

Preparation and UV/visible spectra of fullerenes C₆₀ and C₇₀

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The preparation and isolation of pure fullerene-60 and fullerene-70 is described. The solution UV/visible absorption spectra of the two molecules are presented.

1. Introduction

In 1985, a molecule consisting of sixty carbon atoms was identified in a cluster beam produced by laser ablating graphite [1]. The stability of this novel species was ascribed to the geodesic properties inherent in a truncated icosahedral hollow cage and the molecule was named Buckminsterfullerene (fullerene-60) after the designer of the geodesic domes. Subsequently, a range of experimental observations on carbon clusters was studied and shown to be consistent with the existence of a whole family of closed-cage molecules – the fullerenes [2,3].

In early 1990, Krätschmer et al. [4] detected four very weak IR bands, commensurate with the presence of fullerene-60, in a sample of solid material obtained from discharge-processed graphite. Recently, Krätschmer et al. [5] isolated crystalline material by extracting the solid with organic solvents and showed, from mass spectrometric, X-ray and electron diffraction studies, that it consists of hexagonally packed spheroidal molecules with a 10 Å array spacing, a result beautifully consistent with the proposed structure. In a recent communication we [6] reported the successful chromatographic resolution of a mixture of fullerene-60 and fullerene-70 obtained from an analogous red extract, and we provided definitive proof, on the basis of ¹³C NMR spectroscopy, that both molecules possessed structures as expected [1–3,7]. Bethune et al. [8] have also used the discharge processing technique and have obtained Raman spectra from partly separated fullerene-60 and -70

samples produced by differential sublimation. We describe below more complete details of the preparation and chromatographic separation of pure fullerene-60 and fullerene-70 [6] and present their UV/visible spectra.

The new advances have confirmed the potential importance of the fullerenes in diverse areas from fundamental chemistry, through materials science to astrophysics [1,9].

2. Experimental

A scale diagram of the apparatus used to process carbon is given in fig. 1. The water-cooled evacuable stainless-steel cylinder 28 cm × 8 cm inner diameter (11.5 cm outer diameter) was fitted with two graphite electrodes (5 cm × 0.5 cm diameter type E430, Agar Aids Limited) press-fitted into carbon holders which can be moved horizontally by a screw drive. The electrodes were connected to a standard 200 amp ac welding unit power supply. The gas was introduced via a liquid-nitrogen trap into the cylinder and the pressure was maintained at circa 50 Torr by pumping (flow rate circa 1 Torr s⁻¹) via an additional liquid-nitrogen trap. At the start, the rods were slightly separated, the power supply was activated and the gap between the rods was slowly reduced until the arc struck. If the rods touch, virtually no material vaporises. The arc is maintained for circa 25 s and, on average, a pair of rods survives five such discharges repeated at 2 min intervals to facilitate cool-

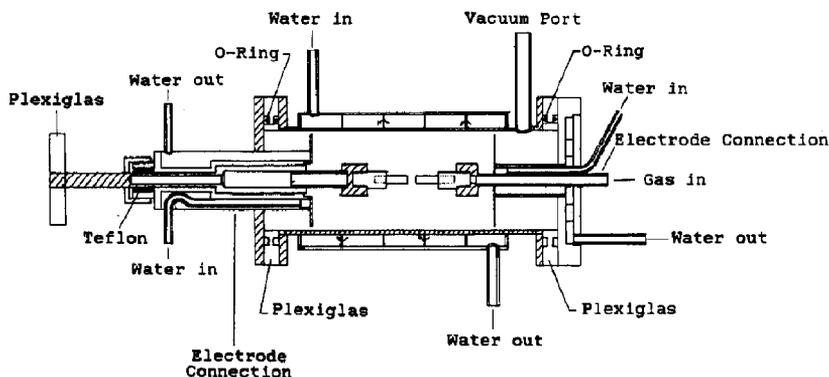


Fig. 1. Scale diagram of carbon arc evaporator.

ing. The resulting carbon deposit was scraped from the inside of the cylinder and in a typical run, 2.69 g of material was collected from 4 rods. The whole operation takes circa 1–2 h. Partly enriched ^{13}C samples were also made by the same procedure using axially drilled rods (1.5 mm diameter, 2 cm deep), packed with 99% enriched ^{13}C powder (Aldrich).

Soluble products were extracted from the deposit by the Soxhlet method, using hot HCCl_3 . Extraction was judged to be complete (4 h) when red material ceased to leach from the Soxhlet thimble. Subsequent removal of the solvent in vacuo yielded 150 mg of solid, containing C_{60} and C_{70} in a 5:1 ratio as estimated by ^{13}C NMR spectroscopy (fig. 2). Successive batches of processed graphite may be extracted with a single charge of HCCl_3 (250 ml); if this is done, granular deposits gradually precipitate from solution and may be removed by filtration if desired. The amount of soluble extract depends on the type of graphite rod, but routinely constituted circa 5–10% of the total mass.

