Isolation, Separation and Characterisation of the Fullerenes C_{60} and C_{70}: The Third Form of Carbon

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Pure samples of the species C_{60} (Buckminsterfullerene) and C_{70} (fullerene-70) have been prepared, and their structures characterised by their mass and ^{13}C NMR spectra; the results indicate the existence of a family of stable fullerenes, thus confirming that carbon possesses a third form in addition to diamond and graphite.

Following the proposal in 1985 that the ultra-stable molecule, C_{60}, Buckminsterfullerene, forms spontaneously when carbon is laser vaporised,[1] much effort has been expended on finding support for the original suggestion.[2,3] In early 1990 Kraetschmer *et al*,[4,5] provided spectroscopic evidence for the presence of trace amounts of C_{60} in smoke obtained from a carbon arc; their observation of four weak but distinct IR bands being consistent with theory.[6–10] We confirmed this result; however, mass spectrometry showed that the material from similarly processed carbon gave rise to strong peaks at *m/z* 720 and 840, commensurate with C_{60} and C_{70}. Kraetschmer and co-workers[11] have now obtained unequivocal evidence for the structure of C_{60}, thus confirming our original proposal that it is Buckminsterfullerene.[1] We describe here the results of a parallel study in which pure C_{60} and C_{70} are isolated, separated and characterised. These results not only confirm the results of Kraetschmer *et al.* on C_{60} but show that C_{70} is also a closed cage and thus provide compelling evidence for the stability of the fullerene family in general.[12–14] The separation of new forms of an element by chromatography is believed to be unique.

Graphite rods were resistively heated in a vessel to deposit carbon smoke under Ar between 50—100 mbar. The films that result from this rudimentary production technique tend to be of somewhat variable quality. However, the four IR bands, first seen by Kraetschmer *et al.*,[4,5] are usually observed weakly; at best they sometimes appear at about half the

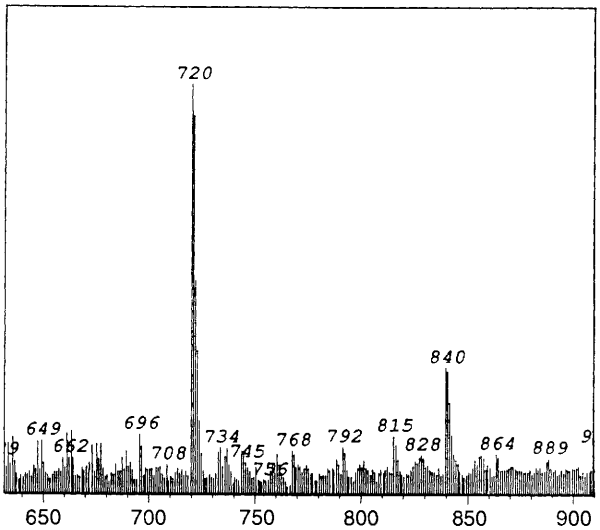

Fig. 1 Mass spectrum of extract from discharge processed carbon

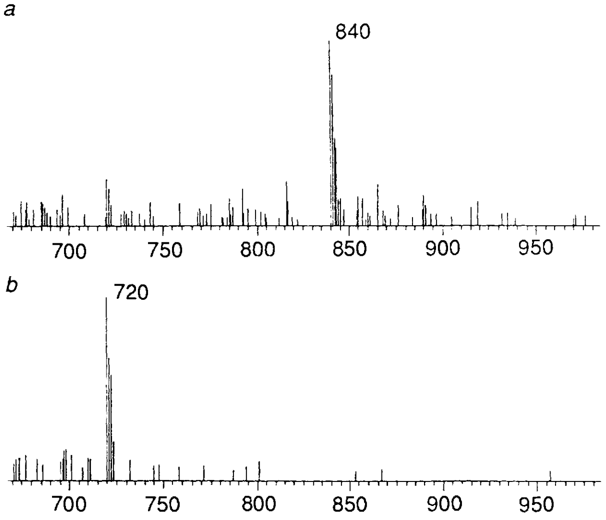

Fig. 2 *a* Mass spectrum of the separated red solid. *b* Mass spectrum of the mustard coloured solid

intensity/signal-to-noise in their spectrum.[4,5] Solid black soot-like material is collected by scraping it from all parts of the apparatus.[15] This material when placed in benzene readily gives rise to a red solution which can be decanted from the black insoluble soot-like material.

The mass spectrum of the smoke produced directly without further processing gives strong peaks at $m/z = 720$ and 840. However, the material which is solvent extracted gives the spectrum shown in Fig. 1. This should be compared with the laser vaporisation results[1–3] and shows that the fullerenes C_n ($n = 62, 64, 66, 68,$ *etc.*) are also present and apparently stable in air.

