

5. Radical **4** is presumed to be the rearrangement intermediate for the production of **2** from **1** under radical-generating conditions, and **5** is the proposed lysine-pyridoxyl radical intermediate in the lysine 2,3-aminomutase reaction. Rearrangements via **4** are azo analogues of the well-known cyclopropyl carbinyl rearrangements.¹⁶

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C₆₀ Has Icosahedral Symmetry

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The class of molecules with icosahedral symmetry, the highest finite point group symmetry, is a very exclusive one. To date it has only two confirmed members—the borohydride anion^{1,2} (B₁₂H₁₂²⁻) and dodecahedrane³ (C₂₀H₂₀), both with symmetry *I_h*. A new candidate molecule, dubbed Buckminsterfullerene, was proposed in 1985 by Kroto, Heath, O'Brien, Curl, and Smalley;⁴ a 60-atom, pure carbon, truncated icosahedron with the geometry of a soccerball. They hit upon this remarkable structure in their struggle to understand the origin of the extraordinary abundance and inertness of C₆₀, observed in pioneering carbon cluster beam experiments carried out at Exxon⁵ and Rice.⁴ The idea that such a spectacular structure might be possible was considered as early as 1966 by Jones,⁶ who mused about the problem of constructing closed two-dimensional nets of atoms. Other authors discussed this structure for a hypothetical C₆₀ molecule as a purely theoretical possibility shortly thereafter.⁷ Following the proposal of Kroto et al., Buckminsterfullerene immediately became the subject of intense theoretical study, and experimentalists vigorously sought evidence that C₆₀ did indeed have the structure of a soccerball. This evidence proved difficult to come by in carbon cluster beam experiments, where the molecules are available in small quantities for short times.

Recently, Krätschmer, Fostiropoulos, and Huffman⁸ reported the observation of four sharp lines in the IR spectrum of carbon dust. This led them to believe that carbon dust, produced by resistively heating graphite in a He atmosphere, contains a significant amount (1%) of C₆₀. We were soon able to directly confirm this belief using a surface analytical mass spectrometer,⁹ and we began producing quantities of carbon dust on the order

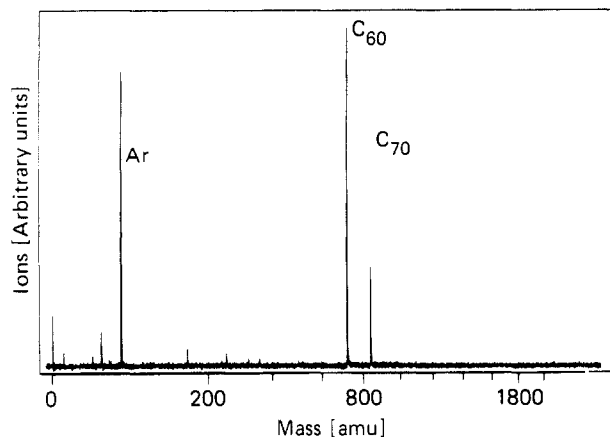


Figure 1. Time-of-flight mass spectrum of the C₆₀/C₇₀ mixture used in the NMR experiment. A 10- μ L drop of the CCl₄ solution was allowed to evaporate on a tantalum foil, and the spectrum was obtained with use of the surface analytical mass spectrometer. The horizontal axis is linear in time-of-flight and the corresponding (nonlinear) mass scale is indicated.

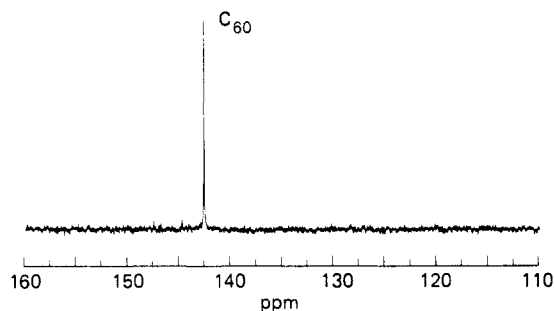


Figure 2. Aromatic region of the ¹³C NMR spectrum of ~200 μ g of C₆₀/C₇₀ in CCl₄, without ¹H decoupling, obtained with a Bruker AM-500 NMR spectrometer operating at 125.7 MHz at 25 °C, with 13 000 scans over a 14 kHz bandwidth digitized into a 64 kword dataset; chemical shift referenced to CCl₄ at 96.1 ppm. The resonance at 142.5 ppm is assigned to C₆₀.

