

Isolation and characterisation of the two major isomers of [84]fullerene (C₈₄)

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We report the first successful separation of the two major isomers of C₈₄, *i.e.* [84-*D*₂]fullerene and [84-*D*_{2d}(II)]fullerene, and ¹³C NMR and UV-VIS-near IR absorption spectra of the purified materials.

[84]Fullerene, C₈₄, is one of the first higher fullerenes found in arc-processed soot, and solvent extracted in macroscopic amounts.¹ C₈₄ has 24 structural isomers obeying the isolated pentagon rule (IPR).² Early ¹³C NMR studies^{3,4} indicated that the two major isomers of [84]fullerene have *D*₂ and *D*_{2d}(II) symmetry and a 2:1 abundance ratio. Theoretical calculations^{5,6} predict that the *D*₂(IV) and *D*_{2d}(II) isomers are the most stable of the 24 IPR isomers. A number of spectroscopic and structural studies have been carried out on [84]fullerene during the last seven years.⁷ However, since the separation of the *D*₂ and *D*_{2d}(II) isomers had not been achieved, none of these experiments have been carried out on isomer-free samples. Here we report the first successful isolation of the two major isomers of [84]fullerene.

Separation of C₈₄ isomers was achieved by recycling HPLC using a Cosmosil 5PPE column and toluene as eluent (20 mm × 250 mm; 10 ml injections of C₈₄ solution; 18 ml min⁻¹ flow rate).⁸ Fig. 1 shows the resulting first-recycling-phase HPLC profile. In this figure, the *D*₂ and *D*_{2d} isomers are seen to be partially separated. Complete separation could not be achieved at this stage by continuing to recycle due to peak spreading. However, by cutting the sample at the line marked in Fig. 1, fractions greatly enriched in each of the two isomers were obtained. Further enrichment resulted from repeating the 20 cycle HPLC and cutting technique, and pure *D*₂ isomer was obtained after a third treatment. The *D*₂ isomer has the shorter retention time on this column, and because of the tailing of the *D*₂ fraction into the *D*_{2d}, two further recycling HPLC treatments are required to produce pure *D*_{2d} isomer.

Fig. 2 shows the ¹³C NMR spectra of the purified *D*₂ and *D*_{2d} fractions. These spectra give a good indication of the purity of our samples, as there is no detectable contamination of the *D*₂ C₈₄ fraction by the *D*_{2d}, or *vice versa*. Fig. 2(a) contains 21 lines

of almost equal intensity, and Fig. 2(b) contains 11 lines with one being of roughly half the intensity of the others. These correspond to the *D*₂ and *D*_{2d}(II) isomers, respectively. We can confirm that the previous ¹³C NMR spectra^{3,4} of the mixture are convolutions of the present isomer-free spectra. However, owing to the 2:1 *D*₂:*D*_{2d} isomer abundance ratio, in the spectrum of the mixture all lines due to the *D*₂ isomer and ten of the eleven lines due to the *D*_{2d} isomer have the same intensity. Therefore, we are also able to show for the first time which lines belong to which isomer. Since the submission of the present communication, an attempt to assign these 31 lines, on the basis of a comparison of ¹³C NMR spectra of a central and tail cut from the main C₈₄ band in an HPLC profile, has appeared in the literature.⁹ This was only moderately successful, having six incorrect assignments.

Among the 24 possible IPR isomers of C₈₄, four have *D*₂ symmetry and two have *D*_{2d} symmetry. The present *D*_{2d} isomer can be unambiguously assigned to C₈₄ isomer II. This isomer possesses 11 different carbon atom environments. One of these

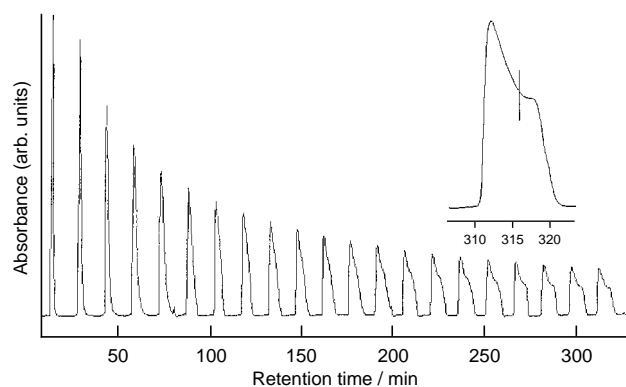


Fig. 1 HPLC profile taken from the second recycling-phase. The insert is an expanded view of the 20th cycle. Partial separation of the two major isomers of C₈₄ has occurred, and by cutting at the line shown in the insert, fractions enriched in the *D*₂ and *D*_{2d} isomers are obtained. Several more recycling HPLC treatments are required to produce pure materials.

