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Synthesis of the C₅₉N⁺ Carbocation. A Monomeric Azafullerene Isoelectronic to C₆₀

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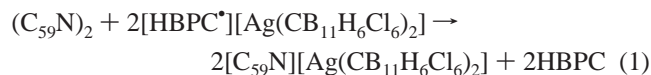
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By isoelectronic analogy to C₆₀, heterofullerenes such as C₅₉N⁺, C₅₉B⁻, C₅₉Si, and C₅₉P⁺ should be stable entities. Differences in size and electronegativity between C and its neighboring nonmetallic elements are unlikely to be large enough to disrupt 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 C₆₀ has been carried to the level of practical synthesis and compositional purity, the N-heterofullerene C₅₉N. With one more electron than C₆₀, its stable form is a C–C bonded dimer, (C₅₉N)₂.^{5–8} The C–H bonded monomer, HC₅₉N, has also been characterized.⁹ We now report that the monomeric C₅₉N⁺ cation, which is isoelectronic with C₆₀, can be isolated as a carborane anion salt. The synthesis involves a rare example of oxidation of an sp³–sp³ C–C bond to produce a carbenium ion.

Fullerenes are typically easy to reduce but hard to oxidize¹⁰ and (C₅₉N)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, (C₅₉N)₂ has an sp³–sp³ C–C bond and such bonds typically present high barriers to oxidation. Chemistry has few “electron–hole” oxidants that operate above ca. +0.7 V¹¹ because most strong oxidants (e.g., Cl₂, SbF₅, XeF₂) 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 CB₁₁H₆Cl₆⁻, stable radical cations can be used to extend the range to +1.34 V, sufficient to oxidize C₆₀ to the C₆₀^{•+} radical cation.¹⁴

The radical cation of crude hexabromo(phenyl)carbazole (HBPC^{•+})^{14,15} oxidizes (C₅₉N)₂⁶ to C₅₉N⁺ in dry *o*-dichlorobenzene (eq 1). The counterion is the silver(I) bis-carborane complex ion



[Ag(CB₁₁H₆Cl₆)₂]⁻. [C₅₉N][Ag(CB₁₁H₆Cl₆)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 C₆₁H₁₂NB₂₂Cl₁₂Ag: 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 (C₅₉N)₂ in *o*-dichlorobenzene lightens slightly upon oxidation. The visible spectrum of C₅₉N⁺ is quite featureless (blue line in Figure 1) compared to that of (C₅₉N)₂.

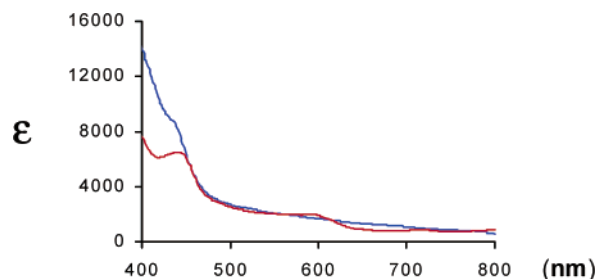


Figure 1. Visible spectra of C₅₉N⁺ (blue, 1.38 × 10⁻³ M) and (C₅₉N)₂ (red, 6.90 × 10⁻⁴ M) in *o*-dichlorobenzene.

Stirring solutions of the C₅₉N⁺ salt over Hg-amalgamated zinc pellets slowly returned the spectrum to that of (C₅₉N)₂, indicating reversibility of the redox chemistry.