of tens of milligrams using the method of Krätschmer et al. We then found that the collected raw carbon dust could be purified by fractional distillation and that refined films consisting almost entirely of C₆₀ and C₇₀ could thereby be produced. The relative proportion of these two species was checked with use of the mass spectrometer and could be controlled by varying the sublimation temperature. Using such purified films we were able to measure vibrational Raman spectra of C₆₀ and C₇₀, as reported elsewhere.¹⁰ A preliminary comparison of both the available IR data⁸ and these recent Raman data for C₆₀ with vibrational spectra calculated for the soccerball structure already strongly suggests that this is likely to be the correct structure.

One particular aspect of the proposed soccerball geometry, the exact equivalence of all 60 atoms implied by the *I_h* symmetry, can be directly tested with NMR spectroscopy. The NMR spectrum of Buckminsterfullerene containing a single ¹³C atom should consist of a single sharp line. In this communication we present NMR data which show that this is indeed the case, thus confirming the icosahedral symmetry of C₆₀.

In the experiments reported here, purified films of C₆₀/C₇₀ were deposited on cooled suprasil slides by fractional sublimation of carbon dust at 600 °C. Part of the deposited material was dissolved in 1.6 mL of carbon tetrachloride. Cr(ac)₃ was added, to a concentration of 0.028 mM, to minimize saturation. The composition of the sample was determined by evaporating a 10 μ L drop of the CCl₄ solution on a tantalum foil and analyzing the residual material with the surface mass spectrometer.¹¹ A

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KrF laser (60 μJ in a 0.25-mm spot) was used for desorption, and ionization was accomplished with an ArF laser (200 μJ in a 1.5-mm spot). The mass spectrum obtained is displayed in Figure 1. The observed $\text{C}_{60}^+/\text{C}_{70}^+$ peak ratio is 3.3.

^{13}C NMR spectra were obtained without ^1H decoupling, and Figure 2 shows the downfield portion of $\text{C}_{60}/\text{C}_{70}$ in CCl_4 . An extremely sharp single resonance is observed at 142.5 ppm. The line shape of this resonance is independent of magnetic field strength, and a similar resonance at 142.6 ppm is obtained with some of the same $\text{C}_{60}/\text{C}_{70}$ material dissolved in benzene. The line width of the resonance is limited by magnetic field inhomogeneity, and we note the absence of any appreciable ^1H J coupling in the resonance line shape. The line intensity is consistent with the amount of C_{60} estimated to be present in the sample (~ 200 μg). The observed chemical shift is in the range reported for non-protonated, aromatic carbons, ca. 155–130 ppm.¹² These results lead us to conclude that the observed resonance is due to C_{60} . The sensitivity of ^{13}C NMR chemical shifts to chemical structure is well-known, and from the appearance of a single resonance for C_{60} we conclude that all 60 carbon atoms are chemically equivalent, implying that the structure must necessarily have icosahedral symmetry.

Several weak resonances can be seen downfield from the C_{60} resonance. The strength of these resonances is consistent with estimates of C_{70} NMR line intensities based on the composition of the sample as reflected in Figure 1 and the reduced symmetry expected for this molecule.

In conclusion, the NMR spectrum of a purified $\text{C}_{60}/\text{C}_{70}$ solution has been obtained, and a single line is found for C_{60} . This is conclusive evidence for its icosahedral symmetry.

Note Added in Proof. Independent measurements of the NMR spectra of C_{60} and C_{70} will be published by Taylor, R.; Hare, J. P.; Abdul-Sade, A. K.; Kroto, H. W. *Chem. Commun.* In press.

