
C₃₆, a new carbon solid

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Under appropriate non-equilibrium growth conditions, carbon atoms form relatively stable hollow clusters of well-defined mass number¹, collectively known as fullerenes. The mass production, purification and condensation of such clusters into a molecular solid is generally essential to full experimental characterization: the initial discovery² of C₆₀, for example, had to await a bulk synthesis method³ six years later before detailed characterization of the molecule was possible. Gas-phase experiments^{1,4,5} have indicated the existence of a wide range of fullerene clusters, but beyond C₆₀ only a few pure fullerene solids have been obtained⁶, most notably C₇₀. Low-mass fullerenes are of particular interest because their high curvature and increased strain energy owing to adjacent pentagonal rings could lead to solids with unusual

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intermolecular bonding and electronic properties. Here we report the synthesis of the solid form of C_{36} by the arc-discharge method³. We have developed purification methods that separate C_{36} from amorphous carbon and other fullerenes, to yield saturated solutions, thin films and polycrystalline powders of the pure solid form. Solid-state NMR measurements suggest that the molecule has D_{6h} symmetry, and electron-diffraction patterns are consistent with a tightly bound molecular solid with an intermolecular spacing of 6.68 Å. We observe large increases in the electrical conductivity of the solid on doping with alkali metals.

To determine the optimum parameters for C_{36} production, we performed a series of experiments in a helium-environment arc-discharge chamber originally designed for C_{60} production. An arc was started between two 1/4-inch-diameter graphite electrodes, using a d.c. current of 100 A while maintaining a 1-mm gap between electrodes. A removable metal substrate, designed for subsequent direct insertion into a mass spectrometer, was placed 10 cm from the discharge region on the wall of the water-cooled chamber. Arcing was maintained for several minutes until a uniform carbon film of approximate thickness 10 μm coated the substrate. A series of experimental runs was carried out at different fixed static helium pressures between 50 and 1,500 torr. Each of the substrates was then

loaded into a Micromass laser desorption/ionization time-of-flight mass spectrometer.

Figure 1a shows the mass spectrum of one of these films grown in 400 torr helium. The dominant peaks in the spectrum are at 720 and 432 atomic mass units (a.m.u.). The former peak corresponds to 60 carbon atoms, while the latter corresponds to 36 carbon atoms. The C_{60} and C_{36} peaks are of comparable magnitude and these molecular species appear to be the most prominent in the sample. Lesser peaks are also observed, for example at 840 a.m.u. (C_{70}). The synthesis of C_{36} is very sensitive to experimental conditions, notably the helium pressure: runs in this series at pressures significantly different from 400 torr failed to produce prominent peaks below 720 a.m.u. in the mass spectrum.

To produce bulk amounts of C_{36} suitable for purification, arcing runs in 400 torr helium were repeated and the resulting 'soot' was collected from the synthesis chamber walls. The soot was initially washed with toluene in a standard Soxhlet extractor which removed C_{60} , C_{70} and trace amounts of even higher-order fullerenes. Mass spectrometry on the toluene-soluble extract showed the expected fullerene peaks but no peak at 432 a.m.u., indicating that C_{36} is not soluble in toluene.

Two methods were subsequently used to separate C_{36} from the remaining toluene-insoluble material. In the first, sublimation-purification was used to produce thin films of C_{36} . Here the toluene-insoluble material was dried in vacuum at 150 °C for two hours and placed in the tungsten boat of a thermal evaporator. No precautionary steps were taken to protect the material from ambient moisture. The evaporator boat was heated under a pressure of less than 1 μtorr , ultimately reaching a temperature in excess of 1,500 °C. A metal substrate was suspended over the boat at a height of about 5 cm. In about 20 minutes, films of the order of 100 nm thick could be grown on the substrate. Notably, the black films were highly resistant to scratching, unlike amorphous carbon or C_{60} films.

Figure 1b shows the time-of-flight mass spectrum for the material of a thermally evaporated film. The film contains essentially a single molecular component of mass 438 a.m.u., 6 a.m.u. higher than the mass of C_{36} . Almost certainly the discrepancy is due to the partial hydrogenation of the C_{36} clusters through reaction with adsorbed moisture at the elevated temperature of evaporation. As expected, C_{36} is a fairly reactive material, more so than C_{60} or C_{70} .

To establish a purification method based on 'wet chemistry' rather than thermal evaporation, we tested sublimation-generated films prepared as above in a variety of organic solvents. The films were found to be insoluble in toluene and benzene, but soluble in pyridine and carbon disulphide (CS_2). However, unlike C_{60} and C_{70} , C_{36} is very slow to dissolve in either of these solvents and extensive heating and exposure to ultrasound are required to obtain a saturated solution. This is consistent with the strong, almost covalent bonding expected⁷ between C_{36} molecules: C_{36} is not simply a van der Waals solid as is C_{60} .

