

Production of C₅₉N:C₆₀ Solid Solution

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Abstract. We describe a simple way to produce large quantities of solid solutions of monomer C₅₉N in pure C₆₀ using an electric gas discharge tube. Typical concentrations are 10⁻⁵ to 10⁻⁴ C₅₉N with respect to C₆₀. The ¹⁴N and several ¹³C hyperfine constants were measured by ESR. These are a sensitive test for electronic structure calculations of the monomer. As the temperature is raised towards the *sc* to *fcc* structural transition at 261 K, the ESR spectrum motionally narrows and the activation energy for reorientation is measured. The rotational dynamics of the C₅₉N monomer between 130 and 600 K parallels that of C₆₀ in the bulk thus interactions between C₅₉N and C₆₀ are surprisingly weak.

INTRODUCTION

Azafullerene, C₅₉N, is one of the most interesting chemical modifications of the fullerene C₆₀ as it carries magnetic and electric dipole moments and is only slightly deformed¹. The solid is formed of (C₅₉N)₂ dimers and is non-magnetic². Dimerization has been a major obstacle to the study of monomeric C₅₉N and although several calculations of the electronic and molecular structure of C₅₉N were published³ the extent of delocalization of the charge over the cage could not be measured as the monomer was not available in sufficient amounts.

Here we describe a simple way to produce solid solutions of C₅₉N in C₆₀ (C₅₉N:C₆₀) in an electric gas discharge tube. We find that monomeric C₅₉N is stable in this solid solution and its rotational dynamics parallels that of C₆₀ in the bulk. The production of C₅₉N:C₆₀ in large quantities allowed us to measure the various ¹⁴N and ¹³C hyperfine constants that are a sensitive test of electronic structure calculations. A more detailed account of this work is published in Ref. 4.

PRODUCTION OF C₅₉N IN A N₂ GAS DISCHARGE TUBE

We produced C₅₉N in a N₂ gas discharge tube originally designed for the production of endohedral N@C₆₀ following the method of Pietzak et al.⁵. The set-up is shown in Fig. 1. Typical experimental conditions were: 1 mbar N₂ pressure, 1 mA

discharge current, 10 cm electrode distance. The tube is heated to about 550 °C at one electrode (usually the anode) while the other electrode is water-cooled and is at ambient temperature. C₆₀ powder placed between the electrodes at the bottom of the tube is sublimed and deposited onto the wall of the quartz tube and the cooled electrode. As the electric discharge is turned on, N ions in the plasma react with C₆₀ to form N@C₆₀ and C₅₉N simultaneously. Endohedral N@C₆₀ is collected from the water-cooled electrode. C₅₉N:C₆₀ is collected from the heated surface of the quartz tube. The highest concentration of C₅₉N in C₆₀ of about 100 ppm (determined from the ESR intensity) was found in narrow stripes on the quartz tube at the hottest regions where deposition still occurred i.e. where the temperature is roughly 400 °C. The yield of C₅₉N:C₆₀ (with concentration of 100 ppm) is about 5% of the starting C₆₀ material. After deposition, the discharge tube was opened to air before sealing the samples in quartz tubes under helium. The material is stable in He atmosphere. In air, C₅₉N decays at ambient temperatures in about a week. X-ray diffraction showed that the deposited powder mainly consists of crystalline C₆₀. The ESR spectrum shows a low concentration of unknown free radicals formed during the production. We have not attempted to purify the material.

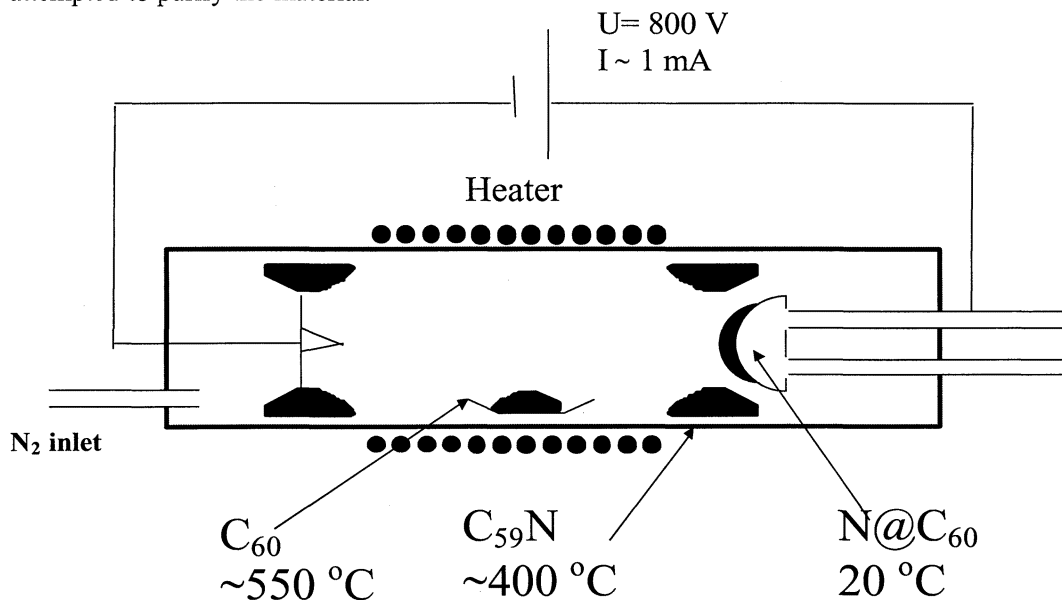


FIGURE 1. C₅₉N:C₆₀ production in a N₂ gas electric discharge tube.

