Separation, isolation and characterisation of two minor isomers of the [84]fullerene C_{84}

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The first successful separation and isolation from arc-burned soot of Gd-doped composite rods of a mixture (in an abundance ratio of 3 : 2) of two minor isomers of C_{84} with molecular symmetry D_{6h} and D_{3d}, and their characterisation by ^{13}C NMR and UV-VIS-NIR absorption spectroscopy, are described.

Following the discovery and isolation in pure form of macroscopic amounts of C_{60} and C_{70}, the presence of the so-called higher fullerenes (C_n, $n > 70$) was also identified in the soot obtained by the resistive heating of graphite under an inert atmosphere. Advances in the chromatographic separation of the higher fullerenes and their endohedrally-coordinated metal complexes have allowed the quantitative isolation and characterisation of certain higher fullerenes, even in isomer-pure form.[1] Examples of these include the molecular systems C_{76}, C_{78} and C_{84}, which have all been isolated quantitatively. While C_{76} exists as a single isomer with D_2 symmetry,[2] only three of the five possible isomers of C_{78} with isolated pentagons (IPR) and symmetry C_{2v}, C_{2v}', and D_3 have been studied.[3] The situation is even more complicated for the higher fullerene C_{84}. The C_{84} molecule can exist in 24 different structural isomers obeying the 'isolated pentagon rule'. However, two of the isomers with symmetry D_2 and D_{2d} (in the ratio 2 : 1) constitute the bulk of the material and these have been isolated and characterised in isomer-pure form by ^{13}C NMR and UV-VIS-NIR absorption spectroscopy.[4] The structural properties of the pristine [84]fullerene solid ($D_2 : D_{2d} \approx 2 : 1$) have also been reported as a function of temperature[5] together with the first results of the intercalation chemistry of both isomer-pure and mixed isomer solids with potassium.[6] In addition, the two dominant isomers have been separated chemically and the structure of the D_{2d} isomer has been determined by single crystal X-ray diffraction.[7] The structural solid state properties of the isomer-pure D_2 and D_{2d} C_{84} solids also exhibit a series of structural phase transitions on cooling.[8] An attempt to identify and characterise the major and minor isomers present in the main and tail HPLC fractions of C_{84} has been already reported in the literature.[9] However, the large number of lines (one hundred and fifty four) present in the ^{13}C NMR spectra has precluded reliable identification of isomers and correct assignment of the observed lines. Here we report the first successful isolation and characterisation of [84]fullerene comprising a mixture of only two of the minor isomers with symmetry D_{6h} and D_{3d}.

Fullerenes were produced by the dc arc discharge technique and extracted with CS_2 and pyridine. In the present experiments, we have used arc-burned soot of Gd-doped (0.8 wt%) composite rods. Similar experiments employing pure or Ca-doped graphite rods did not produce similar amounts of minor isomers of C_{84}, implying a catalytic effect for the Gd atoms in the early stage of the growth of these isomers. The separation of the C_{84} isomers was achieved by the technique of recycling HPLC using a Cosmosil 5PYE column and toluene as eluent (Fig. 1). Following recycling of the sample for 135 min, we succeeded in separating a fraction of minor isomers from the two major isomers of symmetry D_2 and D_{2d}. Further recycling of the fraction of the major isomers for an additional 70 min did not reveal the presence of other isomers of C_{84}.† Theoretical calculations[10] of the stability of C_{84} isomers predict that the most stable isomers after D_2 and D_{2d} should be those with symmetry (11)C_2, (16)C_s, (19)D_{3d} and (24)D_{6h}. From the above symmetries of the minor isomers, we expect in the ^{13}C NMR spectra the appearance of 42 (×2 C), 43 (41 × 2 C + 2 × 1 C), 8 (6 × 12 C + 2 × 6 C) and 5 (3 × 12 C + 2 × 24 C) lines, respectively for each of these isomers.[11]

The ^{13}C NMR spectrum of our purified sample after accumulating 200 000 scans for ten days showed 13 single distinct lines (Fig. 2) which are attributed to a mixture of the D_{6h} and D_{3d} isomers of C_{84} in the ratio 3 : 2. The observed pattern can be classified as comprising of two groups of lines whose intensity ratio is almost in the ratio 2 : 1. The group of eight intense lines can be further divided into two subgroups, one with two lines (δ 139.50, 144.78) slightly more intense, assigned to the D_{6h} isomer, and one with the remaining six lines (δ 135.23, 139.41, 139.60, 139.64, 141.34, 147.49) with slightly lower intensity, assigned to the D_{3d} isomer, in an abundance ratio of 3 : 2. The group of five less intense lines can be also divided into two subgroups; three of them have slightly higher intensity than the other two and they can be assigned to the D_{6h} isomer (δ 135.70, 138.56, 148.14). The remaining two lines (δ 136.39, 147.81) are then assigned to the D_{3d} isomer.

