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Synthesis of the $C_{59}N^+$ Carbocation. A Monomeric Azafullerene Isoelectronic to C_{60}

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By isoelectronic analogy to C_{60}, heterofullerenes such as $C_{59}N^+$, $C_{59}B^-$, $C_{59}Si$, and $C_{59}P^+$ should be stable entities. Differences in size and electronegativity between C and its neighboring nonmetallic elements are unlikely to be large enough to disrupt covalent bonding in the icosahedral cage. Indeed, ions having these elemental compositions have been relatively easy to detect via mass spectrometry on fullerene soots prepared in the presence of heteroatom sources.[1−4] Nevertheless, only one analogue of C_{60} has been carried to the level of practical synthesis and compositional purity, the *N*-heterofullerene $C_{59}N$. With one more electron than C_{60}, its stable form is a C−C bonded dimer, $(C_{59}N)_2$.[5−8] The C−H bonded monomer, $HC_{59}N$, has also been characterized.[9] We now report that the monomeric $C_{59}N^+$ cation, which is isoelectronic with C_{60}, can be isolated as a carborane anion salt. The synthesis involves a rare example of oxidation of an sp^3-sp^3 C−C bond to produce a carbenium ion.

Fullerenes are typically easy to reduce but hard to oxidize[10] and $(C_{59}N)_2$ is no exception. A threshold oxidation potential of ca. +0.9 V (vs Fc/Fc^+) has been reported in its irreversible anodic cyclic voltammetry.[9] In addition, $(C_{59}N)_2$ has an sp^3-sp^3 C−C bond and such bonds typically present high barriers to oxidation. Chemistry has few "electron−hole" oxidants that operate above ca. +0.7 V[11] because most strong oxidants (e.g., Cl_2, SbF_5, XeF_2) come partnered with nucleophiles (e.g., halides) that immediately react with oxidized species. However, when partnered with exceptionally inert carborane anions[12,13] such as $CB_{11}H_6Cl_6^-$, stable radical cations can be used to extend the range to +1.34 V, sufficient to oxidize C_{60} to the $C_{60}^{+\bullet}$ radical cation.[14]

The radical cation of crude hexabromo(phenyl)carbazole ($HBPC^{\bullet+}$)[14,15] oxidizes $(C_{59}N)_2$[6] to $C_{59}N^+$ in dry *o*-dichlorobenzene (eq 1). The counterion is the silver(I) bis-carborane complex ion

$$(C_{59}N)_2 + 2[HBPC^\bullet][Ag(CB_{11}H_6Cl_6)_2] \rightarrow 2[C_{59}N][Ag(CB_{11}H_6Cl_6)_2] + 2HBPC \quad (1)$$

$[Ag(CB_{11}H_6Cl_6)_2]^-$. $[C_{59}N][Ag(CB_{11}H_6Cl_6)_2]$, **1**, was isolated as a brown precipitate in good yield (>75%) by addition of hexane or crystallized as dark green crystals by diffusion of hexane vapor.[15] Anal. Calcd for $C_{61}H_{12}NB_{22}Cl_{12}Ag$: C, 47.89; H, 0.79; N, 0.92. Found: C, 47.49; H, 0.92; N, 1.10. The solid is reasonably air stable.

The dark green color of $(C_{59}N)_2$ in *o*-dichlorobenzene lightens slightly upon oxidation. The visible spectrum of $C_{59}N^+$ is quite featureless (blue line in Figure 1) compared to that of $(C_{59}N)_2$.

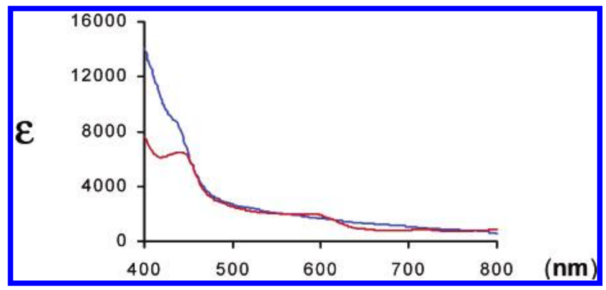

Figure 1. Visible spectra of $C_{59}N^+$ (blue, 1.38×10^{-3} M) and $(C_{59}N)_2$ (red, 6.90×10^{-4} M) in *o*-dichlorobenzene.

