

An NMR Study of He₂ Inside C₇₀Anthony Khong,[†] Hugo A. Jiménez-Vázquez,^{†,‡} Martín Saunders,^{*,†} R. James Cross,^{*,†} Julia Laskin,[§] Tikva Peres,[§] Chava Lifshitz,[§] Rob Strongin,[⊥] and Amos B. Smith III[⊥]

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Received January 13, 1998

Abstract: A peak in the helium NMR spectrum of ³He labeled C₇₀ is assigned to molecules containing two helium atoms. The concentration of the dihelium species is about 1/20th that of molecules containing a single helium, and the helium shift of this new species is 0.014 ppm (5.6 Hz) downfield from the resonance for molecules containing one helium. Mass spectrometry confirms the presence of dilabeled molecules. A Hirsch-Bingel transformation of the C₇₀ to a malonate diethyl ester increases the chemical shift difference between the mono- and dihelium species.

Introduction

Noble gas atoms can be inserted into the cages of fullerene molecules to form stable compounds by heating the fullerenes in the presence of the gas at high pressure.^{1–4} ³He is an excellent NMR nucleus, and when it is incorporated into fullerenes, the products yield helium NMR spectra.^{3,5} Each helium-labeled fullerene yields a distinct, narrow line reflecting the magnetic field inside. Adding chemical groups to the outside of a fullerene alters the π -electron structure, which, in turn, changes the field and the helium chemical shift.^{3,6}

Recently, Lifshitz et al.⁷ found in a mass spectrometric analysis of neon-labeled C₇₀ clear evidence of a species containing two neon atoms. About 2% of the neon-containing molecules had two neon atoms inside. Since helium is smaller than neon, we expected that C₇₀ labeled with ³He would contain an even higher portion of a dihelium species. We report here both NMR and mass spectrometric evidence that this is the case.

Results and Discussion

Subjecting fullerenes to high-temperature, high-pressure treatment with noble gases, reisolating the fullerene, and repeating the labeling leads to an increase in the amount of incorporated

noble gas which, initially, is linear in the number of repetitions.⁸ In our case, the C₇₀ was labeled four times. The NMR solvent consists of a 3:1 solution of methylnaphthalene and CD₂Cl₂. Dissolved ³He gas was used as a reference.

Figure 1 shows the entire NMR spectrum. Peak A at 0 ppm is due to ³He in solution. Peak F at –28.716 ppm is due to ³He@C₇₀ reported earlier at –28.8.⁵ The small change in chemical shift is most likely the result of a solvent effect on the dissolved ³He. Other peaks in the spectrum are also shifted downfield from their literature values by a similar amount.

Apart from the ³He@C₇₀ spectrum, peaks were also observed at –16.803 (B), –17.488 (C), and –18.616 ppm (D). These are due to higher fullerenes, C₇₆ and C₇₈, which are present as impurities in the C₇₀ starting material and have all been seen previously.⁹ Peaks B and D are due to C₇₈ and C₇₆, respectively. Peak C had been observed in a sample of C₇₈ isomers containing a trace of C₇₆. It has not been determined which fullerene it is due to. No ³He@C₈₄ was detected in our sample.

Figure 2 is an enlargement of the region around –28.7 showing a small peak at –28.702 ppm (E) very near the main C₇₀ signal at –28.716 ppm (F). The peaks are separated by 0.014 ppm or approximately 5.6 Hz. Peak E has about 10% the intensity of peak F. We believe that this small peak is due to molecules containing two helium atoms. We have seen this peak previously in other samples of C₇₀ when we were studying the formation of its epoxides¹⁰ but did not understand where it came from.

We considered and ruled out several possible explanations for this peak at that time. We looked at the ¹³C NMR spectrum of an isotopically enriched sample of C₇₀. No peaks attributable