We also measured the UV-VIS-NIR absorption spectrum (Fig. 3) of the purified sample of the mixture of the D_{6h} and D_{3d} isomers of C_{84}. The major features of the spectra appear at 492, 578, 649, 757 and 914 nm. The absorption dip near 750 nm in the spectrum accounts for the sample being of golden yellow colour in toluene.

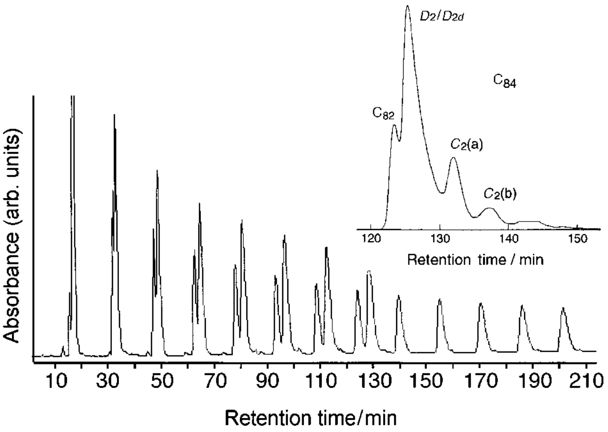

Fig. 1 HPLC profile of the second recycling phase, showing the separation of the mixture of the minor D_{6h} and D_{3d} isomers of C_{84} (second fraction with longer retention time) from its major D_2 and D_{2d} isomers (first fraction that elutes earlier). The second fraction was collected after 135 min and the first fraction was recycled for an additional 70 min. The inset shows part of an HPLC profile of the mixture obtained by using undoped graphite rods. The D_{6h} and D_{3d} isomers are absent and should have appeared between the major D_2/D_{2d} and C_2(a) isomers.

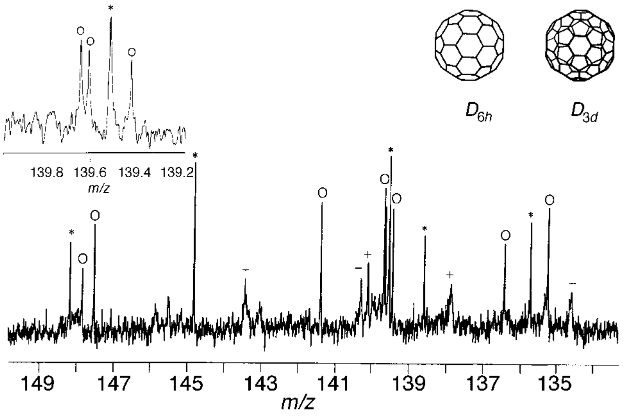

Fig. 2 ^{13}C NMR spectra [500 MHz, CS_2 solution with few drops of deuterated acetone as lock signal and $Cr(acac)_3$ as relaxant] of the purified mixture of the minor isomers D_{6h} (*) and D_{3d} (○) of C_{84}. Peaks labelled as (+) arise from the solvent (toluene) and other impurities. The region around δ139 is expanded for clarity. The inset shows the molecular structures of the two isomers.

In conclusion, we have succeeded in separating, isolating and fully characterising by ^{13}C NMR spectroscopy a 3 : 2 mixture of the minor isomers D_{6h} and D_{3h} of the higher fullerene C_{84}.

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Notes and references

† *Note added at proof*: Further repeated HPLC recycling of the present sample results in the separation of an additional minor fraction, which is assigned to the C_2(a) isomer of C_{84} by comparison with earlier work (T. J. S. Dennis, T. Kai, T. Tomiyama, H. Shinohara, Y. Kobayashi, H. Ishiwatari, Y. Miyake, K. Kikuchi and Y. Achiba, to be published).

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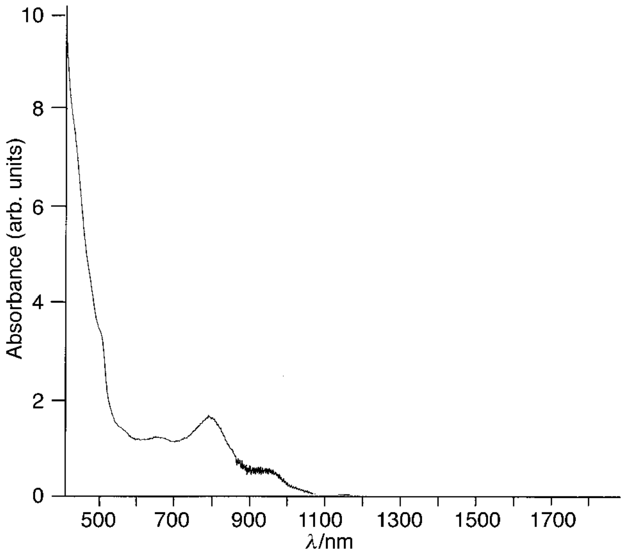

Fig. 3 UV-VIS-NIR absorption spectra of the purified mixture of the minor isomers D_{6h} and D_{3d} of C_{84}.