Stirring solutions of the $C_{59}N^+$ salt over Hg-amalgamated zinc pellets slowly returned the spectrum to that of $(C_{59}N)_2$, indicating reversibility of the redox chemistry.

The infrared spectrum of the $C_{59}N^+$ ion can be distinguished from that of $(C_{59}N)_2$ and $HC_{59}N$ in the 1600−1150 and 600−500 cm^{-1} regions. Bands at 1586, 1580, 1575; 1468, 1455, 1434; ∼1183 sh, 1178, 1165; 579, 537, 532, 527, 525, 519 cm^{-1} in **1**[15] contrast with those at 1574, 1565; 1460, 1443, 1423, 1416; 1196, 1186, 1174; 579, 576, 568, 529, 523 cm^{-1} in $(C_{59}N)_2$ and 1574, 1565, 1461, 1443, 1422, 1414; 1197, 1186, 1174; 579, 574, 568, 529, 523 cm^{-1} in $HC_{59}N$.[16] Other fingerprint bands for the $C_{59}N$ moiety near 800 cm^{-1} are masked by bands from the carborane anion. In the resonance Raman spectrum of **1** with 488 nm excitation, the prominent $A_g(2)$ global breathing mode appears at 1467 cm^{-1}.[15] This is higher in energy than that of $(C_{59}N)_2$ (1462 cm^{-1}),[16] consistent with a tightening of cage bonding from the sp^3 to sp^2 bonding change at C. The frequency in $C_{59}N^+$ is essentially the same as that in C_{60} (1466 cm^{-1}). More bands appear in $C_{59}N^+$ because of lower symmetry.

Consistent with a positive ion already being present, MALDI mass spectroscopy of **1** in positive ion mode gave a dominant peak at $m/z = 722$ for the $C_{59}N^+$ cation using low laser powers.[15] Under comparable conditions, $(C_{59}N)_2$ gave no signal. The isotope pattern confirms the formulation as $C_{59}N^+$.[17] In negative ion mode, a broad, strong peak centered at $m/z = 350$ identifies the carborane anion $CB_{11}H_6Cl_6^-$, indicating expected dissociation of the weakly bound $Ag(CB_{11}H_6Cl_6)_2^-$ complex anion.

As expected from C_s symmetry, the ^{13}C NMR spectrum of **1** in tetrachloroethane-d_2 shows 31 peaks that can be ascribed to the $C_{59}N^+$ ion (Figure 2). A near accidental degeneracy occurs at 142.7/142.8 ppm. Because solubility is higher, a spectrum with a better signal-to-noise ratio could be obtained in *o*-dichlorobenzene-d_2 but slight solvent shifts in the resonances exacerbate the problem of accidental degeneracies.[15] Peak positions distinguish $C_{59}N^+$ from $(C_{59}N)_2$ and $HC_{59}N$. Consistent with the overall positive charge on

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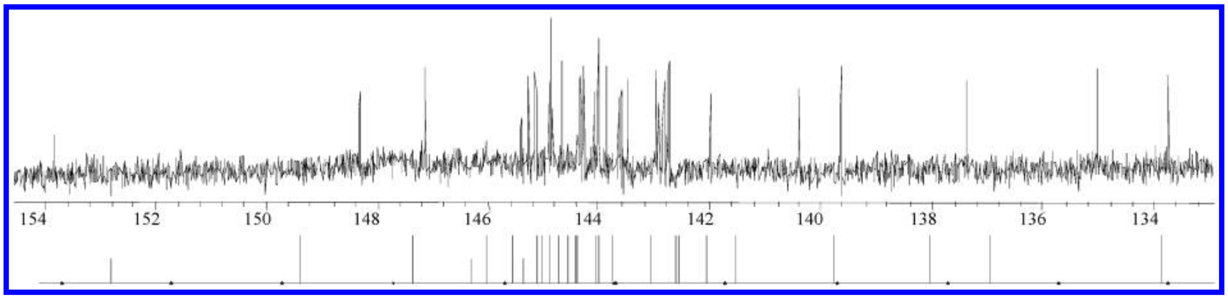

Figure 2. Experimental ^{13}C NMR spectrum of $C_{59}N^+$ in **1** in TCE-d_2 (above) and calculated spectrum (stick diagram below).