[†] Yale University.[‡] Present address: Departamento de Química Organica, ENCB-IPN, Mexico.[§] The Hebrew University of Jerusalem.[⊥] University of Pennsylvania.(1) Saunders, M.; Jiménez-Vázquez, H. A.; Cross, R. J.; Poreda, R. J. *Science* **1993**, *259*, 1428.(2) Saunders, M.; Jiménez-Vázquez, H. A.; Cross, R. J.; Mroczkowski, S.; Gross, M. L.; Giblin, D. E.; Poreda, R. J. *J. Am. Chem. Soc.* **1994**, *116*, 2193.(3) Saunders, M.; Cross, R. J.; Jiménez-Vázquez, H. A.; Shimshi, R.; Khong, A. *Science* **1996**, *271*, 1693.(4) Shimshi, R.; Khong, A.; Jiménez-Vázquez, H. A.; Cross, R. J.; Saunders, M. *Tetrahedron* **1996**, *52*, 5143.(5) Saunders, M.; Jiménez-Vázquez, H. A.; Cross, R. J.; Mroczkowski, S.; Freedberg, D. I.; Anet, F. A. L. *Nature* **1994**, *367*, 256.(6) Saunders, M.; Jiménez-Vázquez, H. A.; Bangert, B. W.; Cross, R. J.; Mroczkowski, S.; Freedberg, D. I.; Anet, F. A. L. *J. Am. Chem. Soc.* **1994**, *116*, 3621.(7) Laskin, J.; Peres, T.; Lifshitz, C.; Saunders, M.; Cross, R. J.; Khong, A. *Chem. Phys. Lett.* In press.(8) In our study with neon and C₆₀, we found that repeating the high pressure, high-temperature treatment on the purified material after each cycle increases the neon content linearly. The neon incorporation increased from 0.1% to 0.3% after four successive treatments. The neon was analyzed by first pyrolyzing the solid material at 1000 °C, which releases the neon and is detected with a quadrupole mass spectrometer.(9) Saunders, M.; Jiménez-Vázquez, H. A.; Cross, R. J.; Billups, W. E.; Gesenberg, C.; Gonzalez, A.; Luo, W.; Haddon, R. C.; Diederich, F.; Herrmann, A. *J. Am. Chem. Soc.* **1995**, *117*, 9305.(10) Smith, A. B.; Strongin, R. M.; Brard, L.; Furst, G. T.; Atkins, J. H.; Romanow, W. J.; Saunders, M.; Jiménez-Vázquez, H. A.; Owens, K. G.; Goldschmidt, R. J. *J. Org. Chem.* **1996**, *61*, 1904.

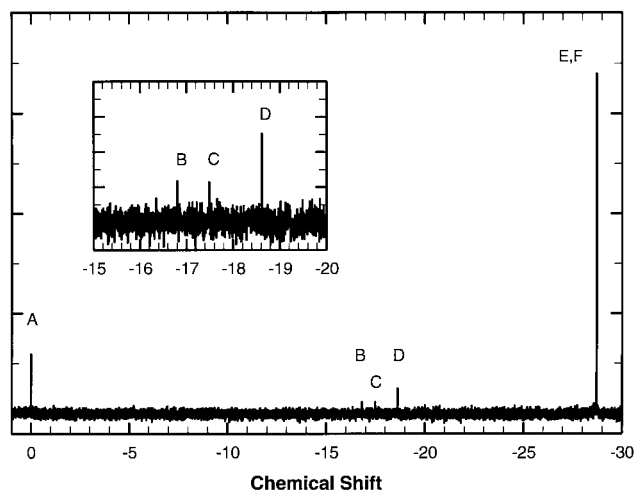


Figure 1. The full ³He NMR spectrum. Peak A at 0 ppm is the reference due to dissolved ³He gas. Peak E,F at -28.716 ppm is due to ³He@C₇₀, and the three peaks B, C, and D, and between -16.8 and -18.6 ppm, are due to higher fullerenes. The inset shows the higher fullerene region more clearly.

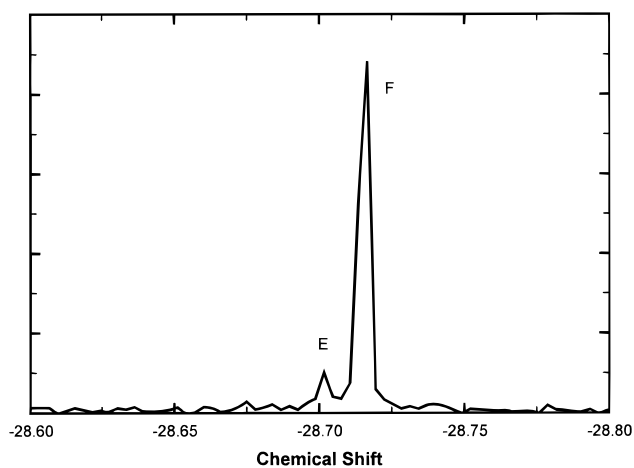


Figure 2. A zoom of the NMR spectrum near the peak for ³He@C₇₀. The small peak E, downfield by 5.6 Hz (0.014 ppm), is due to the dihelium species ³He₂@C₇₀.

to an isomeric form of C₇₀ were seen. We consider it very unlikely that the small peak in the helium spectrum is due to a higher fullerene. Assignment to a derivative of C₇₀ is unlikely, since adding a single functional group to fullerenes typically produces a chemical shift of ~3 ppm upfield³ in C₆₀ and ~1 ppm downfield in C₇₀—2 orders of magnitude larger than the observed shift of the new peak.

