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Production and isolation of an ellipsoidal C_{80} fullerene

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We report the first successful production and isolation of a new C_{80} isomer together with ^{13}C NMR structural and UV–VIS–NIR spectroscopic studies of the purified sample; ^{13}C NMR results unambiguously suggest that the new C_{80} isomer has an ellipsoidal structure with D_{5d} symmetry.

C_{80} has seven structural isomers satisfying the isolated pentagon rule (IPR).[1,2] However, owing to its extremely low abundance in arc-burning soot, this fullerene has long been known as one of the three 'missing' fullerenes[3] between C_{70} and C_{96} (the other two fullerenes are C_{72} and C_{74}).[3] It was not until recently that a small quantity of $C_{80}(D_2)$ was isolated by Henrich *et al.*[4] Here, we report the production, isolation and ^{13}C NMR structural analysis of a new C_{80} isomer.

Fullerene soot containing C_{80} was produced by the dc arc discharge method. Graphite/iron composite rods (12.5 × 12.5 × 300 mm, 0.7 atom% Fe/C, Toyo Tanso Co.Ltd.) were used for the arc discharge at 350 A and 23 V under a 12 l min^{-1} He flow (90–100 Torr). The resulting soot was succesively extracted with carbon disulfide and pyridine for 20 h. The separation of C_{80} was achieved by a multi-stage HPLC method[5,6] using a Buckyprep column (nacalai Cosmosil, 25 × 250 mm, toluene eluent) at 16.5 ml min^{-1} flow rate and a Buckyclutcher column (Regis, 20 × 300 mm) at 10 ml min^{-1} flow rate. The first stage was performed on the Buckyprep column which roughly separates C_{80}(I) and C_{80}(II) from other fullerenes by collecting the corresponding C_{80}-containing fractions. In the second stage, the HPLC fractions collected in stage 1 were re-injected into a 5PYE column (nacalai Cosmosil, 25 × 250 mm, toluene eluent) and recycling HPLC was performed. The third stage was again a recycling HPLC process on the Buckyclutcher column which can finally isolate C_{80}(I) and C_{80}(II) obtained from stage 2. The purity of the isolated samples [C_{80}(I): >98%, *ca.* 5 mg; C_{80}(II): >98%, *ca.* 2 mg] was determined by both positive and negative laser-desorption time-of-flight (LD-TOF) mass spectrometry.

On the 5PYE column, the C_{80} isomers I and II have different HPLC retention times. C_{80}(I) appears immediately after C_{78}. A ^{13}C NMR spectrum of this fullerene has already been reported by Henrich *et al.*[4] to have 20 near-equal signals, suggesting D_2 symmetry. C_{80}(II) has a much longer retention time than C_{80}(I) and appeared after C_{86}. The relative abundance of C_{80}(I) to C_{80}(II) is *ca.* 30 : 1. C_{80}(II) is light green in carbon disulfide solution. Fig. 1 shows the VIS–NIR absorption spectra of C_{80}(II) together with that of $C_{80}(D_2)$ for comparison. Aside from the relative intensity, the band positions in the two absorption spectra are similar. The characteristic peaks of $C_{80}(D_2)$ are seen at 420(sh), 466(sh), 596, 775, 860, and 882 nm, whereas for C_{80}(II) the main peaks are observed at 446(sh), 484(sh), 589, 606, 845 and 880 nm. C_{80}(II) shows a strong absorption band at *ca.* 600 nm which accounts for the greenish color of this fullerene in CS_2 solution.

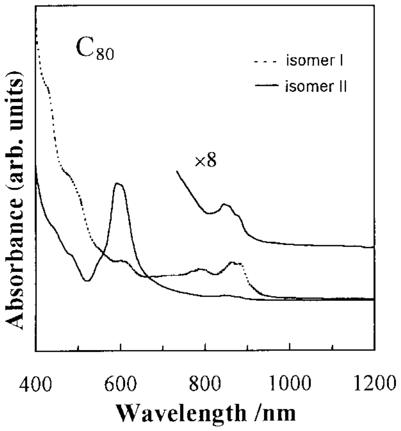

Fig. 1 VIS–NIR absorption spectra of C_{80}(I) and C_{80}(II) in CS_2 solution.

Fig. 2 shows a ^{13}C NMR spectrum of C_{80}(II) in carbon disulfide solution with chromium(III) tris(acetylacetonate) as a relaxant and benzene-d$_6$ as the internal lock. The spectrum consists of a series of three distinct lines of near-equal intensity (lines 1,2,3) and two additional lines at half the intensity (lines 4* and 5*). The position of line 1 (δ 128.9) is very close to that of benzene-d$_6$ (δ 128.5). However, its characteristic fullerene linewidth (*ca.* 0.02 ppm) unambiguously distinguishes it from other solvent signals (linewidth > 0.1 ppm). We also performed ^{13}C NMR measurements by using acetone-d$_6$ instead of benzene-d$_6$ as an internal lock. The results confirm the five NMR lines and show that no C_{80} resonant lines were hidden by the benzene signals. The five signals cover a wide chemical shift range (δ 128.9–163.9), suggesting that C_{80}(II) has an ellipsoidal shape. C_{80} has seven IPR isomers (D_2, D_{5d}, C_{2v}, C_{2v}', D_3, D_{5h} and I_h)[2,4]. The present ^{13}C NMR result unambiguously assigns C_{80}(II) as the D_{5d} isomer (3 × 20; 2×10), where (a × b) indicates (number of NMR lines × relative intensity).