The wet-chemistry purification method was used to produce bulk quantities of refined C_{36} powder. The crude arc-chamber soot was first Soxhlet-extracted with toluene to remove higher-order fullerenes, followed by Soxhlet extraction with pyridine. The pyridine-soluble extract forms a yellow-brown solution, as opposed to the toluene-soluble extract which is red-brown in colour. Overall, the crude soot was found to contain ~10% toluene-soluble material (C_{60} and C_{70}) and about 1–2% pyridine-soluble material (C_{36}). After evaporating the pyridine from the pyridine-soluble fraction, a black solid was obtained. This solid differs from that of the previously reported $C_{36}\text{H}_{12}$ bowl-shaped molecule in both colour and solubility⁸.

To investigate the structure of the individual C_{36} molecules and the C_{36} molecular solid, we used solid-state ^{13}C NMR, bulk electron diffraction, mid-infrared transmission, and solid-state transport studies. It has been shown that for a 36-atom carbon cage with

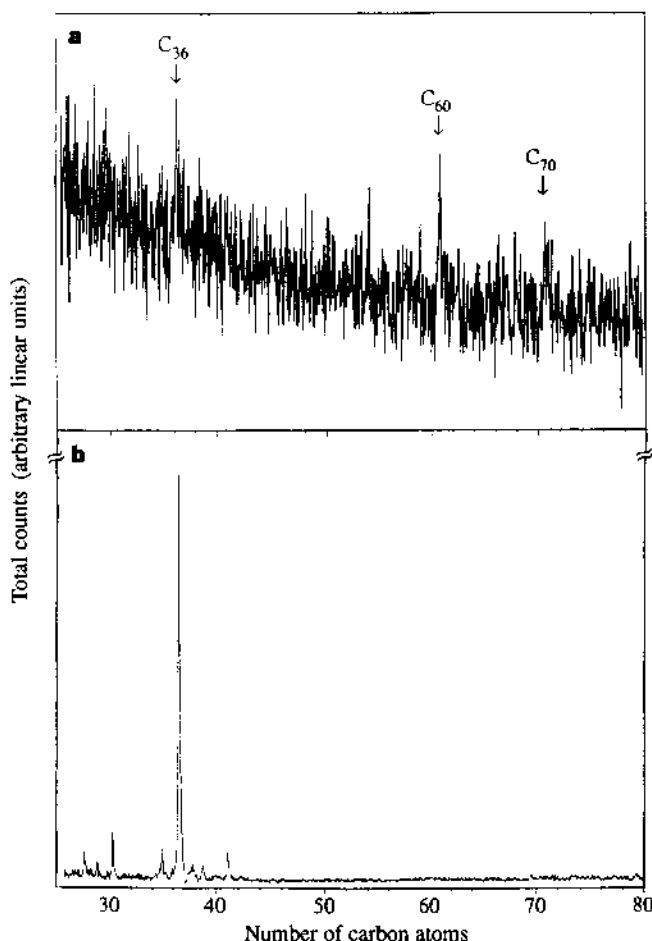


Figure 1 Mass spectra of films prepared in this study. **a**, Time-of-flight mass spectrum of a sample of crude fullerene soot produced at a helium pressure of 400 torr. The data show the presence of a peak at the mass of C_{36} (432 a.m.u.) with approximately the same intensity as the peak due to C_{60} (720 a.m.u.). **b**, Time-of-flight mass spectrum of material from a film evaporated from crude soot which had been depleted of C_{60} and C_{70} by toluene extraction. The peak at 438 a.m.u. is due to C_{36} which has been partially hydrogenated (six hydrogens per C_{36} molecule) during the high-temperature evaporation process.

hexagonal and pentagonal faces, 15 different isomers are possible⁹. Recent calculations indicate that of those isomers the lowest in energy are the structures with D_{6h} and D_{2d} symmetry¹⁰. These two molecules can be distinguished via NMR spectroscopy. The D_{6h} structure is expected to show three distinct ^{13}C NMR resonances of equal intensity, whereas the D_{2d} structure is expected to have five resonances, four with equal intensity and the fifth with half the intensity^{9,11}.