The small difference in chemical shift from ³He@C₇₀ suggests a species very closely resembling it. The dihelium species would fit this description. The gradient of the magnetic field along the 5-fold axis of C₇₀ is predicted to be very small,¹¹ and therefore the helium chemical shift difference at the equilibrium position in the dihelium compound and the monohelium compound should also be small. We believe that the peak at -28.702 ppm is due to molecules with two ³He atoms inside C₇₀. The peak intensity ratio of 10% would correspond to a ratio of 5% in the concentrations of ³He₂@C₇₀ to ³He@C₇₀. This is consistent with Lifshitz's results on Ne₂@C₇₀. The higher fraction of dihelium to dioneon material is as expected.

It has been found that addition of a chemical group to C₇₀ normally occurs at one end of the molecule rather than in the

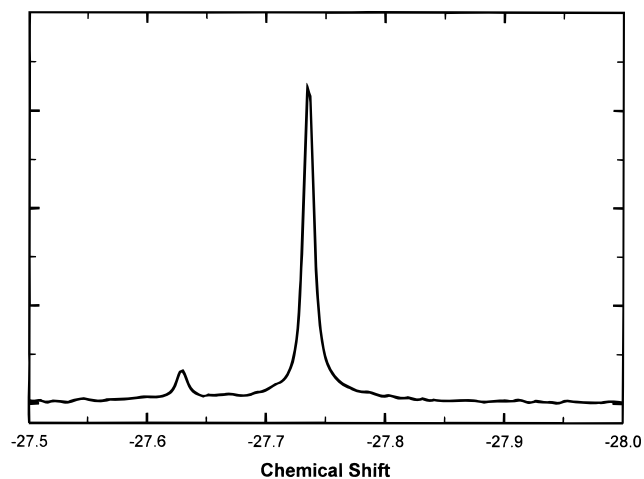
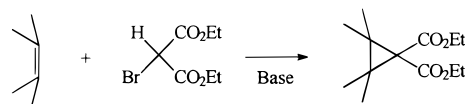


Figure 3. A zoomed NMR spectrum of the C₇₀ monomalonate diethyl ester product. The small peak at -27.636 ppm corresponds to the derivatized dihelium species. Its peak intensity is 10% of the peak at -27.744 ppm due to the same adduct of the monohelium species. The chemical shift difference between the two peaks is 44 Hz, an order of magnitude larger than the same cluster of peaks in the NMR spectrum of ³He@C₇₀.

middle. In the case of ³He₂@C₇₀, functionalization at one end alters the π-ring currents to produce a substantial and perhaps nonlinear gradient in the magnetic field inside. This would result in different chemical shifts for the two helium atoms.¹¹ The helium atoms are expected to interchange rapidly so as to yield a single averaged peak, since the predicted barrier for one passing the other is expected to be only 4.5 kcal/mol. We expected that the difference between this average frequency and that for molecules containing one helium would be larger than in C₇₀ alone.



To test this idea, we carried out a Hirsch-Bingel reaction¹² to generate a C₇₀ malonate diethyl ester adduct. Figure 3 shows the NMR analysis of the monoadduct obtained after column chromatography of the crude mixture. Two helium signals were observed at -27.636 and -27.744 ppm. The intensity of the former peak is about 10% of the latter. This is consistent with the peak ratio found for the unfunctionalized C₇₀. The chemical shift difference of 0.11 ppm or 44 Hz is larger than the corresponding difference in ³He@C₇₀.