The concentrated extract was subjected to column chromatography using neutral alumina (Woelm, activity grade 1, 2.5 cm inner diameter \times 36 cm long); however, this process presents certain difficulties. Separation of fullerene-60 and -70 can be satisfactorily achieved using n-hexane as eluent; however, fullerene solubility in this solvent is very low, so that take-up of solute is poor and extremely slow. The fullerenes cannot be separated using solvents (e.g. benzene and HCCl_3) in which they are more soluble. To overcome this problem, HCCl_3 solutions of the fullerenes were evaporated to dryness in the presence

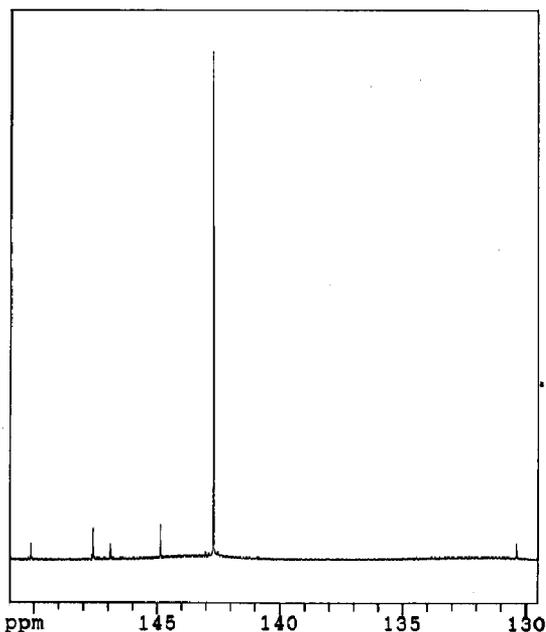


Fig. 2. NMR spectrum of ^{13}C enriched, unseparated extract from which the nascent $\text{C}_{60}/\text{C}_{70}$ ratio of 5/1 is estimated (shift relative to TMS).

of silica, and the resulting mixture was applied to the top of the column. Elution with hexane then produced two coloured bands; the first (magenta) consisting of pure fullerene-60, and the second (pink) a mixture of fullerene-60 and fullerene-70 (the colour of the former is masked by that of the latter). The presence of fullerene-60 in the fullerene-70 band arises, apparently, because the former continues to leach slowly from the solid at the top of the column.

In principle, this problem can be minimised by reducing the initial charge, but as neither fullerene fluoresces, monitoring the resulting very dilute and faintly coloured solutions is extremely difficult. Increasing the column length is counterproductive and leads to band spreading which causes the colours, by which progress is monitored, to become too faint to be seen. Trace hydrocarbons and other impurities are retained at the top of the column in this purification procedure.

Fullerene-70 is reluctant to elute completely from the column, but can be readily removed with CCl_4 . Whilst attempting further to purify fullerene-70 by repeated chromatography, we observed retention of a dark band at the top of the column. We suspect this may arise from decomposition, possibly due to storage between purification runs or because fullerene-70 is inherently unstable on prolonged exposure to alumina. High-pressure liquid chromatography may help to circumvent these problems; results of initial trials, using this separation technique, are shown in fig. 3.

Fullerene-60 is a mustard solid that appears brown or black with increasing film thickness. Fullerene-70 is a reddish-brown solid; thicker films are greyish black. Both compounds are crystalline with high melting points ($>280^\circ$). Fullerene-60 crystals con-

sist of needles and plates, the latter being a mixture of squares, triangles, and trapezia.

The handling of fullerenes presents an additional and most unusual difficulty; the purified (crystalline) products are very reluctant to re-dissolve unless initially isolated as very thin films. This phenomenon is presumably associated with improved molecular packing as purification proceeds. Thus, whereas the crude extract dissolves readily in benzene, purified fullerenes do so only very slowly, although the rate of dissolution can be enhanced using ultrasound. This insolubility of the pure fullerenes can cause difficulty, for instance, in obtaining mass spectra by the FAB technique. Whereas this method works well when crude extracts are submitted to analysis, it can fail due to the reluctance of pure fullerenes to dissolve in the matrix. This problem can be overcome by injecting a benzene solution of each fullerene into the matrix.