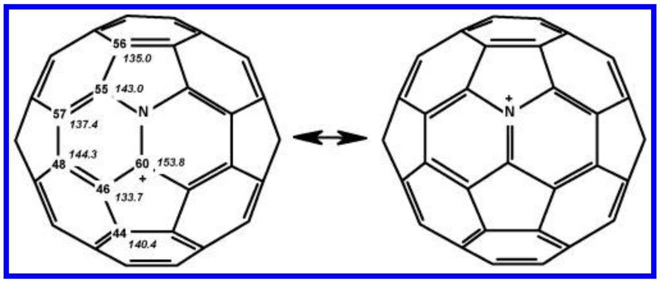

Figure 3. Selected ^{13}C assignments (ppm) in $C_{59}N^+$ and resonance forms showing both carbenium and iminium ion character.

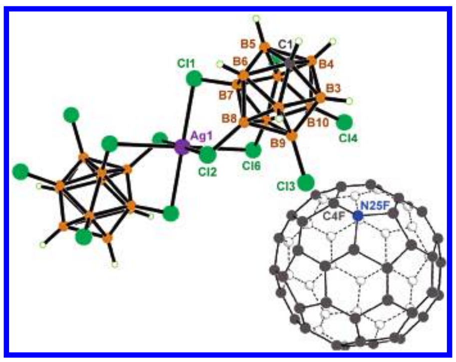

Figure 4. Perspective view of $[C_{59}N^+][Ag(CB_{11}H_6Cl_6)_2^-]$ in **1**. Three lattice *o*-dichlorobenzene molecules are omitted for clarity.

the ion, the majority of the peaks cluster around 144 ppm, somewhat downfield of 142.9 ppm in C_{60}. Individual assignments can be made on the basis of the reasonable agreement with the DFT-calculated spectrum (B3LYP/6-31G*/B3LYP/6-311G(d,p)), shown as a stick diagram in Figure 2. A downfield peak at 153.8 ppm (1C intensity) is ascribed to the formal carbenium ion center (atom 60 in Figure 3). This compares to 182 ppm in the isoelectronic HC_{60}^+ ion,[14] indicating greater delocalization of the positive charge in $C_{59}N^+$ and iminium ion character, favored by NBO analysis[15] (Figure 3). The most upfield shifted resonances (133.7, 135.0, 137.4 ppm) arise from C atoms β to the N atom (C46, C56, C57, respectively).

The X-ray crystal structure of **1** with three *o*-dichlorobenzene solvate molecules provides final proof of formulation and structure (Figure 4). Although the anion is well ordered, disorder in the cation and the solvate molecules prevents accurate bond length data from being obtained for $C_{59}N^+$. The cation is located on a crystallographic mirror plane that does not bisect the [6,6] C−N bond. It was successfully modeled with 50:50 site occupancies and the assumption that the closest anion/cation contact identifies the carbocationic C atom (C4F in Figure 4).

In conclusion, an azafullerene analogue of C_{60} is accessible via chemical oxidation of dimeric $(C_{59}N)_2$ with a strong electron−hole oxidant. As with reactive carbocations such as the benzenium ion $(C_6H_7^+)$[18] and the radical cation $C_{60}^{\bullet+}$,[14] the stabilization of $C_{59}N^+$ as an isolable salt profited from use of an inert carborane as counterion. The properties of $C_{59}N^+$ reflect the isoelectronic analogy to C_{60} and some delocalization of charge.

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Supporting Information Available: Full experimental details, NMR, vis, IR, Raman, and MALDI spectra, and X-ray crystallographic data. This material is available free of charge via the Internet at http://pubs.acs.org.

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