

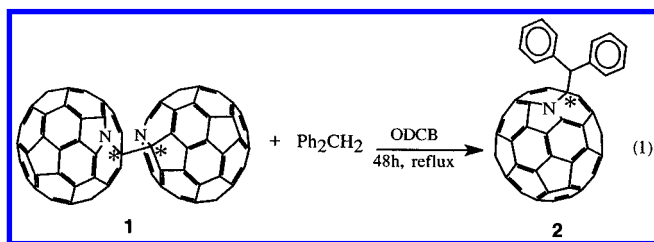
Synthesis of $C_{59}(CHPh_2)N$ from $(C_{59}N)_2$ and $C_{59}HN$. The First Derivatization of $C_{59}N$

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Received December 30, 1996

Since the incorporation of heteroatoms into the fullerene skeleton is expected to modify its structural and electronic properties,¹ we prepared the first heterofullerene, " $C_{59}N$ ", which was isolated as its dimer, $(C_{59}N)_2$.² The isolation in the condensed phase of this nitrogen-substituted fullerene allows for the investigation of the chemical reactivity, physical properties,^{3,4} and possible applications of this new class of fullerenes. As part of our continued interest in the azafullerenes, we have initiated studies to prepare derivatives. Even though ^{15}N -labeling experiments⁵ and the isolation and full characterization of $C_{59}HN$ have given us confidence that the starred carbons (see eq 1, below) are sp^3 hybridized, a principal reason for derivatization of $C_{59}N$ was to glean information on the variability of the chemical shift of the carbon atoms in question as a function of substitution.



Two possible processes for derivatization of $C_{59}N$ are (1) deprotonation of the azafullerene $C_{59}HN$ ⁶ followed by attack of an electrophile and (2) homolytic dissociation of the interdimer bond of $(C_{59}N)_2$ followed by free radical reactions. Here, we report on the derivatization of azafullerene via homolysis of its dimer.

According to theoretical calculations⁷ the interdimer bond of $(C_{59}N)_2$ is relatively weak (18 kcal/mol) and should, under photolysis or thermolysis conditions, undergo facile homolysis. In the presence of a good hydrogen atom donor or radical source,

the resulting azafullerenyl radical is expected to undergo free radical reactions.

Treatment of $(C_{59}N)_2$ with excess diphenylmethane in refluxing *o*-dichlorobenzene (ODCB) for 48 h afforded, upon chromatography (silica gel, toluene), a crude product. HPLC analysis indicated one major constituent, consisting of 71% of the isolable mixture. This was shown to be the substituted azafullerene $C_{59}(CHPh_2)N$ (**2**) by 1H and ^{13}C NMR, FTIR, UV-vis, mass spectrometry, and cyclic voltammetry. The heterofullerene **2** was obtained in 42% isolated yield after purification by HPLC on a Cosmosil Buckyprep semiprep column.⁸

The 1H NMR spectrum of **2** showed signals corresponding to two equivalent phenyl groups and a singlet corresponding to the methine hydrogen at 6.09 ppm. The 34 lines observed between 156 and 124 ppm (30 from the $C_{59}N$ moiety and 4 from the phenyl groups) in the ^{13}C NMR spectrum are consistent with the expected C_s symmetry of **2** depicted in eq 1. Another peak at 65.2 ppm corresponds to the methine carbon atom and a signal at 86.3 ppm must be due to the starred sp^3 carbon atom on the buckyball moiety. This carbon resonance is downfield shifted by 14 ppm relative to the sp^3 carbon of $C_{59}HN$,⁶ as expected on going from hydrogen to alkyl substitution. This is in agreement with a "closed" structure in which the sp^3 carbon atom is bound to the nitrogen atom and the $CHPh_2$ substituent, as shown in **2** above.

While the NOE effect identifies most of the phenyl resonances in the ^{13}C NMR spectrum, proton-coupled ^{13}C NMR distinguishes the resonance of the quaternary carbon of the phenyl group (quartet at 139 ppm) from the surrounding fullerene resonances. The coupled spectrum also supports the assignment of the methine carbon, revealing a doublet at 65.2 ($^1J_{CH} = 127$ Hz) and a β -coupled doublet at 86.7 ($^2J_{CH} = 5$ Hz) for the sp^3 carbon of the fullerene cage. Finally, positive ion electrospray MS shows a molecular ion at $m/z = 889$ and a strong peak at $m/z = 722$ corresponding to $C_{59}N^+$.

The UV-vis absorption of $C_{59}(Ph_2CH)N$ is almost identical to that of $(C_{59}N)_2$ and $C_{59}HN$ showing a broad band in the visible at 448 nm; all three compounds are green in solution. The similarities of the electronic spectra of the azafullerenes supports the closed structure assigned to $(C_{59}N)_2$ ⁶ depicted for **1**, above.

The FTIR spectrum shows a typical pattern for a fullerene derivative, in particular having absorptions similar to $C_{59}HN$ in the fingerprint region ($480\text{--}590\text{ cm}^{-1}$), where the strongest peak is at 529.3 cm^{-1} .

The diphenylmethane adduct of $C_{59}N$ exhibits two quasi-reversible one-electron reduction waves; a third wave, which is completely irreversible was also observed. This contrasts the behavior of $C_{59}HN$ in which the reduction processes are chemically irreversible. We interpreted the properties of the latter as arising from facile hydrogen atom loss on reduction, which is not possible in the diphenylmethane derivative. The reduction potentials are presented in Table 1, along with those of C_{60} , $(C_{59}N)_2$, and $C_{59}HN$ for comparison. The potentials of the (diphenylmethyl)azafullerene and hydroazafullerene are comparable, and both are significantly more difficult to reduce than the dimer, an observation consistent with the high electronegativity of a heterofullerene "substituent". All of the azafullerene compounds possess irreversible oxidation waves at much lower potentials compared to those of C_{60} .

