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 carbonyl 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(12) \( \ce{BH_4^-} \) and dodecahedrane(13) \( \ce{C_{20}H_{20}} \), both with symmetry \( I_5 \). 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 \( \ce{C_{60}} \) observed in pioneering carbon cluster beam experiments. This evidence proved difficult to come by in carbon cluster beam experiments, where the molecules are available in small quantities and we began producing quantities of carbon dust on the order of tens of milligrams using the method of Kratschmer 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 \( \ce{C_{60}} \) and \( \ce{C_{70}} \) 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 \( \ce{C_{60}} \) and \( \ce{C_{70}} \), as reported elsewhere.10 A preliminary comparison of both the available IR data8 and these recent Raman data for \( \ce{C_{60}} \) 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 \( I_5 \) symmetry, can be directly tested with NMR spectroscopy. The NMR spectrum of Buckminsterfullerene containing a single \(^{13}C \) 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 \( \ce{C_{60}} \).

In the experiments reported here, purified films of \( \ce{C_{60}}/\ce{C_{70}} \) 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. \( \text{Cr(acac)} \) was added, to a concentration of 0.028 mM, to minimize saturation. The composition of the sample was determined by evaporating a 10 \( \mu \)L drop of the CCl₄ solution on a tantalum foil and analyzing the residual material with the surface mass spectrometer.11 A

![Figure 1](image1)

Figure 1. Time-of-flight mass spectrum of the \( \ce{C_{60}}/\ce{C_{70}} \) mixture used in the NMR experiment. A 10-\( \mu \)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](image2)

Figure 2. Aromatic region of the \(^{13}C \) NMR spectrum of ~200 \( \mu \)g of \( \ce{C_{60}}/\ce{C_{70}} \) in CCl₄, without \(^1H \) decoupling, obtained with a Bruker AM-500 NMR spectrometer operating at 125.7 MHz at 25 °C, with 13000 scans over a 14 kHz bandwidth digitized into a 64 kword dataset; chemical shift referenced to CCI₄ at 96.1 ppm. The resonance at 142.5 ppm is assigned to \( \ce{C_{70}} \).

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(7) For this history, see the review by: Kroto, H. Science 1988, 242, 1139.
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 C60+/C70+ peak ratio is 3.3.

13C NMR spectra were obtained without 1H decoupling, and Figure 2 shows the downfield portion of C60/C70 in CCl4. 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 C60/C70 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 C60 estimated to be present in the sample (≈200 μg). The observed chemical shift is in the range reported for non-protonated, aromatic carbons, ca. 155–160 ppm.12 These results lead us to conclude that the observed resonance is due to C60. The sensitivity of 13C NMR chemical shifts to chemical structure is well-known, and from the appearance of a single resonance for C60 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 C60 resonance. The strength of these resonances is consistent with estimates of C70 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 C60/C70 solution has been obtained, and a single line is found for C60. This is conclusive evidence for its icosahedral symmetry.


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. 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 prepared crown ethers with six (18C6A6)4 and four (18C6A3)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.4 In 18C6A6, a water dimer fills the cavity prepared crown ethers with six (18C6A6)4 and four (18C6A3)5 carboxylic acid groups attached to the macrocycle. When deprotonated, these macrocycles strongly bind metal ions in water. Crystal structures of the fully protonated acids encapsulate two water molecules. In 18C6A6, a water dimer fills the cavity

Table I. Comparison of Selected Parameters of Water Dimersa

<table>
<thead>
<tr>
<th>structure</th>
<th>O–O, Å</th>
<th>H–O–O, deg</th>
<th>tilt, deg</th>
</tr>
</thead>
<tbody>
<tr>
<td>18C6A6, complex</td>
<td>2.805 (5)</td>
<td>4.8</td>
<td>71.8</td>
</tr>
<tr>
<td>Ice XI (neutron)</td>
<td>2.750 (3)</td>
<td>8.3</td>
<td>31.0</td>
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<tr>
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<td>dimer 3</td>
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<tr>
<td>(H2O)2 (microwave)</td>
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<td>3.5</td>
<td>69.8</td>
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<tr>
<td>(H2O)2 (computational)</td>
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<td>3.5</td>
<td>66</td>
</tr>
</tbody>
</table>

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

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3 For a review of the early history, see: Chadwell, H. M. Chem. Rev. 1927, 4, 375-398.

Figure 2. Structure of the hydrate of 18C6A6 showing atom numbering. Hydrogen atoms bonded to carbon are omitted for clarity.