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A Host for the Water Dimer

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The water dimer has intrigued chemists for the past century. Early workers saw it as a model for water aggregates and the hydrogen bond.¹ More recently it has become a benchmark for computational and spectroscopic techniques.² We have discovered a macrocyclic host for the water dimer and report the crystal structures of the host-guest complex, and of a related host hydrate, which cannot recognize the water dimer.

In the course of our work to construct ion channels,³ we have

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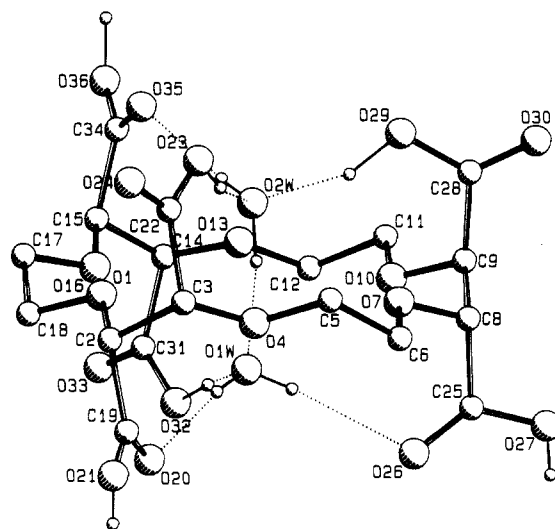


Figure 1. Structure of the water dimer inclusion complex of $18\text{C}_6\text{A}_6$ showing atom numbering. Two water molecules in the lattice and hydrogen atoms bonded to carbon are omitted for clarity. One water bridges between O36 and an O30' on an adjacent molecule, the other bridges between O21 and an O33 on an adjacent molecule.

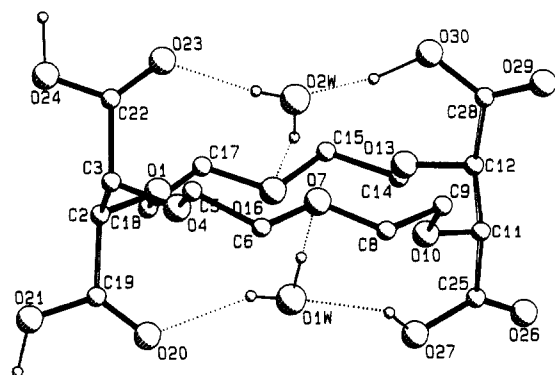


Figure 2. Structure of the hydrate of $18\text{C}_6\text{A}_4$ showing atom numbering. Hydrogen atoms bonded to carbon are omitted for clarity.

Table 1. Comparison of Selected Parameters of Water Dimers^a

structure	O...O, Å	H-O...O, deg	tilt, ^b deg
$18\text{C}_6\text{A}_6$ complex ⁶	2.805 (5)	4.8	71.8
Ice XI (neutron) ⁹			
dimer 1	2.750 (3)	8.3	31.0
dimer 2	2.763 (3)	9.8	45.5
dimer 3	2.793 (3)	3.5	69.8
$(\text{H}_2\text{O})_2$ (microwave) ¹²	2.976 (3)	6	57
$(\text{H}_2\text{O})_2$ (computational) ¹³	3.01	6	56
α -cyclodextrin inclusion hydrate ¹⁰	2.931		

^a O...O distances for other structures (Å): Ice Ih (X-ray),¹⁴ 2.751 (3); amorphous solid water (X-ray), 2.76 (1); liquid water (X-ray and neutron), 2.85. ^b Angle between the O...O axis and the H-O-H angle bisector of the hydrogen bond acceptor molecule.

prepared crown ethers with six ($18\text{C}_6\text{A}_6$)⁴ and four ($18\text{C}_6\text{A}_4$)⁵ carboxylic acid groups attached to the macrocycle. When deprotonated, these macrocycles strongly bind metal ions in water.⁴ Crystal structures of the fully protonated acids encapsulate two water molecules.⁶ In $18\text{C}_6\text{A}_6$, a water dimer fills the cavity

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