The most stable structure of C_{80} as D_{5d} is inferred from theoretical optimization by a nonlocal density function B3LYP/3-21G calculation using the Gaussian 98W program.[7] As shown in Fig. 3, $C_{80}(D_{5d})$ has an ellipsoidal structure with an aspect ratio (long axis/short axis) of *ca.*1.3. $C_{80}(D_{5d})$ can easily be obtained by adding one C_{10} ring on a half cap of $C_{70}(D_{5h})$ (*i.e.*, C_{30} or C_{40}) or adding two C_{10} rings successively on a $C_{60}(I_h)$ hemisphere (*i.e.*, C_{30}). As proposed by Curl,[8] $C_{70}(D_{5h})$ is formed by dissecting C_{60} into two C_{30} hemispheres along a suitable orientation (rotating one hemisphere 36° with respect to another hemisphere), and then by adding a ring of 10 carbon

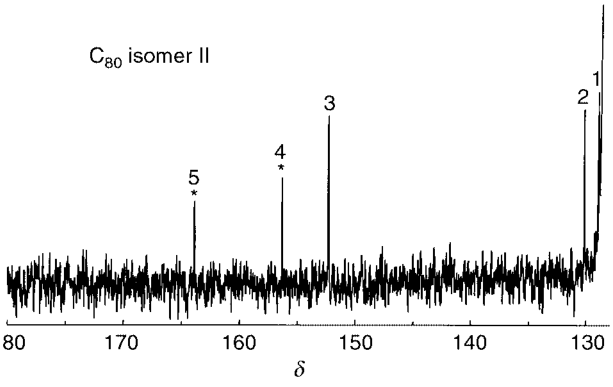

Fig. 2 ^{13}C NMR spectrum of purified C_{80}(II). The spectrum consists of five signals: 1(128.9, 13.9), 2(130.2, 12.7), 3(152.4, 12.2), 4*(156.3, 7.6), 5*(163.9, 6.0), in which (δ, I_{rel}) represent measured chemical shifts δ and relative intensity I_{rel}, and where lines indicated by * are half-intensity lines.

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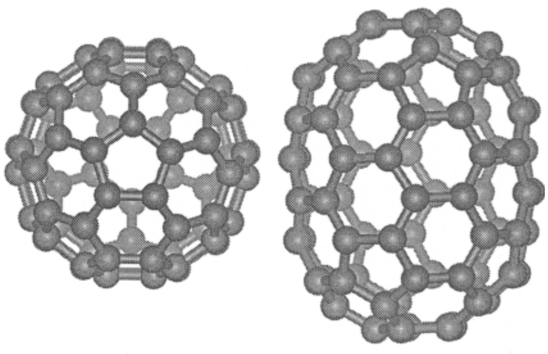

(a) (b)

Fig. 3 The optimized structure of the $C_{80}(D_{5d})$ isomer based on *ab initio* calculation at the B3LYP/3-21G level by Gaussian 98W. (a) Top view along the main C_5 axis and (b) side view. The short/long axis ratio (a)/(b) is *ca.* 1/1.3.

atoms at the equator to combine the two hemispheres. The $C_{80}(D_{5d})$ fullerene is formed in a similar way by adding two C_{10} ring successively at the equator of C_{60} (*i.e.*, $C_{30} + C_{10} + C_{10} + C_{30}$). On going from $C_{60}(I_h)$ to $C_{70}(D_{5h})$ to $C_{80}(D_{5d})$, the fullerene structure, therefore, progressively acquires tubular and cap (hemisphere) parts, which leads to ^{13}C NMR lines spread over a wide range of chemical shift values.

The calculated energy ordering of the seven C_{80} isomers at the HF/Am1 level is: $D_5(D_{5d}) < D_2[+2.3] << C_{2v}[+23.6] < C_3(D_3)[+36] < C_s(C_{2v'})[+38.5] < C_s(D_{5h})[+49.9] << D_2(I_h)[+102 \text{ kcal mol}^{-1}]$, where the stabilization energies are given relative to the most stable $D_5(D_{5d})$ isomer.[4,9] The $D_5(D_{5d})$-C_{80} and D_2-C_{80} isomers are nearly isoenergetic and their relative energies are much smaller than those of the other five isomers. The currently isolated $C_{80}(D_{5d})$ is one of the most ellipsoidal fullerenes so far produced and isolated.

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