The infrared spectrum of the C₅₉N⁺ ion can be distinguished from that of (C₅₉N)₂ and HC₅₉N 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 (C₅₉N)₂ and 1574, 1565, 1461, 1443, 1422, 1414; 1197, 1186, 1174; 579, 574, 568, 529, 523 cm⁻¹ in HC₅₉N.¹⁶ Other fingerprint bands for the C₅₉N 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 (C₅₉N)₂ (1462 cm⁻¹),¹⁶ consistent with a tightening of cage bonding from the sp³ to sp² bonding change at C. The frequency in C₅₉N⁺ is essentially the same as that in C₆₀ (1466 cm⁻¹). More bands appear in C₅₉N⁺ 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 C₅₉N⁺ cation using low laser powers.¹⁵ Under comparable conditions, (C₅₉N)₂ gave no signal. The isotope pattern confirms the formulation as C₅₉N⁺.¹⁷ In negative ion mode, a broad, strong peak centered at *m/z* = 350 identifies the carborane anion CB₁₁H₆Cl₆⁻, indicating expected dissociation of the weakly bound Ag(CB₁₁H₆Cl₆)₂⁻ complex anion.

As expected from C_s symmetry, the ¹³C NMR spectrum of **1** in tetrachloroethane-*d*₂ shows 31 peaks that can be ascribed to the C₅₉N⁺ 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 C₅₉N⁺ from (C₅₉N)₂ and HC₅₉N. Consistent with the overall positive charge on

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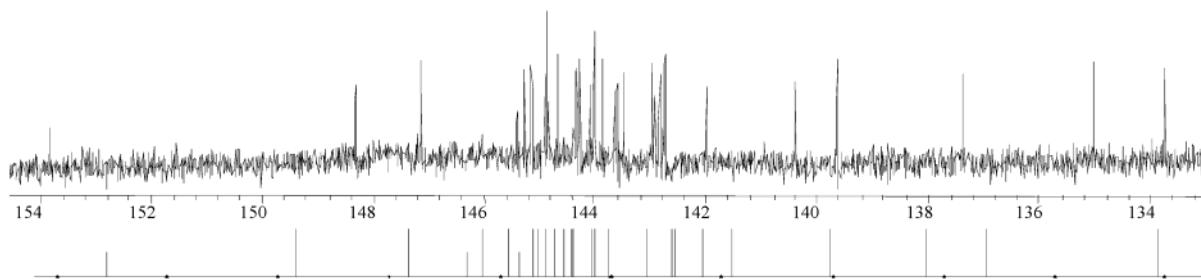


Figure 2. Experimental ^{13}C NMR spectrum of C_{59}N^+ in **1** in TCE-d_2 (above) and calculated spectrum (stick diagram below).

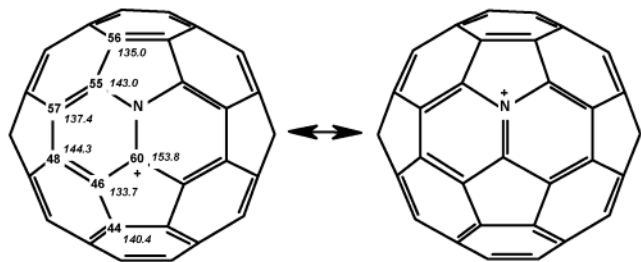


Figure 3. Selected ^{13}C assignments (ppm) in C_{59}N^+ and resonance forms showing both carbenium and iminium ion character.

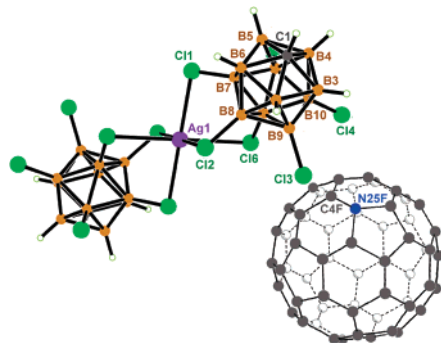


Figure 4. Perspective view of $[\text{C}_{59}\text{N}^+][\text{Ag}(\text{CB}_{11}\text{H}_6\text{Cl}_6)_2^-]$ in **1**. Three lattice *o*-dichlorobenzene molecules are omitted for clarity.

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 analysis¹⁵ (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 assump-

tion 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 $(\text{C}_{59}\text{N})_2$ with a strong electron–hole oxidant. As with reactive carbocations such as the benzenium ion (C_6H_7^+)¹⁸ and the radical cation $\text{C}_{60}^{\bullet+}$,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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