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### Isolation and Characterization by $^{13}\text{C}$ NMR Spectroscopy of [84]Fullerene Minor Isomers

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The isolation of minor isomers of [84]fullerene ( $\text{C}_{84}$ ), five in total, and their characterization by  $^{13}\text{C}$  NMR spectroscopy, have been reported for the first time. The vis—near-infrared absorption spectra for these isomers are also reported. The  $^{13}\text{C}$  NMR results indicate that the isolated  $\text{C}_{84}$  isomers have, in order of decreasing abundance,  $\text{C}_2$ ,  $\text{C}_s(\text{a})$ ,  $\text{C}_s(\text{b})$ ,  $D_{2d}(\text{I})$ , and  $D_2(\text{II})$  molecular point group symmetry. In addition, we have found another  $\text{C}_{84}$  minor isomer adjacent to  $\text{C}_s(\text{b})\text{-C}_{84}$  in the HPLC chromatogram.

#### Introduction

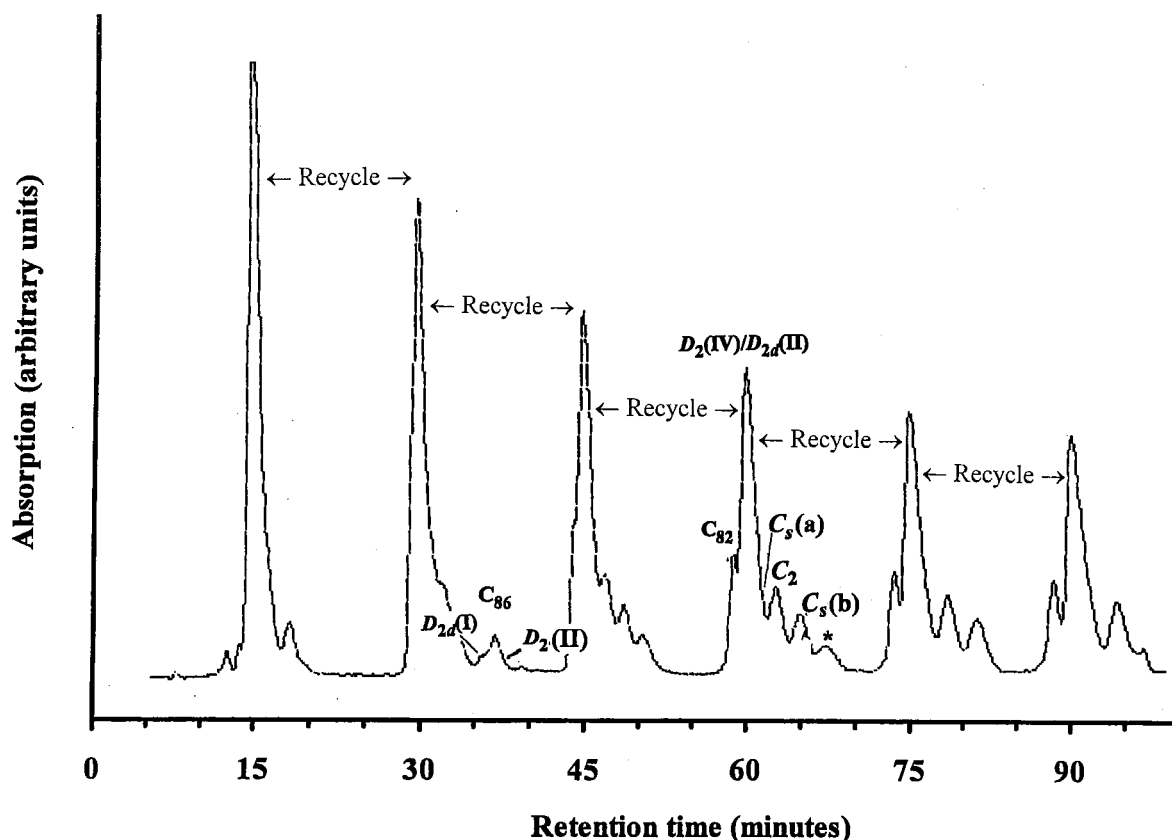
[84]Fullerene ( $\text{C}_{84}$ ) is the third most abundant fullerene solvent extractable from arc-processed soot. Early  $^{13}\text{C}$  NMR studies<sup>1–3</sup> indicated it exists as two isomers with  $D_2$  and  $D_{2d}(\text{II})$  symmetry with a 2:1 abundance ratio. The complete separation of these two isomers was finally achieved only last year.<sup>4</sup> One of the early studies reported the presence of several minor isomers,<sup>3</sup> and Saunders et al.<sup>5</sup> then suggested there are as many as eight isomers based on the  $^3\text{He}$  NMR spectrum of  $^3\text{He@C}_{84}$  (isomer mixture). However, it was not until 1997 that an attempt was made to identify these minor isomers by  $^{13}\text{C}$  NMR spectroscopy. During the HPLC (high-performance liquid chromatography) separation, Taylor and co-workers cut the main

