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Putting Ammonia into a Chemically Opened Fullerene

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Abstract: We put ammonia into an open-cage fullerene with a 20-membered ring (**1**) as the orifice and examined the properties of the complex using NMR and MALDI-TOF mass spectroscopy. The proton NMR shows a broad resonance corresponding to endohedral NH_3 at $\delta_H = -12.3$ ppm relative to TMS. This resonance was seen to narrow when a ^{14}N decoupling frequency was applied. MALDI spectroscopy confirmed the presence of both **1** ($m/z = 1172$) and **1** + NH_3 ($m/z = 1189$), and integrated intensities of MALDI peak trains and NMR resonances indicate an incorporation fraction of 35–50% under our experimental conditions. NMR observations showed a diminished incorporation fraction after 6 months of storage at -10 °C, which indicates that ammonia slowly escapes from the open-cage fullerene.

Introduction

Ever since the discovery of fullerenes in 1985,[1] it was realized that the space inside could hold atoms and even small molecules. Several methods have been developed for producing endohedrally doped fullerenes, including ion bombardment and high-pressure/high-temperature techniques.[2–9] The main drawbacks of these methods are low yield (<1%) and the need for extreme reaction conditions. A relatively new approach to producing endohedral fullerenes has been the "molecular surgery" method, whereby a hole is chemically opened on the surface of the fullerene cage, and a gas molecule is inserted reversibly through the orifice.[10–24] This method avoids the drawbacks of the others because the orifice in the fullerene considerably lowers the

activation barrier for insertion of the dopant molecule. A high incorporation fraction of small molecules into the fullerene can thus be achieved under relatively mild reaction conditions. Komatsu et al. added groups to C_{60} to create a 13-membered ring in the carbon cage.[14] This is large enough to permit H_2 and He to enter.[15,16] They then devised a sequence of reactions that closed the hole, trapping H_2 inside to produce $H_2@C_{60}$ in high yield.[17]

Several synthetic groups have been working to produce novel open-cage fullerene derivatives with various orifice sizes.[12,13,16,19–22] In particular, Iwamatsu et al.[20,21] have succeeded in synthesizing a fullerene with a 20-membered ring as the orifice (**1**), the largest opening synthesized on a fullerene to date; see Figure 1.

The size of this orifice is such that a water molecule spontaneously incorporates into the fullerene cage at room temperature.[21] Furthermore, it has been shown that, under suitable reaction conditions, CO can be incorporated into **1**.[23] We report here the synthesis of a new endohedral fullerene,

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Figure 1. Iwamatsu's open-cage fullerene, **1**.

NH$_3$@**1**, and confirm its existence via NMR and MALDI mass spectroscopy.

Experimental Section

Sample Preparation. The open-cage fullerene **1** was prepared as described in the literature.[19,22] Liquid ammonia was prepared from an ammonium salt. Briefly, an aqueous solution of ammonium sulfate and sodium hydroxide was refluxed. A vessel attached to the top of the condenser was immersed in a dry ice/acetone bath to condense ammonia from the reflux vapors. About 2 mL of liquid ammonia was obtained in this way. The ammonia was then transferred to a cooled sample tube containing **1** (10 mg) dissolved in 3 mL of 1,1,2,2-tetrachloroethane. The tube was placed into a high pressure vessel (Autoclave Engineering), and the vessel was sealed. The vessel was left at room temperature and allowed to remain under pressure for 20 h. The pressure of ammonia gas inside the vessel was about 7 atm, the vapor pressure at room temperature. After 20 h, the sample was removed and purified on a short (10 cm) silica gel column eluting with 50% toluene in ethyl acetate. The crude material was brown and opaque with some solid material suspended in the solution. The purified material was a clear red solution. The solvent was removed without heating, yielding a red powder, which was stored under nitrogen at −10 °C. The yield of **1** is about 50%. About 35−50% contains an ammonia molecule (see below). Increasing the temperature causes increased decomposition of **1** but gives a higher incorporation of ammonia. NMR spectroscopy of the purified material revealed no trace of free ammonia dissolved in solution, indicating that the purification process removes any ammonia that is not incorporated into **1**.

NMR Spectroscopy. All spectra were taken in a solution of CDCl$_3$ except for the low-temperature spectra, which were taken in a solution of CD$_2$Cl$_2$.

^{1}H Spectroscopy. The ^{1}H NMR spectrum was taken on a Bruker Avance 500 MHz spectrometer running at a ^{1}H frequency of 499.95 MHz. Typically, 32 pulses were used with a width of 9.45 μs and a recycling delay of 0.5 s. All chemical shifts were relative to TMS. Line broadening of up to 0.3 Hz was used to improve the signal-to-noise ratio.