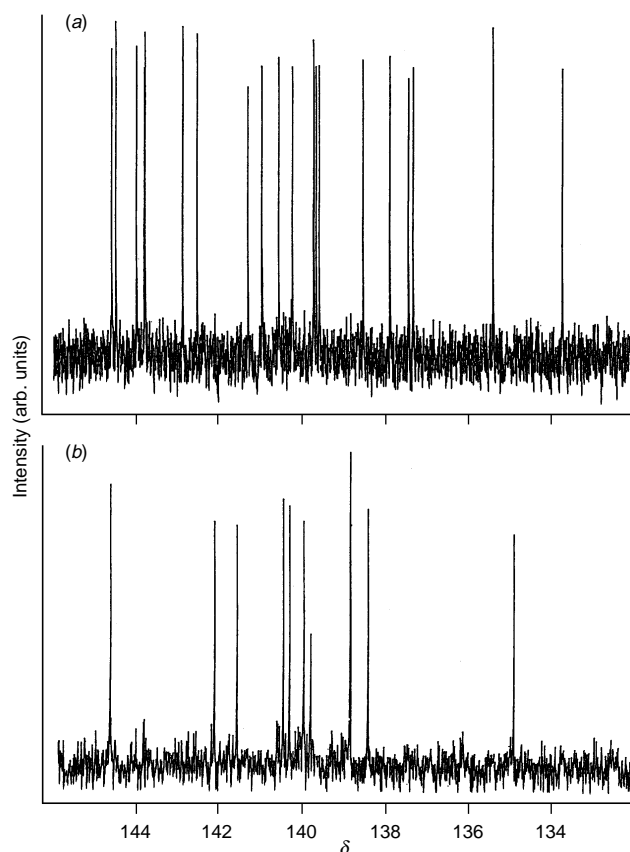


Fig. 2 ¹³C NMR spectra of the purified two major isomers C₈₄: (a) one of the four *D*₂ IPR isomers, and (b) [84-*D*_{2d}(II)]fullerene. The measured chemical shifts for the present C₈₄ isomers are: *D*₂ δ 133.81, 135.48, 137.39, 137.50, 137.91, 138.58, 139.63, 139.74, 139.77, 139.79, 140.32, 140.60, 141.00, 141.33, 142.58, 142.89, 143.78, 143.81, 143.98, 144.48, 144.58; *D*_{2d}: δ 134.98, 138.48, 138.87, 138.88, 139.82, 140.00, 140.37, 140.50, 141.57, 142.13, 144.60.

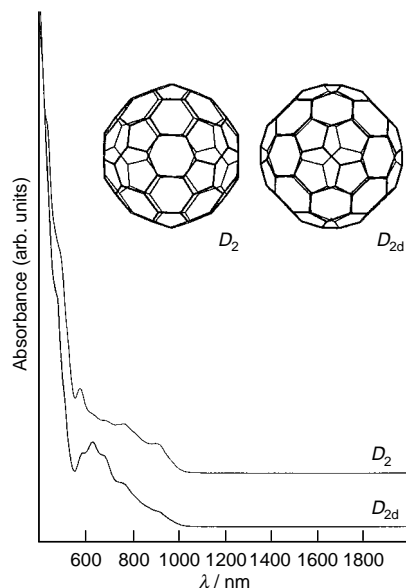


Fig. 3 UV-VIS-near IR absorption spectra of the D_2 and D_{2d} (II) isomers of C_{84}

occurs four times, and the other ten each occur eight times. This fits perfectly with the spectrum given in Fig. 2(b), both in terms of the number of lines and their relative intensities. An unambiguous assignment cannot be given to the D_2 isomer, as all four IPR D_2 isomers would have a one-dimensional ^{13}C NMR spectrum consisting of 21 equal-intensity lines. However, a recent two-dimensional ^{13}C NMR study¹⁰ suggests that the present sample corresponds to $C_{84}\{D_2(\text{IV})\}$.

Fig. 3 shows the UV-VIS-near IR absorption spectra of the purified C_{84} D_2 and D_{2d} (II) isomers. The absorption dip near 600 nm in the spectrum of the present D_{2d} (II) C_{84} sample accounts for this isomer being green; the D_2 isomer is yellow-brown in CS_2 solution.

The UV-VIS-near IR absorption spectrum of [84- D_2 (II)] fullerene is considerably different from the scandium *incarcer*-fullerene $i\text{Sc}_2\text{C}_{84}\{D_2(\text{II})\}$,^{11,12} even though they share the same C_{84} isomer. This indicates that metal encapsulation alters substantially the electronic structure of the host fullerene.

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