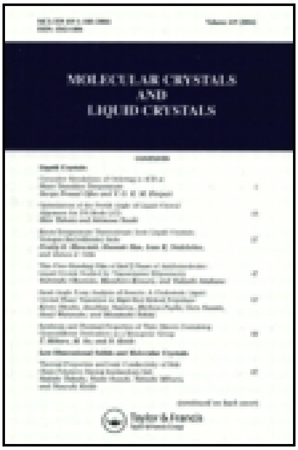

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Yoko Miyake [a] , Tsuyoshi Minami [a] , Kouichi Kikuchi [a] , Masatsune Kainosho [a] & Yohji Achiba [a]

[a] Department of Chemistry, Tokyo Metropolitan University, Hachioji, 1920397, Tokyo, Japan

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Trends in Structure and Growth of Higher Fullerenes Isomer Structure of C_{86} and C_{88}-

YOKO MIYAKE, TSUYOSHI MINAMI, KOUICHI KIKUCHI,
MASATSUNE KAINOSHO and YOHJI ACHIBA

*Department of Chemistry, Tokyo Metropolitan University, Hachioji,
1920397 Tokyo, Japan*

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The isomer structure and stability of higher fullerenes is one of the most interesting issues which might be closely related with general question how a fullerene cage structure is formed. In the present study, the structures of the higher fullerenes with the sizes of C_{86} and C_{88} are described based on UV/Visible/nearIR absorption spectra and ^{13}C NMR measurements in solution. For well-understanding the structure and growth of higher fullerenes, the isomer-free samples were prepared for all isomers associated with the C_{86} and C_{88} cages by means of a multiple stage high performance liquid chromatography (HPLC). As a result, five different isomers for C_{86} and C_{88} were successfully isolated and characterized. For these five different isomers studied in the present work, ^{13}C NMR measurements in solution straightforwardly gave a conclusion that three of them possess the cage structures with a C_2 molecular symmetry and two with a C_s molecular symmetry. The possible specific candidates for these five isomers will be discussed on the basis of both the present experimental results and recent theoretical predictions.

Keywords: Fullerenes; Higher Fullerenes; ^{13}C NMR spectroscopy; Isomer Separation; C_{86} fullerene; C_{88} fullerene

INTRODUCTION

Soon after the discovery of large-scale preparation of C_{60} fullerene[1], the presence of much larger all carbon molecules has been found and identified in the carbon soot[2]. From mass spectroscopic characterization, it has been suggested that these all carbon molecules possess a similar cage structure like C_{60} and C_{70}. Actually soon later, several kinds of stable higher fullerenes, C_{76}, C_{78}, C_{82} and C_{84} were isolated and characterized by means of ^{13}C NMR spectroscopy[3,4], revealing the presence of a cage structure with a five and six-membered ring systems. On the basis of NMR measurements, it was also found that C_{76} and C_{82} consist of only single isomer, while C_{78} and C_{84}, three and two isomers, respectively[4].

For the higher fullerenes larger than C_{86}, our preliminary investigations have been performed on the fullerenes up to C_{94} by Achiba et al[5,6]. However, because the samples used in the previous work contained two or three isomers which were not fully isolated from each other, the obtained ^{13}C NMR spectra showed significant overlapping lines caused by the mixture of several isomers, resulting in some ambiguities in determining individual isomer structures.

Very recently, the isomers with C_{84} closed cages have been reinvestigated[7], and it was found that seven different isomers are able to be isolated from each other as an isomer-free sample. The ^{13}C NMR characterization in solution for these samples straightforwardly gave a conclusion that the seven isomers of C_{84} consist of two D_2, two D_{2d}, two C_s, and one C_2 as a molecular symmetry. Furthermore, the investigation of higher fullerenes have been placed much attention on the research field associated with the formation of ehdohedral metallofullerenes, in which, for example, La metal has been known to be stably trapped in the C_{82} specific fullerene cage. So far many other exapmles have also been demonstarted that very specific isomers of higher fullerenes play an important role on the stabilization of metallofullerenes. Here in the present work, we will demonstrate the isomer-free sample preparation of C_{86} and C_{88} by means of multi-stage HPLC method and the ^{13}C NMR characterizations for five different isomers of these specific fullerenes will be shown.

EXPERIMENTAL

The fullerene soot containing higher fullerenes was prepared by a conventional arc-discharge method with a graphite rod in He. Following carbon disulfide extraction of the fullerene containing soots, the extracts were treated separately by filteration. The initial automated chromatographic separation stage was performed by a 5PBB (Cosmosil, Nakarai Tesque Inc., 250 mm x 10 mm i.d.) colomn with CS_2 as the mobile phase. In the second and third stages, preparative Buckyprep (Cosmosil, Nakarai Tesque Inc., 250 mm x 10 mm i.d.), and 5PBB (Cosmosil, Nakarai Tesque Inc., 250 mm x 10 mm i.d.) colomns were utilized with toluene as the solvent for isolation of a single isomer from the size separated fullerene samples from C_{86} to C_{90}. In this manner, the isomer-free samples were separately isolated.

