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LETTERS

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

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The isolation of minor isomers of [84]fullerene (C_{84}), five in total, and their characterization by ^{13}C NMR spectroscopy, have been reported for the first time. The vis−near-infrared absorption spectra for these isomers are also reported. The ^{13}C NMR results indicate that the isolated C_{84} isomers have, in order of decreasing abundance, C_2, C_s(a), C_s(b), D_{2d}(I), and D_2(II) molecular point group symmetry. In addition, we have found another C_{84} minor isomer adjacent to C_s(b)-C_{84} in the HPLC chromatogram.

Introduction

[84]Fullerene (C_{84}) is the third most abundant fullerene solvent extractable from arc-processed soot. Early ^{13}C NMR studies[1−3] indicated it exists as two isomers with D_2 and D_{2d}(II) symmetry with a 2:1 abundance ratio. The complete separation of these two isomers was finally achieved only last year.[4] One of the early studies reported the presence of several minor isomers,[3] and Saunders et al.[5] then suggested there are as many as eight isomers based on the ^3He NMR spectrum of $^3He@C_{84}$ (isomer mixture). However, it was not until 1997 that an attempt was made to identify these minor isomers by ^{13}C NMR spectroscopy. During the HPLC (high-performance liquid chromatography) separation, Taylor and co-workers cut the main C_{84}-containing peak into two fractions, center and tail, and assignments were made with reference to comparisons between ^{13}C NMR spectra of these fractions.[6]

A number of spectroscopic and structural studies have been carried out on [84]fullerene during the last eight years.[7] 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 C_{84}.[8−19] There are 24 structural isomers of C_{84} that obey the isolated pentagon rule (IPR).[10] Early Hückel theory calculations suggest D_{6h}, T_d, and D_2(I) to be likely candidates for the most stable isomers.[8,9] However, more elaborate calculations are consistent with experiments,[1−3] indicating that the D_2(IV) and D_{2d}(II) isomers are the most stable C_{84} isomers.[20] The early calculations neglected the curvature of the fullerene cage, and once a curvature correction is made,[11−19] the agreement with the experimental results can be found.

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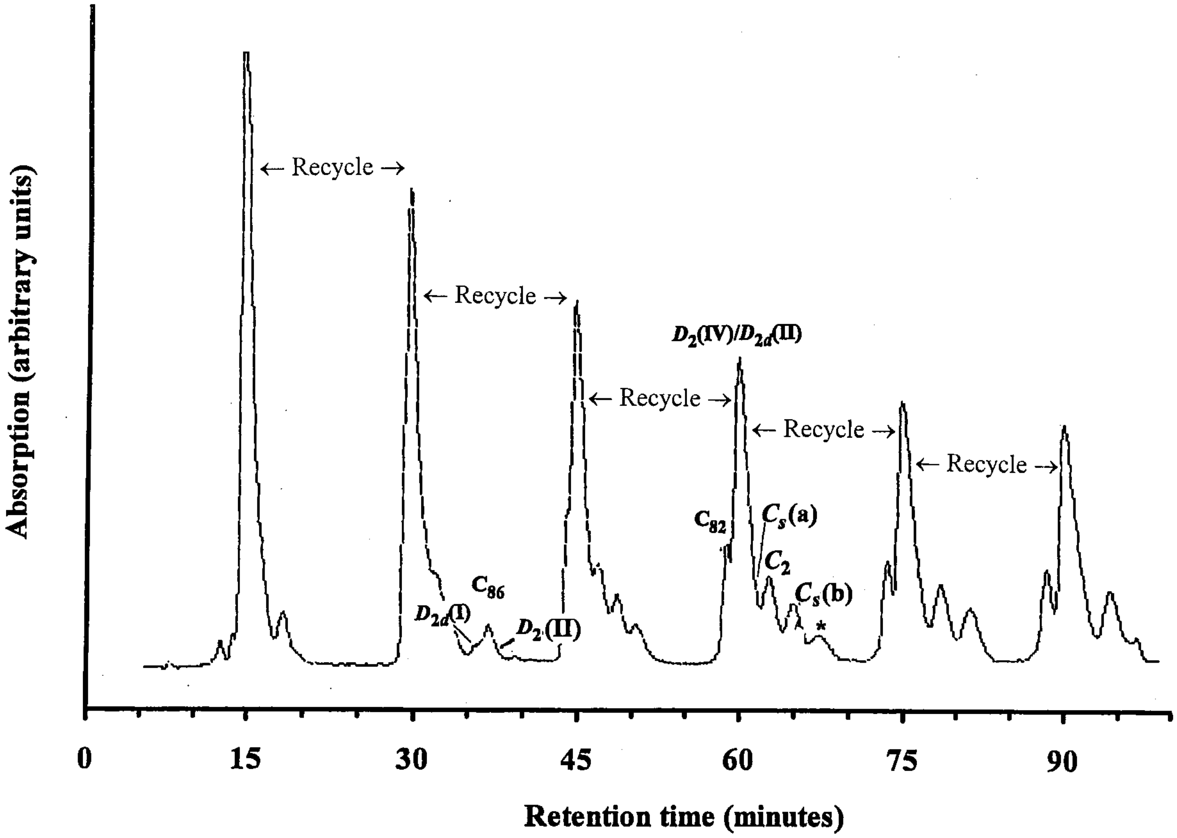

