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

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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. 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. 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 carbocation 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 Fe/Fe⁺) 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)2 to C59N⁺ in dry o-dichlorobenzene (eq 1). The counterion is the silver(I) bis-carborane complex ion

\[
(C59N)2 + 2[HBPC][Ag(CB11H6Cl6)2] \rightarrow 2[C59N][Ag(CB11H6Cl6)2] + 2HBPC
\]

[Ag(CB11H6Cl6)2]⁺. (C59N)[Ag(CB11H6Cl6)2], I, 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 C59H12NB2Cl12Ag: 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 × 10⁻⁴ M) and (C59N)2 (red, 6.90 × 10⁻⁴ M) in o-dichlorobenzene.

Stirring solutions of the C59N⁺ cation 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; 1178, 1165; 579, 537, 532, 527, 525, 519 cm⁻¹ in I¹5 contrast with those at 1574, 1565; 1460, 1433, 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 in (C59N)2 show 31 peaks that can be ascribed to the C59N radical anion. In the resonance Raman spectrum of I with 488 nm excitation, the prominent Ag(2) global breathing mode appears at 1467 cm⁻¹.¹⁵ This is higher in energy than that of (C59N)2 (1462 cm⁻¹),¹⁵ 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 I 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 carbocation anion CB11H6Cl6−, indicating expected dissociation of the weakly bound Ag(CB11H6Cl6)− complex anion.

As expected from C₁ symmetry, the ¹³C NMR spectrum of I in tetrachloroethane-d₂ 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-d₂ 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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the ion, the majority of the peaks cluster around 144 ppm, somewhat downfield of 142.9 ppm in C₆₀. 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 HC₆₀⁺ ion, indicating greater delocalization of the positive charge in C₅₉N⁺ and iminium ion character, favored by NBO analysis (Figure 3).

Figure 4. Perspective view of [C₅₉N⁺][Ag(CB₁₁H₆Cl₆)₂] in 1. Three lattice o-dichlorobenzene molecules are omitted for clarity.

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 C₅₉N⁺. 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 C₆₀ is accessible via chemical oxidation of dimeric (C₅₉N)₂ with a strong electron−hole oxidant. As with reactive carboxations such as the benzenium ion (C₆H₅⁺)³ and the radical cation C₆₀⁺,¹⁴ the stabilization of C₅₉N⁺ as an isolable salt profited from use of an inert carborane as counterion. The properties of C₅₉N⁺ reflect the isoelectronic analogy to C₆₀ 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.

References

(15) See Supporting Information for details.

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