^{14}N Spectroscopy. The ^{14}N NMR spectrum was taken on the same spectrometer running at a ^{14}N frequency of 36.11 MHz. Typically, 32 pulses were used with a width of 25 μs and a recycling delay of 5 s. All chemical shifts were reported relative to tetraethylammonium chloride in D$_2$O. Line broadening of up to 3 Hz was used to improve the signal-to-noise ratio.

^{14}N Decoupling. We modified a standard ^{1}H$-^{13}$C CW decoupling sequence by changing the ^{13}C frequency. This was used to decouple ^{14}N from ^{1}H spins. A ^{14}N pulse width of 10.9 μs was used. The decoupling frequency was set at −87.75 ppm relative to the ^{14}N shift of tetraethylammonium chloride in D$_2$O. The power was attenuated typically by 40 dB.

MALDI-TOF Mass Spectroscopy. MALDI-TOF mass spectra were acquired on an Applied Biosystems Voyager DE Pro MALDI-TOF fitted with a nitrogen laser (337 nm, 3 ns pulses) in negative ion reflector mode and using an accelerating voltage of 25 kV and

Figure 2. Downfield part of the proton NMR spectrum of NH$_3$@**1**.

an extraction delay time of 200 ns. Scans with and without use of 1,8,9-anthracenetriol matrix were performed.

Results and Discussion

The sample of NH$_3$@**1** was prepared as described above. After purification, the incorporation of ammonia into **1** at room temperature is found to be between 35% and 50% by NMR and MALDI-TOF mass spectroscopy. Higher incorporation fractions can be achieved with higher temperature, but the accelerated reaction of ammonia with the external structure of **1** at elevated temperatures destroys a significant fraction of the fullerene. Also, ammonia is observed to incorporate in small quantities (<5%) simply by adding liquid ammonia to an open vessel containing a solution of **1** in 1,1,2,2-tetrachloroethane and letting the mixture warm to room temperature.

The MALDI spectrum of NH$_3$@**1** in a 1,8,9-anthracenetriol matrix reveals the presence of both **1** ($m/z = 1172$) and NH$_3$@**1** ($m/z = 1189$) in a roughly 2:1 ratio. When the matrix is removed or the laser power is increased, the intensity of the NH$_3$@**1** peak is dramatically reduced, indicating that the laser is causing the escape of the gas from the cage. Because this process can be assumed to occur to some extent even in the presence of a matrix, it was concluded that the incorporation fractions obtained from the MALDI spectra were likely unreliable and that NMR studies would give more accurate values.

The downfield part of the proton NMR spectrum of NH$_3$@**1** is shown in Figure 2. The spectrum is almost identical to that of empty **1**. There are two doublets, at 3.0 and 3.5, due to two methylene protons at the throat of **1** (see Figure 1). These peaks have been previously shown to shift by small amounts when an atom or molecule is put inside **1**.[23] In the present case, the peaks show a small splitting because some of the open-cage fullerene is filled and some is empty (see the inset in Figure 2). However, the splitting is not large enough to get a good ratio of peak areas to determine the incorporation fraction.

The upfield region of the proton NMR is shown in the top panel of Figure 3. There is a very broad peak at $\delta_H = -12.3$ ppm, fwhm ≈ 45 Hz (peak B). This is contrasted with the peak at $\delta_H = -11.4$ ppm due to H$_2$O@**1**, which has been previously seen and which has a fwhm of less than 1 Hz (peak A). The integrated intensity of the peak at $\delta_H = -12.3$ ppm in the spectrum indicated that the incorporation fraction of ammonia was between 35% and 50%. The dramatic upfield shift from

Figure 3. Upfield region of the proton NMR of NH$_3$@**1**. Top panel: Undecoupled spectrum. Bottom panel: With ^{14}N decoupling applied. Peak A is due to H$_2$O@**1**, and peak B is due to NH$_3$@**1**. Note: Spectra have been rescaled (see text).

ammonia dissolved in CDCl$_3$ ($\delta_H = 0.465$ ppm) is characteristic of endohedral molecules inside fullerenes, as the ring currents induced by the external static magnetic field produce an opposing field inside the fullerene, which shields the nuclei inside. This effect has been predicted theoretically and observed experimentally in a number of other endohedral fullerenes.[16,20,25-33] Two potential causes were hypothesized for the significant broadening of the observed proton resonance. First, the broadening could be due to the coupling with the nuclear spin of the nitrogen. Because ^{14}N has a nuclear spin of $I = 1$, the proton peak should be split into a 1:1:1 triplet. However, ^{14}N has a large electric quadrupole moment, and, in an asymmetric environment, the tumbling of the molecule causes rapid enough relaxation of the ^{14}N spin to broaden the three proton peaks to give a single broad line. This effect is common in protons bonded to nitrogen. Second, the umbrella inversion of ammonia inside the open-cage fullerene might be slow on the NMR time scale, leading to a broadening of the line as the protons spend more time in unequal chemical environments.