(8) $(Ph_2CH)C_{59}N$: Diphenylmethane (2.4 mL) was added to a degassed solution of $(C_{59}N)_2$ (30 mg) in HPLC grade 1,2-dichlorobenzene (25 mL). The mixture was refluxed under argon for 48 h and chromatographed on silica gel using toluene as eluent. The product was purified by HPLC using a semipreparative Cosmosil Buckyprep column (30% hexane in toluene, 5 mL/min, UV/326 nm). Solvents were removed under vacuum, and the product was washed with ether, centrifuged, and decanted three times to remove ether-soluble components, including toluene. It was finally dried under vacuum. Yield: 15 mg (42%). Please refer to Supporting Information for spectroscopic data.

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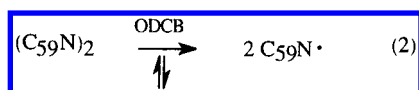
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Table 1. Redox Potentials for C₆₀ and some C₅₉N Derivatives^a

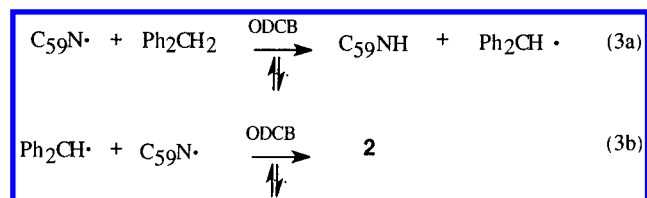
	C ₆₀	(C ₅₉ N) ₂	C ₅₉ HN	C ₅₉ N(CHPh ₂)
<i>E</i> ₁ ^{red}	−1123	−992 −1071	−1106 ^b	−1082
<i>E</i> ₂ ^{red}	−1450	−1424 −1485	−1500 ^b	−1470
<i>E</i> ₃ ^{red}	−1913	−1979 −2089		
<i>E</i> ^{ox}	+1300 ^{b,c} +1260 ^d	+886 ^b	+823 ^b	+867 ^b

^a All potentials are in mV vs Ferrocene, in ODCB unless stated otherwise. ^b Chemically irreversible. ^c Dubois, D.; Kadish, K. *J. Am. Chem. Soc.* **1991**, *113*, 7773. ^d Chemically reversible, in 1,1,2,2-tetrachloroethane solvent: Xie, Q.; Arias, F.; Echegoyen, L. *J. Am. Chem. Soc.* **1993**, *115*, 9818.

We can attribute the mechanism of formation of **2** to be a short free radical chain. As illustrated in eq 2, the initiation step is proposed to be the homolysis of the azafullerene dimer to C₅₉N•

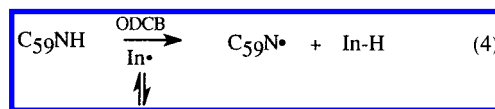


Subsequently, the steps in eqs 3a and 3b are plausible propagation and termination steps. Hence, in the presence of the hydrogen donor diphenylmethane, formation of C₅₉HN was expected to be one of the major products (eq 3a); however, it was only 2% of the reaction mixture. The major product was the diphenylmethane derivative of the azafullerene radical, **2**, (eq 3b).

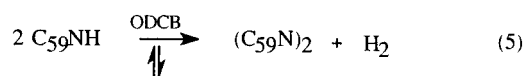


Two possible reasons for the low yield of C₅₉HN are (1) unlike **2**, which appears to be quite stable under the “harsh” reaction conditions, C₅₉HN decomposes or polymerizes to yield insoluble products or (2) C₅₉HN undergoes a free radical reaction to afford C₅₉N• (eq 4). In eq 4, “In•” under the arrow

could be an adventitious initiator or C₅₉N• from (C₅₉N)₂ (see eq 5, below).



In a control experiment, treatment of C₅₉HN⁶ with diphenylmethane in refluxing ODCB for 24 h, afforded, upon chromatography (silica gel, toluene), one isolable band. HPLC analysis of the crude product revealed the presence of **2** (73%), (C₅₉N)₂ (7%), and unreacted C₅₉HN (5%). This experiment proves that equation 4 is operative and that In• is due to a combination of eqs 5 and 2.



In support of the above dimerization, fresh, HPLC single component samples of C₅₉HN were found to dimerize on standing at room temperature even in the solid state.

We have demonstrated above the relatively clean conversion of (C₅₉N)₂ to a stable, soluble derivative in good yield. This study shows that C₅₉HN can also undergo homolytic cleavage to yield the C₅₉N radical, where all three species C₅₉N•, C₅₉HN, and (C₅₉N)₂ are involved in the process leading to **2**. Full characterization of the title molecule shows remarkable similarities to (C₅₉N)₂ and C₅₉HN, and in particular the UV-vis data demonstrate that the electronic structure of all three molecules is essentially identical. The ¹³C NMR spectra reveal a similar pattern in the sp² region of **2** to that of its precursors and an unmistakable sp³ carbon at 86.1 ppm, illustrating the chemical shift deviation as a result of substitution; an important stepping stone for the absolute determination of the (C₅₉N)₂ structure.⁹ Research is currently in progress utilizing this methodology to derive azafullerenes with unusual properties.

Acknowledgment. We thank the National Science Foundation for support through the Materials Research Laboratory and NSF DMR 95-00888, as well as individual investigator grants. R.G. and A.S. thank the Ministerio de Educación y Cultura (Spain) for postdoctoral fellowships. R.G.H. thanks the National Research Council of Canada for a postdoctoral fellowship.

Supporting Information Available: Experimental details for the preparation, purification, and characterization of **2** (6 pages). See any current masthead page for ordering and Internet access instructions.

JA964447C

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