Figure 2 shows the experimental ^{13}C NMR spectrum for C_{36} powder, obtained using a Chemagnetics 500 MHz instrument with magic-angle spinning. The experimental spectrum contains two prominent peaks, one at 146.1 p.p.m. (relative to tetramethylsilane) and another (with approximately one-half the intensity) at 135.7 p.p.m. The inset to Fig. 2 shows the predicted molecular NMR spectra for the isolated D_{6h} and D_{2d} isomers (along with schematic structure drawings). The experimental spectrum appears inconsistent with predictions for the D_{2d} isomer. On the other hand, taking into account experimental broadening of the peaks, one would expect for the D_{6h} isomer two peaks, one near 135 p.p.m. and another 'double intensity' peak at higher p.p.m. arising from the two higher nearly degenerate resonances. This is precisely what is observed experimentally. The smaller experimentally observed shift of the 'double intensity' peak (at 146 p.p.m. versus the predicted 158 p.p.m.) is accounted for by additional shielding of these reactive carbon atom sites by neighbouring molecules in the solid (this shielding is not considered in the simple molecular calculations). We thus identify our C_{36} cage molecule as having D_{6h} symmetry.

To investigate the crystal structure of solid C_{36} , we performed electron diffraction experiments. A small amount of material obtained from the pyridine extraction was ground up, dispersed on a holey carbon grid, and inserted into a JEOL 200X transmission electron microscope (TEM). The material was observed to be polycrystalline with a crystallite grain size of ~ 100 nm. Using a field limiting aperture, the diffraction pattern of selected crystallites was recorded.

In Fig. 3 we show a TEM diffraction pattern for a C_{36} crystallite. The hexagonal diffraction pattern suggests a close-packing arrangement perpendicular to the zone axis. The pattern is reminiscent of diffraction patterns observed for C_{60} and C_{70} . However, the d -spacing measured from this pattern for the first-order diffracted

spots is 6.68 Å, significantly less than the (100) d -spacing of 8.7 Å reported³ for C_{60} . Unfortunately, because the C_{36} crystallites are platelets with high aspect ratios, this was the only zone axis along which the crystallites were thin enough to allow useful TEM imaging, and thus determination of the detailed C_{36} crystal structure was not possible. Using the C_{36} molecular diameter^{7,10,11} of approximately 5 Å (carbon centre to carbon centre distance) and assuming that C_{36} crystallizes in close-packed planes, the diffraction results imply an intermolecular bond length of 1.7 Å, significantly smaller than the van der Waals distance of 3.4 Å in graphite. This is suggestive of strong crystal bonding.

Like higher-order fullerene solids, C_{36} appears to suffer some TEM-induced damage at an electron beam energy of 200 keV. Under continuous TEM observation, the sharp crystalline diffraction patterns were found to deteriorate for extended irradiation times. Additional studies were performed to investigate the long-term stability of solid C_{36} subject (only) to high ambient temperatures. C_{36} powder was heated in vacuum to 1,350 °C for 48 hours and then characterized by TEM imaging. Over 50% of the diffraction patterns obtained for the heat-treated material were graphitic, indicating that a large amount of the material had converted to the energetically more favourable graphite.

Specimens of solid C_{36} were further characterized by mid-infrared transmission and d.c. electrical resistivity measurements. Figure 4 shows the room temperature mid-infrared transmission spectrum for C_{36} powder dispersed in KBr. Several prominent dips in the transmission are observed. In the simplest interpretation, these dips directly represent absorption bands for the C_{36} solid. The observed absorption resonances are in the fullerene range but, as expected, they do not precisely match those of previously known fullerenes. No additional absorption peaks for C_{36} were observed in the frequency range 2,000–5,000 cm^{-1} .

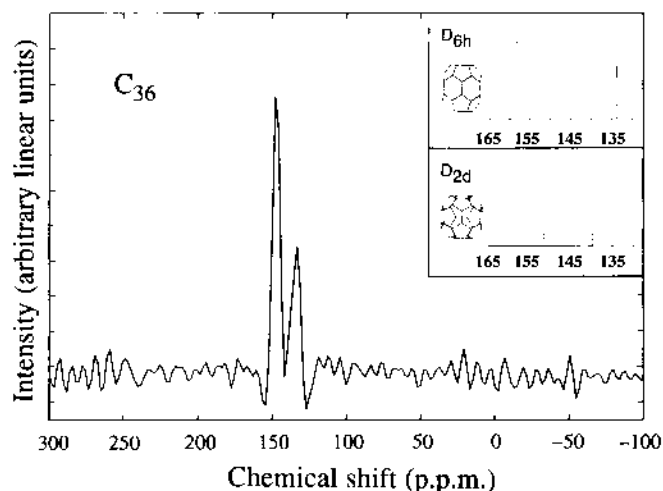


Figure 2 Predicted and observed NMR spectra of C_{36} . Main figure, ^{13}C NMR spectrum of C_{36} powder showing peaks at 146.1 and 137.5 p.p.m. with a 2:1 relative intensity ratio. Inset, the two lowest-energy isomers of the C_{36} molecule (with D_{2d} and D_{6h} symmetry) with the corresponding predicted NMR spectra⁷. Taking into account broadening and shielding for the solid, the experimental data suggest D_{6h} symmetry for the C_{36} molecule.