$\text{C}_{84}$ -containing peak into two fractions, center and tail, and assignments were made with reference to comparisons between  $^{13}\text{C}$  NMR spectra of these fractions.<sup>6</sup>

A number of spectroscopic and structural studies have been carried out on [84]fullerene during the last eight years.<sup>7</sup> However, since the separation of any isomers had not been achieved, none of these experiments was carried out on isomer-free samples. There have been many theoretical calculations of the properties of  $\text{C}_{84}$ .<sup>8–19</sup> There are 24 structural isomers of  $\text{C}_{84}$  that obey the isolated pentagon rule (IPR).<sup>10</sup> Early Hückel theory calculations suggest  $D_{6h}$ ,  $T_d$ , and  $D_2(\text{I})$  to be likely candidates for the most stable isomers.<sup>8,9</sup> However, more elaborate calculations are consistent with experiments,<sup>1–3</sup> indicating that the  $D_2(\text{IV})$  and  $D_{2d}(\text{II})$  isomers are the most stable  $\text{C}_{84}$  isomers.<sup>20</sup> The early calculations neglected the curvature of the fullerene cage, and once a curvature correction is made,<sup>11–19</sup> the agreement with the experimental results can be found.

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**Figure 1.** The first recycling-phase HPLC profile for the  $C_{84}$ -containing fraction. The positions of the seven isolated isomers are indicated. Each isomer-containing fraction was collected, concentrated, and subjected to several further recycling HPLC purification treatments. The \* denotes peaks corresponding to another unidentified  $C_{84}$  minor isomer.

In the previous isolation of calcium-containing *incarc*-fullerenes, an extensive recycling HPLC is employed to separate *i*Ca $C_{82}$  from  $C_{84}$ , and *i*Ca $C_{80}$  and *i*Ca $C_{84}$  from  $C_{86}$ .<sup>21</sup> During these experiments, small quantities of purified  $C_{84}$  minor isomers were obtained, and this gave us the impetus for a concerted effort to isolate ca. 10 mg samples of these materials. Recently we reported the first isolation of the two major  $C_{84}$  isomers,  $D_2(IV)$  and  $D_{2d}(II)$ ,<sup>4</sup> and here we report the isolation of five minor isomers of  $C_{84}$ .

## Experimental Section

Fullerenes were produced by the DC arc discharge method and Soxhlet extracted by carbon disulfide. To enhance the production efficiency of minor isomers of  $C_{84}$ , we have used arc-burned soot of various metal-containing composite rods. Details of the production and extraction procedure have been described elsewhere.<sup>23</sup> Isolation of the  $C_{84}$  isomers was achieved by multi-stage recycling HPLC using a Cosmosil 5PYE column (21 mm  $\times$  250 mm).<sup>4</sup>  $^{13}C$  NMR spectroscopic measurements of the minor isomers were performed on a Varian Inova-600 spectrometer at 600 MHz ( $CS_2$  solution,  $Cr(acac)_3$  relaxant,  $C_6D_6$  lock, at 25  $^{\circ}C$ ). All  $^{13}C$  NMR spectroscopic line positions were referenced with respect to  $C_6D_6$  at 128.00. The purity of the samples was also characterized by laser-desorption time-of-flight (LD-TOF) mass spectrometry.