A portion of the ³He labeled C₇₀ sample was sent to Jerusalem for mass spectrometric analysis. It was found to contain three species: C₇₀, ³He@C₇₀, and ³He₂@C₇₀. Due to the small mass of ³He and the presence of ¹³C at natural abundance, the peaks due to the three species overlap, complicating the analysis. The data are shown in Figure 4. The top panel shows the mass region 839–844 due to C₇₀ and ³He@C₇₀. The middle panel shows the range from 842 to 847 due to all three species. The bottom panel shows the range from 845 to 850 containing all three species. The ordinates are the unnormalized signal intensities spanning 2 orders of magnitude. Calculated spectra are shown for C₇₀, the sum of C₇₀ and ³He@C₇₀, and for all three species. The details of the fitting procedure are given below. It is clear that the peaks at 843 and beyond cannot be

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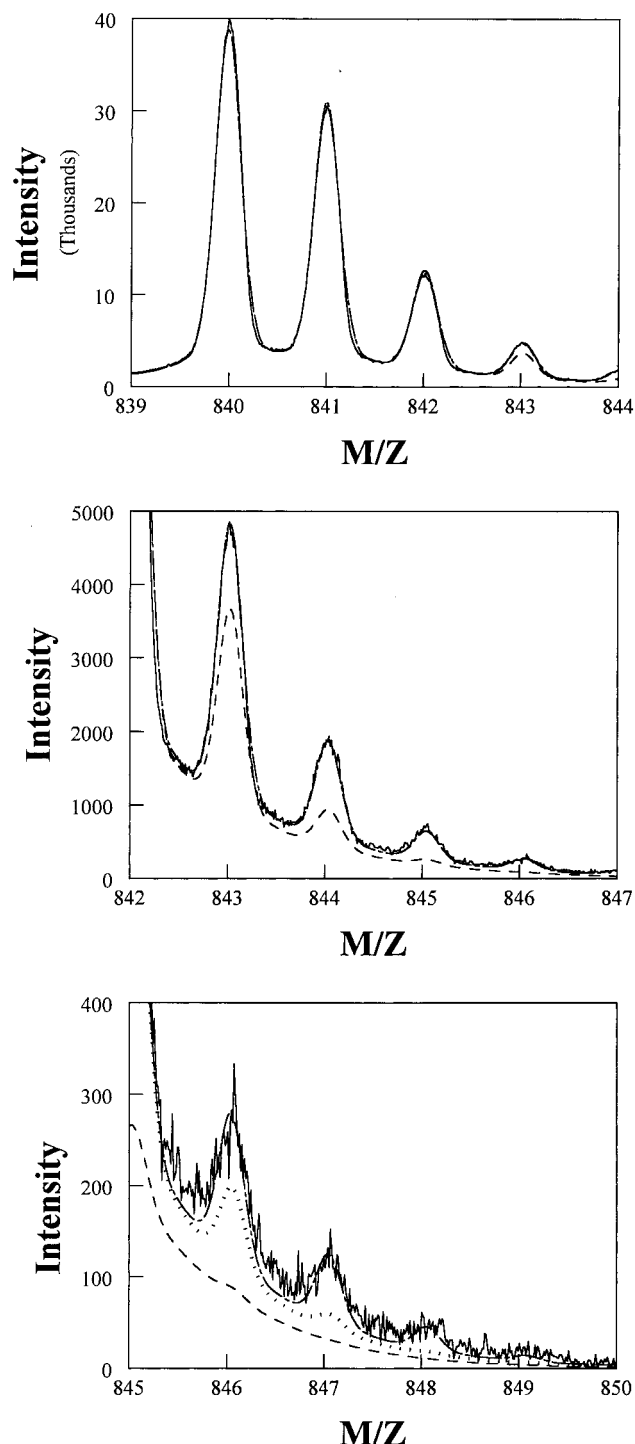


Figure 4. The mass spectrum of the sample. The top panel shows the mass range 839–844, largely due to C_{70} containing varying numbers of ^{13}C 's. The middle panel at higher gain shows the mass range 842–847, and the bottom panel at still higher gain shows the range 845–850. All three panels show the calculated mass spectrum of C_{70} in long dashes (see text). This clearly does not give the correct intensity at mass 843 and beyond due to the presence of $^3He@C_{70}$. Similarly, in the bottom panel, the combined spectra of C_{70} and $^3He@C_{70}$ (short dashes) do not match the measured intensity at masses 846 and 847 due to the presence of $^3He_2@C_{70}$. The calculated curve for all three products (short, long dashes) fits very well.

fit by C_{70} alone, and the peaks at 846 and 847 cannot be fit by C_{70} and $^3He@C_{70}$ alone. The extra intensity at masses 846 and 847 is assigned to $^3He_2@C_{70}$. The curve can be fit with the amounts of the three species as adjustable parameters. The

ratios of intensities for $C_{70}:^3He@C_{70}:^3He_2@C_{70}$ are $37:1:0.05 \pm 0.01$, in good agreement with the NMR data.