Figure 1. The first recycling-phase HPLC profile for the C_{84}-containing fraction. The positions of the seven isolated isomers are indicated. Each isomer-containing fraction was collected, concentrated, and subjected to several further recycling HPLC purification treatments. The * denotes peaks corresponding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

In the previous isolation of calcium-containing *incar*-fullerenes, an extensive recycling HPLC is employed to separate *i*CaC_{82} from C_{84}, and *i*CaC_{80} and *i*CaC_{84} from C_{86}.[21] 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),[4] 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.[23] Isolation of the C_{84} isomers was achieved by multi-stage recycling HPLC using a Cosmosil *5PYE* column (21 mm × 250 mm).[4] ^{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 °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 an 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,[4] 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[12−19] 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}.[24] 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

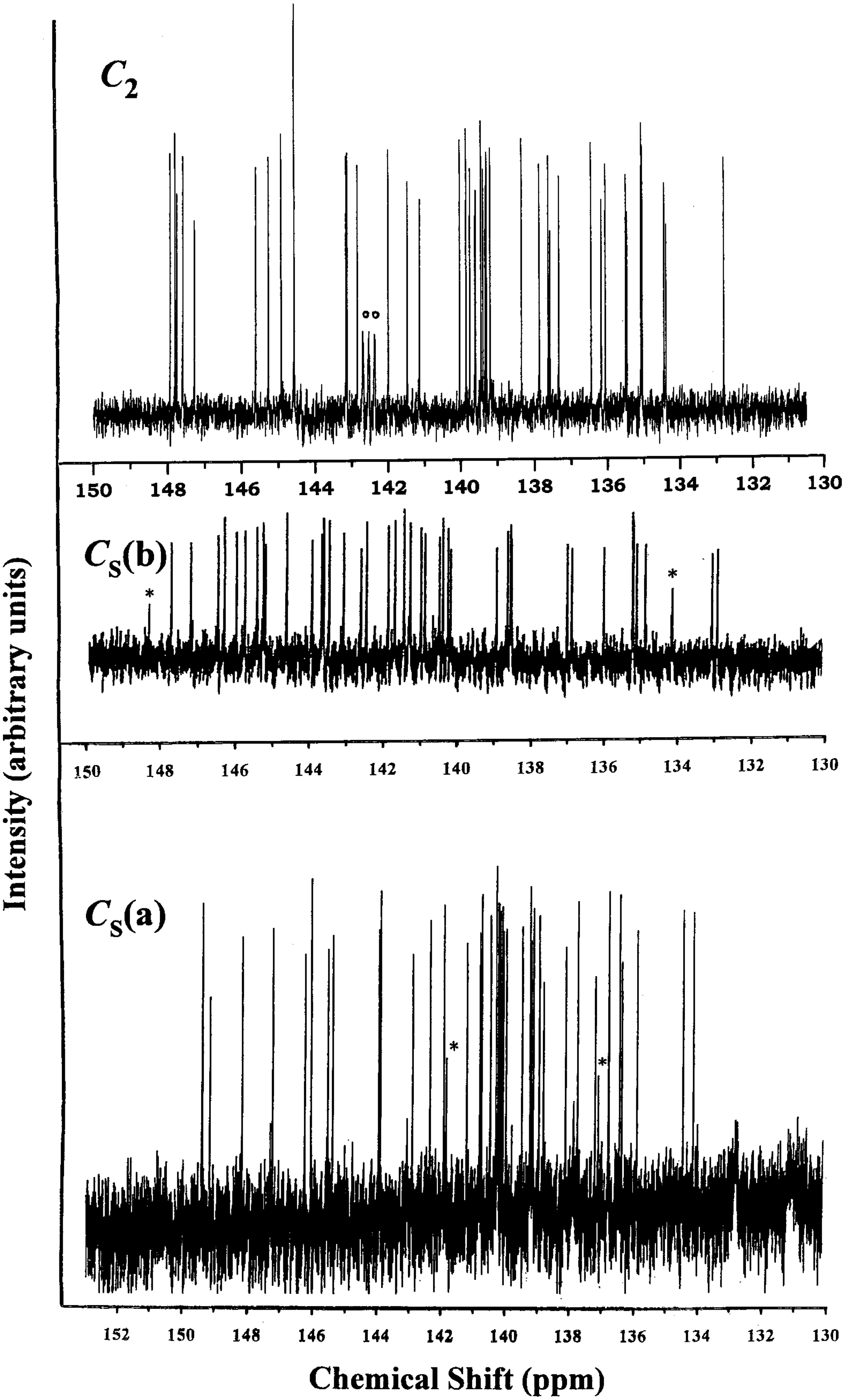

Figure 2. ^{13}C NMR spectra of the three minor isomers eluting with the main C_{84}- containing fraction. In order of increasing retention time on the 5*PYE* column they have C_s(a), C_2, and C_s(b) point group symmetry (see text). The * marks indicate half intensity lines. In the upper spectrum, the three peaks denoted by ° ° indicate sidebands due to the C_6D_6 lock.

separation we have noticed the presence of another minor (eighth) isomer adjacent to C_s(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