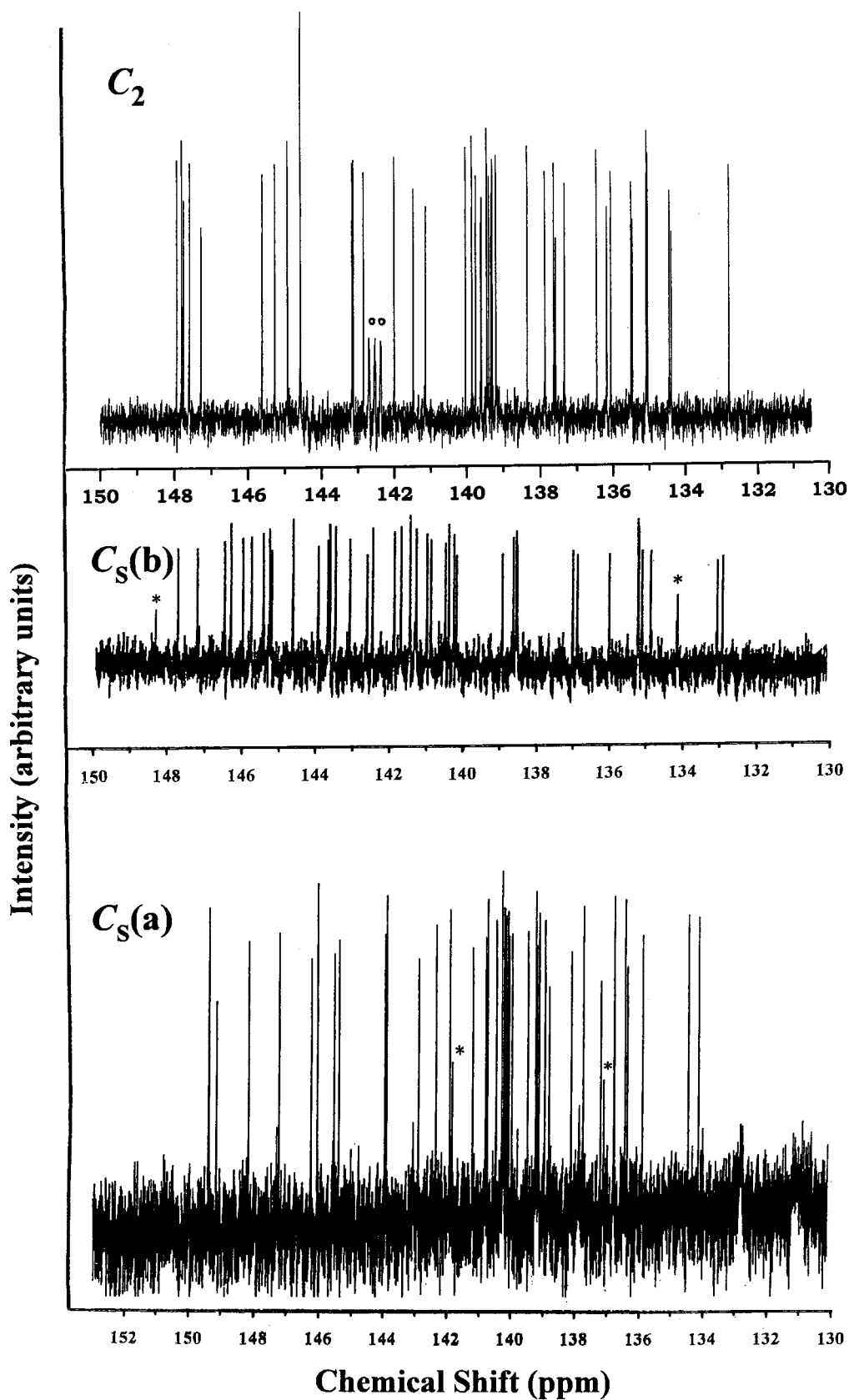
## Results and Discussion

Figure 1 shows a part of the first-stage recycling HPLC profiles for the  $C_{84}$ -containing fractions. The HPLC positions

for the seven isolated isomers are indicated. Each of these subfractions was subjected to further recycling HPLC treatments in order to obtain purified  $C_{84}$  isomers. The  $C_{84}$ -containing fractions can roughly be divided into two. The first contains the main two  $C_{84}$  isomers as well as three minor isomers, whereas the second contains two minor isomers and the main  $C_{86}$  isomer. The LD-TOF mass spectra of all purified  $C_{84}$  fractions showed only a single line, indicating isolation (99% up) of these isomers.