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	NH$_3$	NH$_3$@**1**	$\Delta\delta$
^{1}H	0.465	−12.3	−12.8
^{14}N	−66.7	−87.8	−21.1

The first hypothesis was tested by decoupling the ^{14}N nucleus from the surrounding protons. An rf pulse at the ^{14}N resonant frequency causes rapid transitions among the three *m* states in ^{14}N. The pulse sequence was tested on tetraethylammonium chloride salt dissolved in D$_2$O. Here, the tetrahedral symmetry around the ^{14}N means that the electric field gradient at the nucleus is zero, and the quadrupolar relaxation is not present. The characteristic 1 Hz N−H *j*-coupling in the methyl protons of the salt disappeared when the rf was set to the salt's ^{14}N resonant frequency. Gaussian 03[34] GIAO calculations at the B3LYP/6-311G++(2p,2d) level indicated that the ^{14}N frequencies of the ammonium salt and the endohedral ammonia were separated by ∼100 ppm. A ^{14}N decoupling frequency of $\delta_N = -87.75$ ppm (relative to the ammonium salt) collapsed the large ammonia proton line at $\delta_H = -12.3$ ppm from 45 to 2 Hz fwhm, as seen in the bottom panel of Figure 3. This observation indicates that the extreme broadening of the line is caused mainly by rapid quadrupolar relaxation of the ^{14}N nucleus, which, in turn, relaxes the protons bound to it. It should be noted that the measured intensities of the water peak (peak A) in the two panels are the same; the ordinate has been rescaled on the bottom panel.

We measured the upfield shifts for both protons and ^{14}N caused by putting ammonia into **1** (Table 1). The proton NMR of free ammonia showed a single narrow peak at 0.465 ppm. The peak is narrow and not split by ^{14}N because the protons rapidly exchange with trace amounts of water in the solvent. This difference is yet another proof that the ammonia that we are studying is inside **1** and protected from exchange. The upfield shift due to the incorporation is then 12.8 ppm. As stated above, we find the ^{14}N resonance in NH$_3$@**1** is at −87.75 ppm relative to tetraethylammonium ion. Using ^{14}N NMR, we found the resonance for NH$_3$ is at −66.67 ppm relative to tetraethylammonium ion. This gives an upfield shift for the nitrogen of 21.1 ppm. The difference between the effects on protons and ^{14}N is due to the different positions in the open-cage fullerene cage and to the different effects of the solvent for the dissolved ammonia.

To test the second hypothesis, the sample was cooled to −80 °C without the decoupling field. There are two orientations of the ammonia molecule in the cage: with the hydrogens pointed toward or away from the mouth. If the interconversion is sufficiently slow, the proton peak will broaden. If the temperature is decreased, the interconversion slows still further, and the NMR spectrum would show two peaks. The ammonia proton fwhm decreased from 45 to 13 Hz, probably due to the decreased quadrupole relaxation of the ^{14}N, but did not split into two lines. Also, several other lines too broad to be distinguished from the noise appeared to be sharpened as well, although not as much as when decoupled. When the spectrum was decoupled at −80 °C, no additional effects beyond those reported in the room-temperature decoupling experiment relating to peak height or area were seen. This suggests that the small extra resonances observed at low temperatures are not additional

(34) Frisch, M. J.; *Gaussian 03*; Gaussian, Inc.: Pittsburgh, PA, 2003.

conformations of NH_3 inside **1**, but rather NH_3 inside chemically modified derivatives of **1**, likely byproducts of the reaction of ammonia with the external scaffolding around the orifice of **1**.

After more than 6 months of storage under N_2 at -10 °C, the resonance at $\delta_H = -12.3$ ppm was still observed in the ^1H NMR spectrum of our sample, but at greatly reduced intensity. The small resonance due to $H_2O@\mathbf{1}$, however, remained at roughly the original intensity. These results indicate that the incorporation of ammonia into the open-cage fullerene is reversible and that the incorporated gas leaks out of the cage over a long period of time. Water apparently has a low barrier for going into or out of **1**. Therefore, $H_2O@\mathbf{1}$ rapidly equilibrates with the trace water in the NMR solvent. Ammonia that escapes from **1** diffuses out of the NMR tube and is lost.

Summary

We have demonstrated the incorporation of NH_3 into the open-cage fullerene **1**. NMR and MALDI spectroscopy indicate the formation of $NH_3@\mathbf{1}$ where the ammonia is highly shielded by the fullerene cage and the protons undergo rapid relaxation in the presence of the ^{14}N electric quadrupole moment. The gas is observed to slowly escape over time, reverting to the original empty open-cage fullerene.

Supporting Information Available: Complete ref 34. This material is available free of charge via the Internet at http://pubs.acs.org.

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