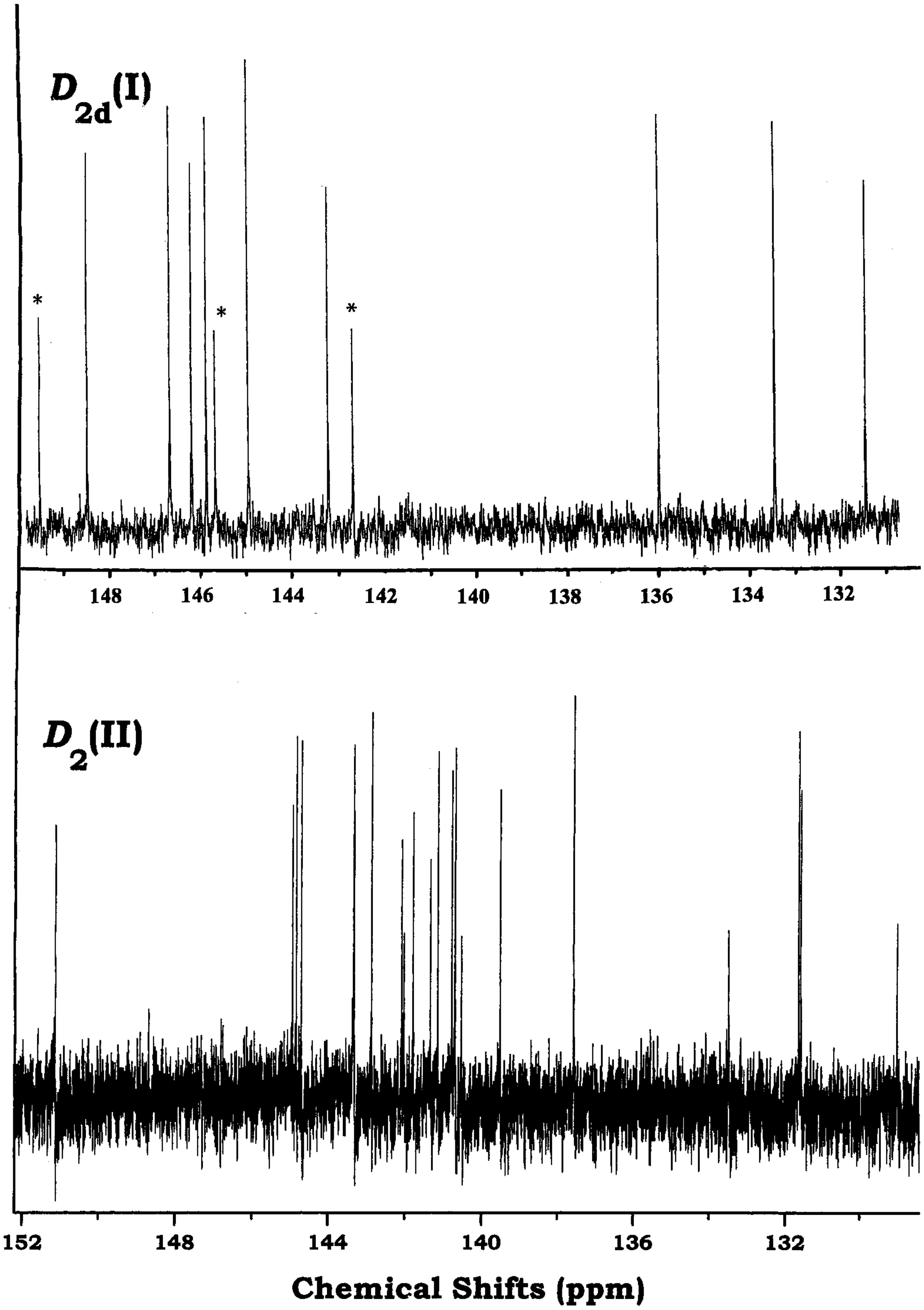

Figure 3. ^{13}C NMR spectra of the two minor isomers eluting with the main C_{86}-containing fraction. The * marks indicate half intensity lines. In order of increasing retention time on the 5*PYE* column they have D_{2d}(I) and D_2(II) point group symmetry.

this HPLC fraction also contains a 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}He@C_{84}[5] obtained from high-pressure helium capture by a 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}C NMR measurements on partially separated C_{84}.[6] The present isolation and identification of C_2, C_s, and D_2 minor isomers is consistent with their reports of C_2 and C_s isomers. However, the current isolation of the minor D_2(II) isomer indicates that this isomer has a greater retention time than that of 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 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}(I) and D_2(II) isomers show sharp peaks around 600 and 700 nm, respectively, whereas those of C_2, C_s(a) and C_s(b) only

TABLE 1: Chemical Shifts (ppm) for Seven Isolated Isomers of C_{84}[a]

D_2 (IV)	D_{2d} (II)	C_2	C_s(a)	C_s(b)	D_{2d} (I)	D_2 (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*		

[a] * denotes half intensity lines where appropriate.

show some broad features. The absorption onsets of these C_{84} minor isomers lie between 1000 and 1500 nm, except for D_{2d}(I) which has an absorption onset at ca. 900 nm.