The  $^{13}C$  NMR spectra of the three minor isomers that elute with the main  $C_{84}$  isomer-containing fraction are shown in Figure 2, while those of the two isomers that coelute with  $C_{86}$  are shown in Figure 3. Their chemical shifts, together with those we previously reported on the major two isomers,<sup>4</sup> are listed in Table 1. These spectra present a good indication of the purity of the samples since there is no detectable contamination by other isomers. The data clearly show the isolated  $C_{84}$  isomers have  $D_2(IV)$ ,  $D_{2d}(II)$ ,  $C_2$ ,  $C_s(a)$ ,  $C_s(b)$ ,  $D_{2d}(I)$ , and  $D_2(II)$  molecular point-group symmetry. Here we have made the provisional assignments on  $C_s$  isomers as  $C_s(a)$  and  $C_s(b)$  (cf., Figure 1), because unambiguous molecular symmetry assignment among  $D_2(I-IV)$ ,  $C_2(I-V)$ , or between  $C_s(III)$  and  $C_s(V)$  isomers cannot be made on the basis of the present one-dimensional  $^{13}C$  NMR study. Previous theoretical calculations<sup>12-19</sup> indicate that  $C_s(V)$ - $C_{84}$  is more stable than  $C_s(III)$ - $C_{84}$ . Unambiguous assignment for the one of the major isomers,  $D_2(IV)$ , was already done by two-dimensional  $^{13}C$  NMR measurements by using  $^{13}C$ -enriched  $C_{84}$ .<sup>24</sup> Interestingly, the order of decreasing abundance is almost the same as the order of increasing retention time.

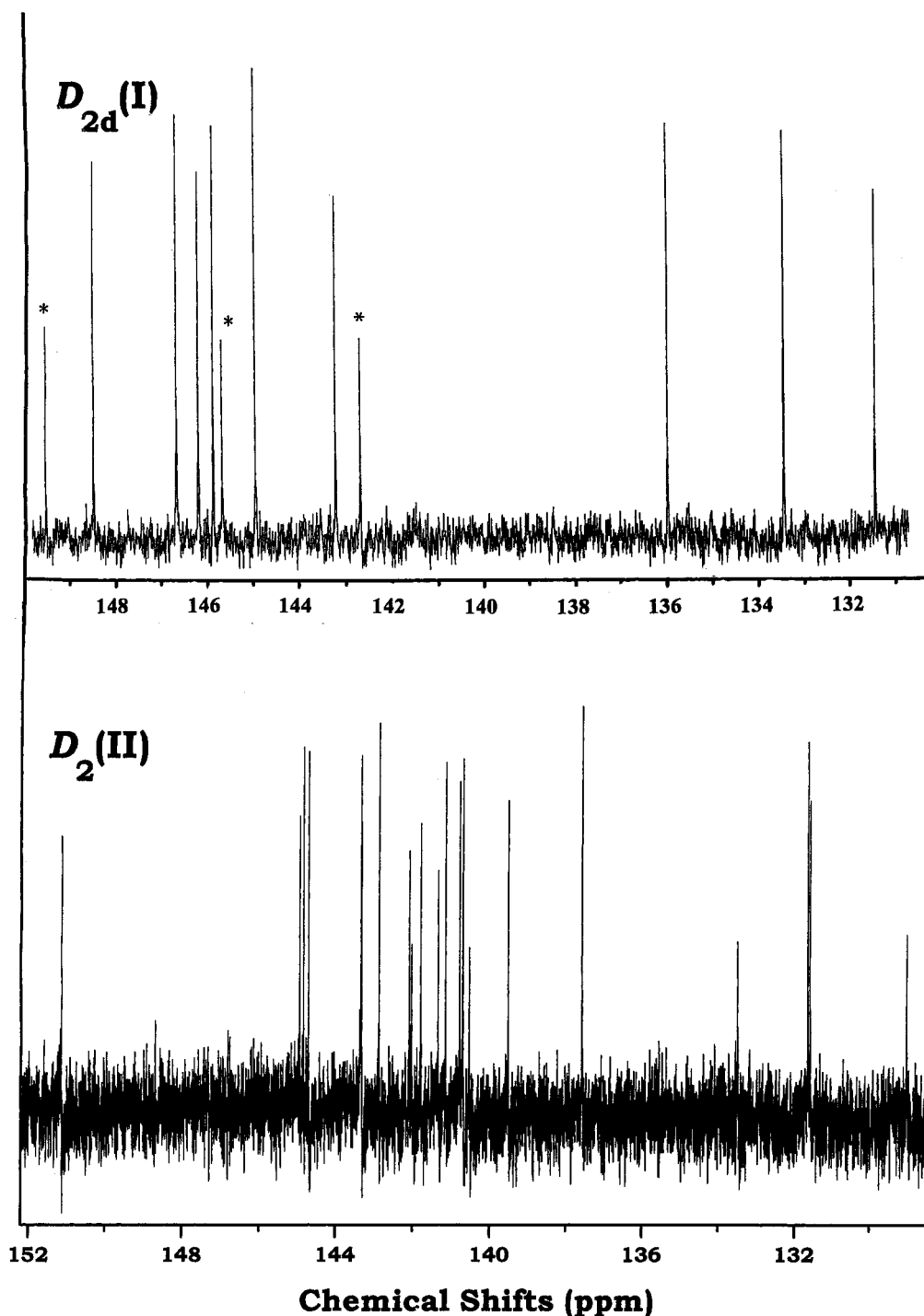
It is possible that there are still other  $C_{84}$  isomers extractable from arc-processed soot. In fact, during the current HPLC