Conclusions

A peak in the helium NMR spectrum of helium-labeled C_{70} is assigned to the novel dihelium species, $^3He_2@C_{70}$. Its presence was confirmed by mass spectrometry. Approximately 5% of the helium-labeled C_{70} contains two helium atoms. The very small difference in chemical shift between the unfunctionalized mono- and dilabeled species indicates that the magnetic field in C_{70} is very nearly independent of the position inside the cage. Adding a chemical group to the outside of the cage on one end substantially increases the separation between the peaks of the mono- and dilabeled species.

These observations are relevant to considerations concerning the mechanism of noble gas incorporation into fullerene cages. It is also useful to be able to anticipate the presence of these peaks in the helium spectra of derivatives of C_{70} and other fullerenes.

Experimental Section

High-Temperature and High-Pressure Labeling of C_{70} . A sample of 200 mg of 96% C_{70} (from the MER Corporation)¹³ was labeled with 3He in a sealed 4 in. copper ampule at 650 °C and a pressure of 3000 atm in a steel high-pressure vessel. The reaction was allowed to proceed for 8 h. The material was extracted for 24 h with CS_2 using a Soxhlet extractor. The solid was obtained, dried and relabeled using identical conditions. The C_{70} was labeled with 3He four times to increase the incorporation of helium.

3He NMR Analysis. Approximately 15 mg of helium-labeled C_{70} was dissolved in a 3:1 mixture of methylnaphthalene and CD_2Cl_2 in a 7 in. by 5 mm NMR tube. 3He gas was bubbled into the solution as a reference. No relaxation agent was added. The sample was examined by using a 384 MHz probe (Nalorac) in a Bruker 500 MHz magnet. Acquisitions were made in 20 h (about 86 000 pulses). The 3He gas resonance is set to 0 ppm when the FID is processed. No line broadening was applied to the data processing.

Synthesis of the Malonate Diethyl Ester Derivative of C_{70} . To a 20 mg sample of enriched $^3He@C_{70}$ dissolved in 20 mL toluene under an argon atmosphere was added one equivalence of diethyl bromomalonate. The reagents were dissolved before one equivalence of DBU, 1,8-diazabicyclo[5.4.0]undec-7-ene, was introduced. The resulting mixture was stirred for 1 h and subsequently concentrated and chromatographed on a 48 in. silica gel column with methylene chloride as the eluant. Three distinct bands were observed. The first band was unreacted C_{70} . A monoadduct was collected from the second fraction. The third band consists of higher functionalized products of the reaction which were discarded. The fraction containing the monofunctionalized C_{70} was stripped of solvent, dried, and analyzed with NMR with conditions described earlier.

Mass Spectrometric Analysis. The mass spectrum was taken on a double focusing spectrometer of reversed geometry, the VG ZAB-2F. The sample was introduced into the mass spectrometer by using the direct insertion probe and evaporated at 400 °C. The electron impact conditions were as follows: electron energy, 70 eV; trap current, 100 μA ; mass resolution 1100 (10% valley definition). The calculated curve for C_{70} was obtained by taking the low-mass half of the peak at 840 and reflecting it to make the whole peak. This procedure eliminates most of the contribution from the tail of the peak at 841. A small correction was made to eliminate the remaining contribution. This peak was then shifted over by one amu and multiplied by the appropriate factor to construct the peak at 841. Repeating this for higher masses generates the calculated spectrum for C_{70} shown in the top two panels of Figure 4. Because the isotopic abundance of ^{13}C is known, only

(13) HPLC analysis at MER corporation of the 96% C_{70} found the remaining constituents of the crude material to consist of 1.5% C_{60} :0.5% $C_{70}O$ and 2% C_{76} , C_{78} , and C_{84} combined. A C_{18} column was used in the analysis.

the overall intensity is an adjustable parameter. The spectrum for ³He@C₇₀ is calculated by taking the spectrum for C₇₀, shifting it over by three mass units, and multiplying it by an adjustable intensity so that the sum of the two fits the measured intensity at masses 843 and 844. The same procedure is applied to the ³He₂@C₇₀ spectrum.

Acknowledgment. This work was supported by the U.S. National Science Foundation through grants CHE-9412768 and

CHE-9610215 and by the United States–Israel Binational Science Foundation under Grant No. 94-00058. The Farkas Research Center is supported by the Minerva Gesellschaft für die Forschung, GmbH, München. We are grateful to Dr. Michael Bühl for comments on his theoretical values for the magnetic field inside C₇₀.

JA980142H