Solvent extraction of batches of these carbon deposits gave plum-coloured solutions which yielded, after solvent removal, a black-brown solid in up to 8% yield. Chromatographic separation (alumina, hexane) then yielded pure C_{60} and C_{70} in a ratio of approximately 5:1, and together these comprised about 15% of the extract; the total yield was 8 mg. In one of the two chromatographically separated samples the dominant peak appears at $m/z = 720$ and in the other it appears at $m/z = 840$ (Figs. 2 *b* and *a*, respectively).

C_{60} is a mustard-coloured solid that appears brown or black with increasing film thickness. It is soluble in the common organic solvents, especially aromatic hydrocarbons, and gives beautiful magenta-coloured solutions. C_{70} is a reddish brown solid, and thicker films are greyish black; its solutions are port-wine red. Solutions of mixtures of C_{60} and C_{70} are red due to C_{70} being more intensely coloured. Both compounds are crystalline with high m.p.'s (>280 °C). Although both compounds are very soluble in, *e.g.*, benzene (C_{60} is the more soluble), they are nevertheless slow to dissolve reflecting the excellent close packing achieved by the spherical and near-spherical molecular structures. Crystals of C_{60} are both needles and plates, the latter being a mixture of squares, triangles and trapezia; the needles consist of a series of overlapping plates.

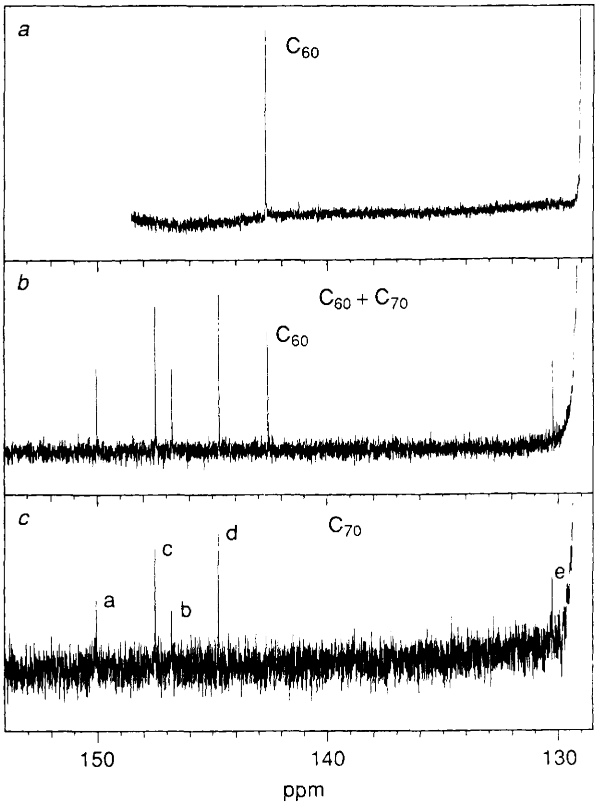

Fig. 3 *a* ^{13}C NMR spectrum of C_{60}, Buckminsterfullerene. *b* ^{13}C NMR spectrum of a mixed sample in which C_{60} is much reduced. *c* ^{13}C NMR spectrum of C_{70}, fullerene-70. The line assignments given are based on the observed intensities and semi-quantitative strain arguments, and are subject to confirmation. The wing of the intense benzene solvent signal lies at the far right hand side

The ^{13}C NMR spectrum for C_{60} (18 h integration) consists of a single line (Fig. 3*a*), as required, at 142.68 ppm, and unaltered by proton decoupling. This is significantly downfield from the peaks for the corresponding positions in naphthalene (133.7 ppm), acenaphthylene (128.65 ppm), and benzo[*g,h,i*,]fluoranthene (126.85, 128.05 and 137.75 ppm).[16] This is not unexpected since strain produces downfield shifts which may be attributed to strain-induced hybridisation changes, as shown for example by the ^{13}C peaks for the bridgehead carbons in tetralin (136.8 ppm), indane (143.9 ppm) and benzcyclobutene (146.3 ppm).[16]

Fig. 3*c* shows the ^{13}C NMR spectrum for C_{70} [run in the presence of $Cr(acac)_3$, Hacac = pentane-2,4-dione, which produces a *ca.* 0.12 ppm upfield shift of the peaks] consisting of five lines as required, at 150.07, 147.52, 146.82, 144.77 and 130.28 ppm, also unaffected by proton decoupling. The number of lines (five) is compelling evidence for the fullerene-70 structure[12,13] depicted in Fig. 4. Fig. 3*b* shows the spectrum of a mixed sample in which C_{60} is much reduced. It is clear from this diagram that fullerene-70 possesses five sets of inequivalent carbon atoms with an $n_a:n_b:n_c:n_d:n_e$ ratio of 10:10:20:20:10 (sighting along vertical planes as indicated in the diagram), and this is precisely the ratio of the line intensities observed in the spectrum. The peak at 130.28 ppm can reasonably be assigned to the equatorial ring of ten carbon atoms (e in Fig. 4), since these correspond to the tertiary carbons in pyrene which appear at 124.6 ppm;[16] strain again produces a downfield shift of the peaks. The peaks at 144.77 and 147.52 ppm arise from carbons d and c (Fig. 4). It is probable that the peak at 144.77 ppm is due to the carbon atoms d since models indicate these to be less strained than carbon atoms c. Similarly we suggest that the lines at 150.07 and 146.82 ppm be assigned to type a and b carbon nuclei respectively as indicated in Fig. 3*c*.