Several theoretical calculations of the relative stabilities of all C_{84} isomers have been carried out.[13,15,17−19] 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_2(IV) and D_{2d}(II) isomers are nearly isoenergetic and most stable, that C_2(IV) and C_s(V) are the next stable, and that C_{3d}, C_{6h}, and C_1 are among the top seven isomers.[12,15,17] There are also some notable exceptions however. The D_{3d} and D_{6h} isomers are calculated to be more stable than D_{2d}(I) and D_2(II), but were not observed among the seven most abundant C_{84} isomers. In particular, the D_{2d}(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.[22] suggested the presence of the D_{2d}(I) isomer may be justified on kinetic grounds. By considering a pathway map of generalized Stone-Wales rearrangements, presumed to occur during annealing immediately after fullerene formation, this isomer is found to occupy a deep energy local-minimum.[22] These authors use a similar argument to suggest the minor D_2 isomer is D_2(II).

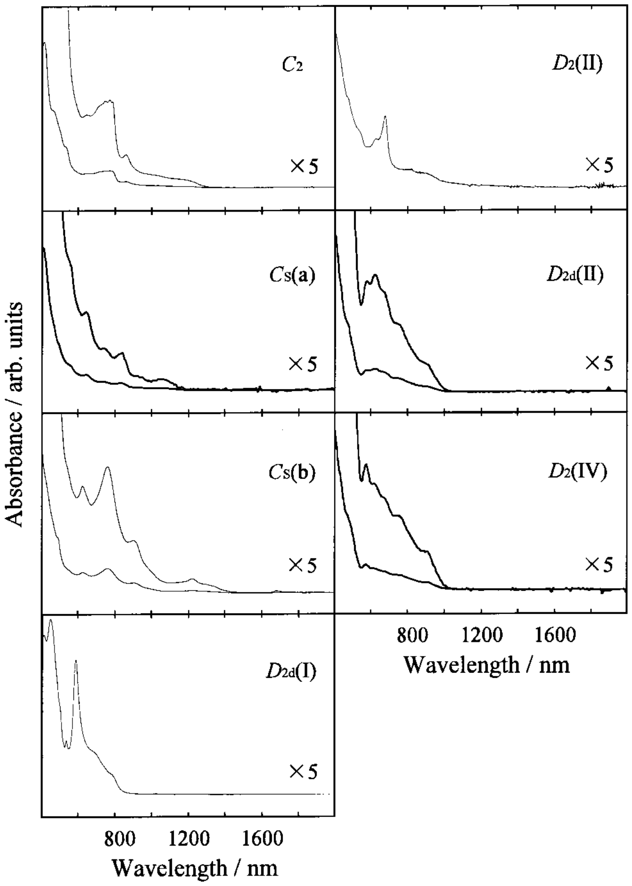

Figure 4. UV−vis−NIR absorption spectra of the five C_{84} minor isomers currently isolated [C_2, C_s(a), C_s(b), D_{2d}(I), D_2(II)] and the two major isomers previously isolated [D_{2d}(II), D_2(IV)][4] for reference.

In conclusion, together with the two main isomers, we have isolated and characterized by ^{13}C NMR spectroscopy seven isomers of the third most abundant fullerene, C_{84}. These isomers have in order of decreasing yield 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. Also we have found another C_{84} minor (eighth) isomer adjacent to C_2(b)-C_{84} in the Buckyprep HPLC chromatogram. The present production, isolation, and characterization on the C_{84} isomers should lead to give valuable information on the growth process of C_{84}.

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TABLE 2: Summary of Several Parameters for the Currently Isolated Seven C_{84} Isomers

	D_2 (IV)	D_{2d} (II)	C_2	C_s (a)	C_s (b)	D_{2d} (I)	D_2 (II)
number of ^{13}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[a]	1	2	4	3	5	6	7
retative abundance[b]	1	0.5	0.2	0.1	0.1	0.05	0.03

[a] With increasing retention times (see text). [b] The values presented here are rough estimates and subject to change depending on the production condition of the C_{84} isomers.

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