**Figure 2.**  $^{13}\text{C}$  NMR spectra of the three minor isomers eluting with the main  $\text{C}_{84}$ -containing fraction. In order of increasing retention time on the 5PVE column they have  $\text{C}_2$ ,  $\text{C}_s(\text{a})$ , and  $\text{C}_s(\text{b})$  point group symmetry (see text). The \* marks indicate half intensity lines. In the upper spectrum, the three peaks denoted by ° ° indicate sidebands due to the  $\text{C}_6\text{D}_6$  lock.

separation we have noticed the presence of another minor (eighth) isomer adjacent to  $\text{C}_s(\text{b})$  in the HPLC chromatogram

in Figure 1 (denoted by \*), which has not yet been fully isolated to the present. (An extensive HPLC recycling has showed that



**Figure 3.**  $^{13}\text{C}$  NMR spectra of the two minor isomers eluting with the main  $\text{C}_{86}$ -containing fraction. The \* marks indicate half intensity lines. In order of increasing retention time on the 5PYE column they have  $D_{2d}(\text{I})$  and  $D_2(\text{II})$  point group symmetry.

this HPLC fraction also contains a  $\text{C}_{82}$  (minor) isomer.) There is a good agreement between the number of isolated isomers presented here and the number of isomers reported for  $^3\text{He}@\text{C}_{84}$ <sup>5</sup> obtained from high-pressure helium capture by a  $\text{C}_{84}$  isomer mixture. Without further improvement in separation techniques, we feel it unlikely that any other sub-minor isomers, if they exist, could be isolated. Recently, Taylor and co-workers reported  $^{13}\text{C}$  NMR measurements on partially separated  $\text{C}_{84}$ .<sup>6</sup> The present isolation and identification of  $\text{C}_2$ ,  $\text{C}_s$ , and  $D_2$  minor isomers is consistent with their reports of  $\text{C}_2$  and  $\text{C}_s$  isomers. However, the current isolation of the minor  $D_2(\text{II})$  isomer

indicates that this isomer has a greater retention time than that of  $\text{C}_{86}$ , and as such, should not be in their HPLC fraction judging from the present identification of its retention time. This explains why many of the lines they assigned to this isomer are not a reasonable match to those presented here on fully isolated materials.