ESR SPECTRUM AND ROTATIONAL DYNAMICS

Electron spin resonance (ESR) was performed at 9 GHz (X-band), 75 and 225 GHz. We identified the material as a solid solution of C₅₉N in C₆₀ from the similarity of the ESR spectrum to that of monomers produced by photo-⁶ or thermolysis⁷. At 300 K

(Fig. 2) the three ^{14}N ($I=1$) hyperfine lines characteristic of rapidly tumbling free radicals are observed with $g_{av}=2.0014(2)$ and an isotropic hyperfine coupling constant, $A_{iso}=0.363(1)$ mT.

The ESR spectrum is temperature independent between 257 and 290 K. As shown in Fig. 2, the spectrum consists of narrow ^{14}N hyperfine and a series of well resolved ^{13}C lines. In this temperature range the C_{59}N molecules are rapidly reorienting in all three directions together with the C_{60} molecules of the matrix. The reorientation is fast on the time scale of the ESR measurement and all anisotropic interactions are averaged to zero. The motional narrowing of the ESR spectrum of the rapidly reorienting C_{59}N molecule remains effective even at high ESR frequencies where relaxation due to g-factor anisotropy is more important. At 290 K and 225 GHz the linewidth was less than the instrumental resolution of 0.05 mT.

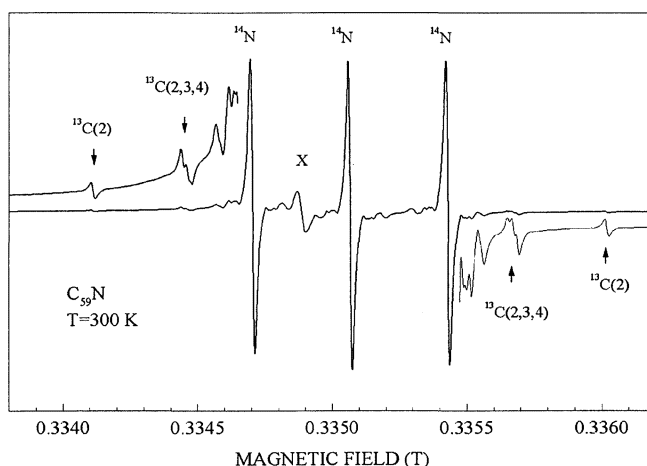


FIGURE 2. Motionally narrowed ESR spectrum of tumbling C_{59}N substituted in C_{60} at 290 K and 9 GHz. Wings are 10 times magnified. The ^{14}N and ^{13}C hyperfine lines of various sites are indicated. Other lines are unassigned ^{13}C lines and an unidentified free radical line, denoted by "X".

Isotropic Fermi contact couplings were calculated by the density functional *ab initio* method, B3LYP with 6-31G* basis set on a PM3 optimized molecular geometry of C_{59}N . The calculations were carried out using the Gaussian 98 software⁸. The electronic structures of the monomer and the dimer forms of C_{59}N were determined previously by Andreoni et al.¹ applying a similar method. The agreement between calculated and measured hyperfine constants is not particularly good. However, the calculation shows, in agreement with the experiment, that the extra spin density is not localized to the first C neighbors of N.

Pure C_{60} has a first order phase transition at 261 K from a low temperature simple cubic (*sc*) to the high temperature face centered cubic (*fcc*) structure. At low temperatures the molecular orientations are arranged preferentially in two standard configurations with respect to each other and there is a merohedral disorder of regions with differing configurations. As the temperature is raised, molecules fluctuate more and more rapidly between the possible orientations with large angle jumps. The

fluctuations shorten the spin lattice relaxation time, T_1 , and above about 200 K motionally narrow the anisotropic ESR spectrum. The width of the spectral components is proportional to the spin-spin relaxation rate $1/T_2$. The activation energy of monomeric $C_{59}N$ in C_{60} measured from T_1 and $1/T_2$ is about $\Delta E_{C_{59}N} / k_B = 2300$ K. This value is remarkably close to $\Delta E_{C_{60}} = 2980$ K, the activation energy of the correlation time of the rotation of C_{60} molecules measured⁹ in pure C_{60} . The close agreement between $\Delta E_{C_{59}N}$ and $\Delta E_{C_{60}}$ indicates that the reorientation dynamics of $C_{59}N$ follows that of the bulk. This would not be so if interactions between $C_{59}N$ and C_{60} were strong.

SUMMARY

In summary, $C_{59}N$ is a stable substituent molecule in C_{60} crystals at all temperatures below the formation of the solid solution at 400 C. Hyperfine interactions of the free radical with ^{14}N and ^{13}C show a partial delocalization of the extra electron over the cage. Interactions with neighboring C_{60} molecules is small and thus rotational dynamics are similar.

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