (3:1), due to the isotopic shift of the ^{15}N -labeled material and the smaller coupling constant of ^{15}N to an α sp^3 carbon.

(11) Carbons “c” and “d” are close and may have the reverse assignment (see ref 12).

deshielding suffered by carbon "a", and as shown below, our skepticism was justified.

To gain information on the chemical shift variation as a function of substituent, the diphenylmethyl azafullerene derivative **4**, labeled and unlabeled, was synthesized from the



corresponding azafullerene dimer **3**.⁷ The ¹³C NMR spectrum of **4** revealed the sp³ carbon α to the nitrogen on the fullerene cage at 86.3 ppm. It seemed unreasonable that the broadened peak at 138 ppm, in the spectrum of **3**, could be the α carbon resonance that we have been searching for. This reasoning stems from the fact that changing the substituent from diphenylmethyl to C₅₉N should not shift the "sp³" resonance downfield by 51.4 ppm, considering that in going from a proton (C₅₉HN) to an alkyl C₅₉(CHPh₂)N substituent the α resonance shifted by only 14.9 ppm. An ¹⁵N-coupled ¹³C NMR spectrum of **4** showed a pattern similar to that of its precursors, splitting at 86.3 and 155.5 corresponding to the sp³ α carbon "a" and the sp² α carbon "e", respectively, as illustrated in **4**. Broadening was observed for β carbon resonances at 137.6 and to a lesser extent at 65.2, 124.7, and 148.9 ppm. The ¹H-coupled ¹³C NMR spectrum of **4** showed that the resonance at 148.9 ppm was also γ-coupled to the methine proton. The assignment of "b" and "c" in **4** is again based on the fact that "c", unlike the other three β carbons, is in conjugation with nitrogen and should exhibit a stronger spin–spin interaction.

After comparison of the three derivatives, it is possible by extrapolation to assign the β carbons of **3** (cf. Table 1). The assignments of the β carbons at 134.9 ppm for **2** and 137.6 ppm for **4** supported the notion that the 138 ppm resonance in the dimer was also due to β-coupling and strongly suggested that the sp³ α carbon of **3** was still unknown.

Re-evaluation of pulse delay times used to record fullerene ¹³C NMR spectra¹⁵ revealed that a 16 s pulse delay, twice the value for a "standard" detection, allowed the observation of a weak resonance in the sp³ region at 90.4 ppm in the ¹³C NMR spectrum of the "unlabeled" (C₅₉N)₂ heterofullerene. Attempts were made to optimize the NMR experimental parameters for a long T₁, i.e., the variation of delay times and pulse angles.¹⁶ Various conditions were tried on the labeled material without

(13) Andreoni, W.; Curioni, A.; Holzer, K.; Prassides, K.; Keshavarz-K, M.; Hummelen, J.-C.; Wudl, F. *J. Am. Chem. Soc.* **1996**, *118*, 11335–11336.

(14) As a result of the minor effect ¹⁵N-coupling had on the resonance at 125.1 ppm, it was ruled out as a possibility.

(15) Bellavia-Lund, C. Wudl, F. *J. Am. Chem. Soc.* **1997**, *119*, 943–946.

success. This is probably due to the mixture of the labeled and unlabeled **3** giving too low a signal to noise ratio (S/N) for signal detection.¹⁷ Table 1 summarizes the NMR results obtained and illustrates a distinct pattern of the azafullerenes.

Table 1. ¹⁵N-Coupled Carbon Atoms a–f as a Function of R on the Fullerene Cage (cf. **4**)

	a	b	c	d	e	f
R = H (2)	71.7 (3.5) ^a	124.3 ^b	134.9 ^b	147.1 ^b	155.3 (12.1) ^a	
R = CHPh ₂ (4) ^c	86.6 (4.5) ^a	124.6 ^b	137.6 ^b	149.1 ^b	155.7 (11.9) ^a	65.4 ^b
R = C ₅₉ N (3)	90.4 ^b	125.1 ^b	138 ^b	148.8 ^b	156.1 (11.6) ^a	

^a ¹⁵N–¹³C coupling constant (Hz) in ODCB-d₄. ^b Broad, low-intensity peaks. ^c Chemical shifts next to the structure drawing differ slightly from those in Table 1 because they were obtained in CS₂.

The numbers in Table 1 indicate that, as the electronegativity of R increases, the chemical shifts of the sp³ and (for the most part) the sp² carbon atoms α and β to the nitrogen atom also increase. In all three cases, the pattern is reproduced and similar coupling constants are observed. The only exception appears to be carbon "d" in **4**, which has approximately the same chemical shift as that of **3**.

In conclusion, a combination of spectroscopic techniques on the structure analysis of ¹⁵N-labeled and unlabeled **2**, **3**, and **4** showed that the α carbon "a" of **3** does not reside in the fullerene region (125–160 ppm), but must lie in the sp³ region. Further, the substituent on the sp³ carbon influences the chemical shifts of the carbon atoms surrounding the heteroatom. After experimental optimization for a long T₁, the signal for the interdimer carbon of **3** was found at 90.4 ppm, unequivocally supporting a "[6,6] closed" structure for (C₅₉N)₂, as depicted in **3**. As a result of this study, any future ¹³C-NMR characterization of azafullerenes will rest on a firm foundation and chemical shift assignments of carbon atoms α and β to the nitrogen atom(s) will now be possible and will be found in the range 155–156 ppm (α as well as 124–125 (β, adjacent to sp² carbon), 135–138 (β, adjacent to sp² carbon), and 144–149 (β, adjacent to sp³ carbon) ppm.

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Supporting Information Available: ¹³C-NMR spectra with and without ¹⁵N-coupling (20 pages). See any current masthead page for ordering and Internet access instructions.

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(16) Chemical shift anisotropy (σ) can account for the long T₁ of the interdimer carbon atoms [(Δσ)² ∝ 1/T₁]. The chemical shift anisotropy for sp² carbons adjacent to nitrogen are larger (e.g., *p*-(dimethylamino)-benzotrile and *N*-butyl-2,4,6-octatrienimine have Δσ ≈ 120 ppm), compared to sp³ carbons adjacent to nitrogen (L-alanine which has Δσ ≈ 20 ppm) (Duncan, T. M. *A Compilation of Chemical Shift Anisotropies*; Farragut: Chicago, 1990). This theory was tested by taking multiple NMR spectra at different pulse delays of a C₆₀ triazolone; the sp³ carbons in the triazolone ring rose in intensity as the delay time was increased using a 45° pulse angle.

(17) Because there exists both α sp³ C–N and β sp³ C–N coupling, both of which are expected to be in close proximity (≤ 5 Hz), we would expect to observe a broad, unresolved peak even if the S/N were excellent.