The UV-vis-NIR absorption spectra of the five  $\text{C}_{84}$  minor isomers are shown in Figure 4. All the absorption spectra are very different in comparison with each other. In particular, the  $D_{2d}(\text{I})$  and  $D_2(\text{II})$  isomers show sharp peaks around 600 and 700 nm, respectively, whereas those of  $\text{C}_2$ ,  $\text{C}_s(\text{a})$  and  $\text{C}_s(\text{b})$  only

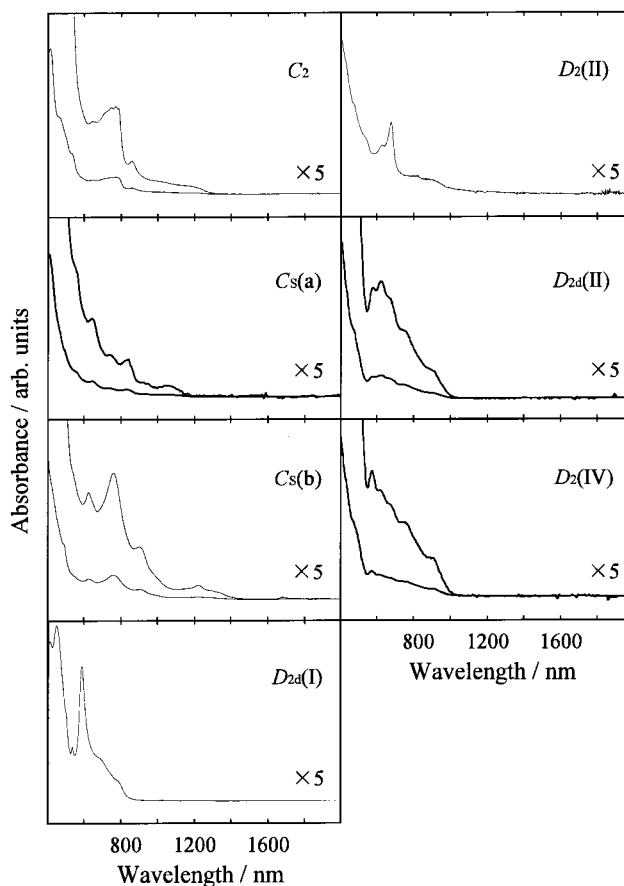
**TABLE 1: Chemical Shifts (ppm) for Seven Isolated Isomers of C<sub>84</sub><sup>a</sup>**

<i>D</i> <sub>2</sub> (IV)	<i>D</i> <sub>2d</sub> (II)	<i>C</i> <sub>2</sub>	<i>C</i> <sub>s</sub> (a)	<i>C</i> <sub>s</sub> (b)	<i>D</i> <sub>2d</sub> (I)	<i>D</i> <sub>2</sub> (II)
133.71	134.88	133.09	134.11	132.93	131.36	129.38
135.38	138.38	134.68	134.43	133.07	133.34	131.95
137.29	138.77	134.74	135.86	134.33*	135.87	132.01
137.40	138.78	135.33	136.33	134.91	142.54*	133.84
137.81	139.72*	135.35	136.40	135.16	143.08	137.93
138.48	139.90	135.37	136.74	135.24	144.80	139.87
139.53	140.17	135.79	136.74	135.25	145.51*	140.88
139.64	140.40	135.75	137.03*	136.04	145.70	141.04
139.67	141.47	136.35	137.17	136.93	146.02	141.06
139.69	142.03	136.47	137.72	137.04	146.49	141.14
140.22	144.50	136.75	138.09	138.56	148.29	141.50
140.50		137.62	138.80	138.59	149.34*	141.69
140.90		137.86	138.93	138.66		142.14
141.23		137.91	139.11	138.97		142.39
142.48		138.16	139.18	140.23		142.44
142.79		138.64	139.22	140.31		143.66
143.68		139.49	139.46	140.34		143.69
143.71		139.59	139.96	140.53		145.05
143.88		139.62	140.04	140.94		145.18
144.38		139.68	140.08	141.05		145.28
144.48		139.74	140.14	141.37		151.48
		139.89	140.19	141.52		
		139.90	140.21	141.76		
		140.05	140.27	141.96		
		140.14	140.44	142.55		
		140.31	140.71	142.72		
		141.43	140.77	143.20		
		141.77	141.17	142.66		
		142.29	141.76*	143.70		
		143.13	141.88	143.74		
		143.41	142.30	143.77		
		143.45	142.85	144.02		
		144.87	143.87	144.71		
		144.87	143.92	145.31		
		145.21	145.36	145.36		
		145.55	145.51	145.53		
		145.90	146.04	145.86		
		147.56	146.23	146.09		
		147.87	147.23	146.42		
		148.03	148.16	146.59		
		148.08	149.15	147.32		
		148.22	149.39	147.84		
			149.40	148.44*		

<sup>a</sup> \* denotes half intensity lines where appropriate.

show some broad features. The absorption onsets of these C<sub>84</sub> minor isomers lie between 1000 and 1500 nm, except for *D*<sub>2d</sub>(I) which has an absorption onset at ca. 900 nm.