Krätschmer et al. [5] have already published the UV/visible absorption spectrum of the nascent extract in which some features belonging to fullerene-70 mask those of fullerene-60, particularly in the visible region. The chromatographic procedure described above has enabled us to obtain the UV/visible spectra of C_{60} and C_{70} separately, and the regions between 200 and 800 nm (hexane solution) are shown in fig. 4; very weak features in the 400–700 nm region for both molecules (benzene solution) are depicted in fig. 5. The strong absorptions for C_{60} lie at 213, 257 and 329 nm (with $\epsilon_{\text{max}} = 135000, 175000$ and 51000, respectively) and there is an interesting weak band, which is unusually sharp, at 404 nm (w). The weak shoulders on the 214 and 329 nm bands appear to be real. A very weak broad absorption is also observed between 440 and 670 nm which exhibits maxima at 500, 540, 570, 600 and 625 nm. This region is shown in more detail in fig. 5. The very weak absorption in this range may be due to first-order forbidden transitions though the possibility that one or more of the other members of the fullerene family, known to be present (see fig. 1, ref. [6]) are responsible cannot be discounted at this stage. Fullerene-70 exhibits pronounced maxima at 214(s), 236(s), 331(mw), 360(mw), 378(mw) and 468 (mw, broad) nm. The long-wavelength shoulder of the broad 468 nm band which starts at 670 nm displays weak structural features (or shoulders) at 550,

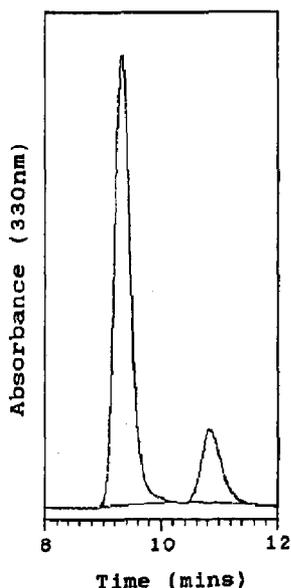


Fig. 3. Result of HPLC study.

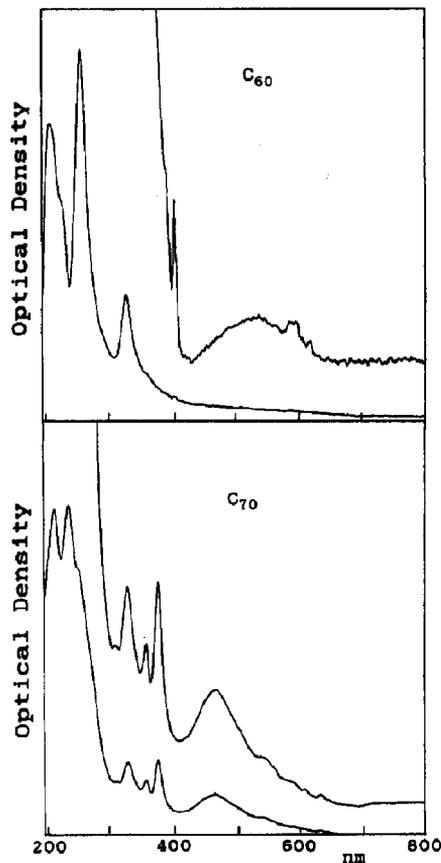


Fig. 4. UV/visible electronic spectra between 200 and 800 nm in spectroscopic hexane solution of (above) C_{60} and (below) C_{70} .

600, 620, 645, and 665 nm. One qualitative difference between the two sets of spectra is the medium-weak broad band centered at circa 468 nm. For fullerene-60, there are only extremely weak features in this region. As Fowler [10] has shown that the LUMO of fullerene-70 should be non-bonding whereas that of fullerene-60 is antibonding, semi-quantitative arguments suggest that the first allowed transition of fullerene-70 should lie to longer wavelengths than the first allowed transition of fullerene-60. Thus, a possible assignment of this band is to a transition, between a high-lying e_g' HOMO and this low-lying non-bonding a_g' LUMO, which is of E_g' symmetry and therefore dipole-allowed [11].

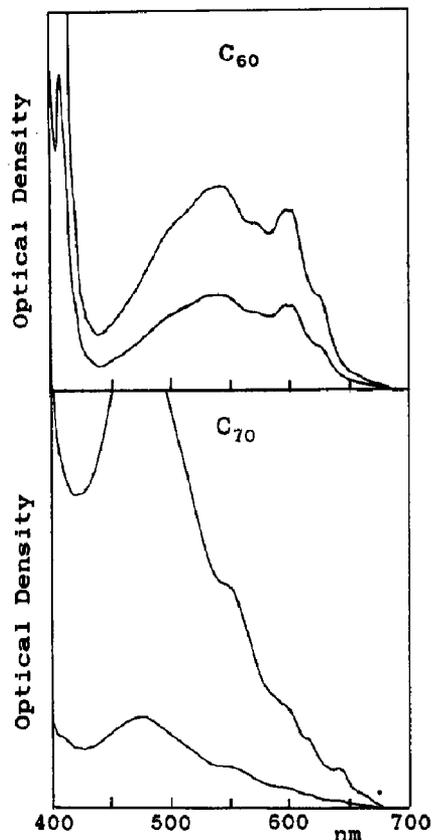


Fig. 5. UV/visible electronic spectra of the very weak features between 400 and 700 nm in benzene solution of (above) C_{60} and (below) C_{70} .

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