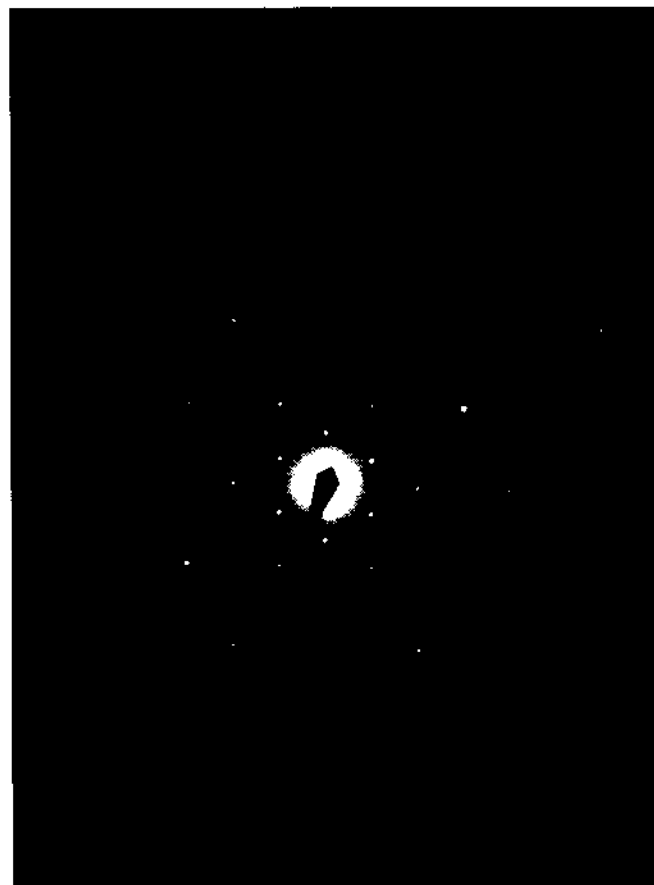


Figure 3 Electron-diffraction pattern of C_{36} crystallite. The pattern is hexagonal with a calculated d -spacing of 6.68 Å.

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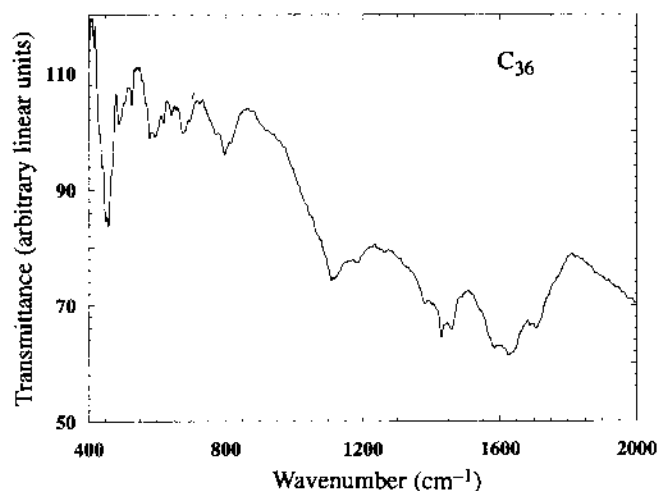


Figure 4 Infrared transmission spectrum of C_{36} powder in KBr.

For d.c. measurements, four-probe contacts were made to polycrystalline specimens with conductive silver paint. At room temperature, the pure samples were insulating with a resistivity in excess of $10^7 \Omega \text{ cm}$. In fullerenes such as C_{60} , it is known that intercalation with alkali metals or alkaline earths drastically improves the electrical conductivity of the solid^{1,2}. We have investigated this effect for C_{36} . Intercalation of the C_{36} solid with alkali metals was carried out using both sodium and potassium, by sealing the sample at one end of an evacuated tube with the alkali metal at the other end. The sample was then heated to $\sim 250^\circ \text{C}$ while the metal was heated to $\sim 175^\circ \text{C}$. In both cases, the resistivity dropped by more than four orders of magnitude, to $\sim 10^3 \Omega \text{ cm}$ at room temperature. The resistivity ρ as a function of temperature T for samples intercalated with either sodium or potassium was not metallic, but obeyed the functional form $\rho \sim \exp[T^{-\alpha}]$, behaviour typical of variable range hopping. At present it is not clear where in the structure, or how uniformly, the alkali metals intercalate.

If C_{36} could be made conducting with a sufficient density of states at the Fermi level—either by doping or by structural rearrangement (for example, induced by pressure)—one might expect, among other things, high-temperature superconductivity¹⁰ with a transition temperature significantly exceeding that of intercalated C_{60} . These possibilities, along with details of the structure, electronic properties, and mechanical response of C_{36} , are at present being investigated. \square

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