Several theoretical calculations of the relative stabilities of all C<sub>84</sub> isomers have been carried out.<sup>13,15,17–19</sup> There is some agreement between the calculated stability order and the observed abundance order for the isomers. For example, the calculations suggest that the *D*<sub>2</sub>(IV) and *D*<sub>2d</sub>(II) isomers are nearly isoenergetic and most stable, that *C*<sub>2</sub>(IV) and *C*<sub>s</sub>(V) are the next stable, and that *C*<sub>3d</sub>, *C*<sub>6h</sub>, and *C*<sub>1</sub> are among the top seven isomers.<sup>12,15,17</sup> There are also some notable exceptions however. The *D*<sub>3d</sub> and *D*<sub>6h</sub> isomers are calculated to be more stable than *D*<sub>2d</sub>(I) and *D*<sub>2</sub>(II), but were not observed among the seven most abundant C<sub>84</sub> isomers. In particular, the *D*<sub>2d</sub>(I) is calculated to be the 12th or 13th most stable isomer, but actually is the sixth most abundant. Recent calculations by Osawa et al.<sup>22</sup> suggested the presence of the *D*<sub>2d</sub>(I) isomer may be justified on kinetic grounds. By considering a pathway map of generalized Stone-Wales rearrangements, presumed to occur during

**Figure 4.** UV-vis-NIR absorption spectra of the five C<sub>84</sub> minor isomers currently isolated [*C*<sub>2</sub>, *C*<sub>s</sub>(a), *C*<sub>s</sub>(b), *D*<sub>2d</sub>(I), *D*<sub>2</sub>(II)] and the two major isomers previously isolated [*D*<sub>2d</sub>(II), *D*<sub>2</sub>(IV)]<sup>4</sup> for reference.

annealing immediately after fullerene formation, this isomer is found to occupy a deep energy local-minimum.<sup>22</sup> These authors use a similar argument to suggest the minor *D*<sub>2</sub> isomer is *D*<sub>2</sub>(II).

In conclusion, together with the two main isomers, we have isolated and characterized by <sup>13</sup>C NMR spectroscopy seven isomers of the third most abundant fullerene, C<sub>84</sub>. These isomers have in order of decreasing yield *D*<sub>2</sub>(IV), *D*<sub>2d</sub>(II), *C*<sub>2</sub>, *C*<sub>s</sub>(a), *C*<sub>s</sub>(b), *D*<sub>2d</sub>(I), and *D*<sub>2</sub>(II) molecular point-group symmetry. Also we have found another C<sub>84</sub> minor (eighth) isomer adjacent to *C*<sub>2</sub>(b)-C<sub>84</sub> in the Buckyprep HPLC chromatogram. The present production, isolation, and characterization on the C<sub>84</sub> isomers should lead to give valuable information on the growth process of C<sub>84</sub>.

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**TABLE 2: Summary of Several Parameters for the Currently Isolated Seven C<sub>84</sub> Isomers**

	<i>D</i> <sub>2</sub> (IV)	<i>D</i> <sub>2d</sub> (II)	<i>C</i> <sub>2</sub>	<i>C</i> <sub>s</sub> (a)	<i>C</i> <sub>s</sub> (b)	<i>D</i> <sub>2d</sub> (I)	<i>D</i> <sub>2</sub> (II)
number of <sup>13</sup> NMR lines	21	11	42	43	43	12	21
absorption onset (nm)	1,050	1,050	1,310	1,200	1,450	900	1,400
HPLC retention-time order on 5-PYE column <sup>a</sup>	1	2	4	3	5	6	7
relative abundance <sup>b</sup>	1	0.5	0.2	0.1	0.1	0.05	0.03

<sup>a</sup> With increasing retention times (see text). <sup>b</sup> The values presented here are rough estimates and subject to change depending on the production condition of the C<sub>84</sub> isomers.

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