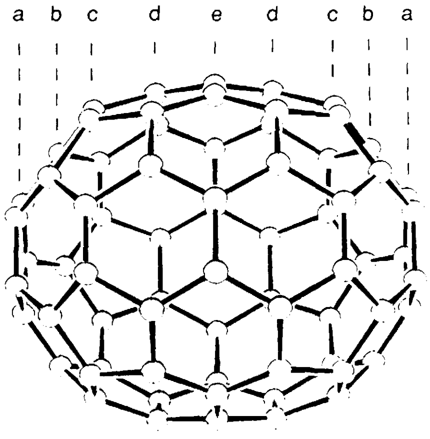

Fig. 4 Schematic diagram of fullerene-70 (based on the diagram in ref. 10). The five sets of identical carbon nuclei a–e lie in the vertical planes as indicated

The mass spectrum of C_{60} (obtained by the FAB method using *m*-nitrobenzyl alcohol as the matrix) exhibits the parent ion at m/z = 720 with complete absence of a peak at m/z = 840, showing the sample to be free from C_{70}, confirming the NMR result. The mass spectrum of C_{70}, similarly obtained, shows the main peak at m/z = 840, but also a small peak at m/z = 720 which we attribute to fragmentation of C_{70} to C_{60}. Analogous fragmentation of fullerenes has been indicated by earlier work.[17]

The electronic spectra for the compounds (UV in hexane and VIS in benzene) are quite different. C_{60} shows peaks at 202.5, 208.3, 211.9, 215.9, 230(sh), 257.6(main), 329.7, 405.7, 408.6, 500(sh), 540.0, 571.0, 596.8, 604.0 and 625(sh) nm. For C_{70} the peaks are at 205.6, 207.3, 210.2(main), 232(sh), 254.8, 322.2, 334.4, 360.0, 378.7, 473.6, 550.0, 600.0, 617.0 and 644.0 nm.

The IR spectra of the separated materials deposited on a KBr plate have been obtained. In the spectrum of the solid obtained from the magenta solution, which gave a very strong m/z 720 mass peak, four strong peaks consistent with the observation of Kraetschmer *et al.* are observed. Normal mode calculations[6–10] predict only four active bands, adding compelling support for the assignment of Kraetschmer *et al.* and supported by the measurements here. The spectrum of fullerene-70 shows many more lines. The calculations of Osawa and co-workers predict 26 allowed vibrations.[14]

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References

1 H. W. Kroto, J. Heath, S. C. O'Brien, R. F. Curl and R. E. Smalley, *Nature (London)*, 1985, **318**, 162.
2 H. W. Kroto, *Science*, 1988, **242**, 1139.
3 R. F. Curl and R. F. Smalley, *Science*, 1988, **242**, 1017.
4 W. Kraetschmer, K. Fostiropoulos and D. R. Huffman, *Dusty Objects in the Universe*, eds. E. Bussoletti and A. A. Vittone, Kluwer, Dordrecht, 1990.
5 W. Kraetschmer, K. Fostiropoulos and D. R. Huffmann, *Chem. Phys. Lett.*, 1990, **170**, 167.
6 M. D. Stanton and R. E. Newton, *J. Phys. Chem.*, 1988, **92**, 2141.
7 Z. C. Wu, D. A. Jelski and T. F. George, *Chem. Phys. Lett.*, 1988, **137**, 291.
8 D. E. Weeks and W. G. Harter, *Chem. Phys. Lett.*, 1988, **144**, 366.
9 D. E. Weeks and W. G. Harter, *J. Chem. Phys.*, 1989, **90**, 4744.
10 Z. Slanina, J. M. Rudzinski, M. Togaso and E. Osawa, *J. Mol. Struct.*, 1989, **202**, 169.
11 W. Kraetschmer, L. D. Lamb, K. Fostiropoulos and D. R. Huffmann, *Nature (London)*, in the press.
12 H. W. Kroto, *Nature (London)*, 1987, **329**, 529.
13 T. G. Schmalz, W. A. Seitz, D. J. Klein and G. E. Hite, *J. Am. Chem. Soc.*, 1988, **110**, 1113.
14 J. M. Rudzinski, Z. Slanina, M. Togaso and E. Osawa, *Thermochim. Acta*, 1988, **125**, 155.
15 W. Kraetschmer, personal communication.
16 E. Breitmaier, G. Haas and W. Voelter, *Atlas of ^{13}C NMR Data*, Heyden, London, 1979.
17 S. C. O'Brien, J. R. Heath, R. F. Curl and R. E. Smalley, *J. Chem. Phys.*, 1985, **88**, 220.