^{13}C NMR spectroscopic measurements of the isomers were performed by a Varian -500 at 500 MHz (CS_2 solution, Cr(acac)3 relaxant, C_2D_4 lock at room temperature). The purity of the samples was also characterized by a laser desorption time-of-flight mass spectrometry.

RESULTS AND DISCUSSION

C_{86} fullerene

Using the three-stage HPLC system, two kinds of isomers (C_{86}-1 and C_{86}-2) were found to be isolated for C_{86} fullerene. In the manner of the HPLC elusion profile in the buckyprep colomn, it was found that both of the two isomers have almost the same retention time, indicating the formation of a similar cage structure for each of them. Furthermore, the similarity in the structure of the molecular framework was also confirmed by comparing elusion behaviors of the two isomers in the different colomn such as the 5-PBB. It was found that the C_{86}-2 isomer moves a little bit faster in the buckyprep colomn but in the 5-PBB colomn, it is reversed.

The ratio of the production yield of these two isomers was about 4:1 for C_{86}-1 and C_{86}-2, respectively. UV/Visible /Near IR absorption spectra of these two isomers were measured separately, and demonstrated that the first absorption band (which may closely be related with the HOMO-LUMO energy gap) appear at 1400 nm and 1000 nm for C_{86}-1 and C_{86}-2, respectively. Therefore, it is concluded that the C_{86}-1 isomer would have the smaller HOMO-LUMO gap than the C_{86}-2.

The ^{13}C NMR spectrum of C_{86}-2 isomer consists of 40 lines with 6 additional lines with a half intensity (total 46 lines), while the one of C_{86}-1 consists of 43 lines with an equal intensity. These data clearly suggest that the molecular symmetries of C_{86}-1 and C_{86}-2 are C_2 and C_s, respetively. For the case of C_s isomer, it is also suggested that the six non-equivalent carbon atoms with a half intensity of C_{86}-2 are sitting on a mirror plane of the C_{86} cage. The chemical shifts of all lines due to these two isomers are summarized in Table 1.

According to the theoretical calculation by Mamolopoulos and Fowler[8], C_{86} fullerene has distinct 19 kinds of structural isomers if we assume an isolated pentagon rule (IPR) for the stability of C_{86} fullerene structure. Among the 19 isomers, there are six isomers possessing a C_2 molecular symmetry, and three isomers, a C_s symmetry. However, in the case of C_s, one of the three candidates can easily be excluded for the present case, because this particular isomer should have 39 full lines and 8 lines with a half intensity. Obviously this is not indeed the case. Therefore, for C_{86}-2 fullerene, there are only two candidates which can reasonably be expected by the ^{13}C NMR spectrum.

Furthermore, very recently the potential candidates for the isomers of C_{86} fullerene has been discussed by Slanina et al.[9]. According to their calculations including semi-ab-initio model as well as ab initio SCF computations, two of 19 different isomers, $C_2(17)$ and $C_s(16)$ (parentheses are the numbering of the isomers used in ref.[8]) were found to be distinguishably stable, not depending on the levels of the computing method. On the basis of these results, they predicted that the isomers $C_2(17)$ and $C_s(16)$ might be preferentially formed in the network formation processes. This conclusion is well consistent with the fact that two isomers C_2 and C_s were actually detected in the present work. Furthermore, the expectation deduced by the present HPLC elusion behavior that the structures of these two isomers might be similar with each other is also consistent with the fact that one of the structures are reproduced from the other only by transforming a pair of pyracylene structure. The structures of $C_2(17)$ and $C_s(16)$ are shown in Fig. 1.

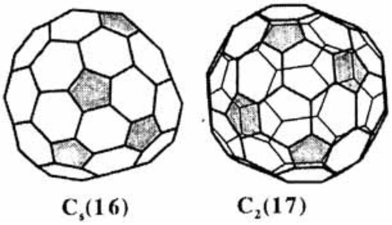
$C_s(16)$ $C_2(17)$

FIGURE 1. Two IPR structures of C_{86}

C_{88} fullerene

The isomers of C_{88} were also examined to isolate the isomer-free samples by the multi-stage HPLC procedures. Using a multi-stage high performance liquid chromatography (HPLC), three kinds of isomers with C_{88} cage were successuly separated. Among these three isomers, one of the isomers, C_{88}-1 was able to be separated only by use of the buckyprep colomn, while the remaining two C_{88}-2 and C_{88}-3 were separated only after the third-stage HPLC procedure.

UV/Visible/nearIR absorption spectra in solution were measured for the sample of C_{88}-1, C_{88}-2 and C_{88}-3, separately. The absorption threshould thus obtained for three isomers, C_{88}-1, C_{88}-2 and C_{88}-3 were 1300 nm, 1300 nm and 1000 nm, respectively. The isomer C_{88}-3 shows the largest energy gap among these three isomers.

Table 1. Chemical shifts(ppm) for isolated isomers of C_{86} and C_{88} (* denote half intensity lines where appropriate).

	C_{86}-1 (C_2)	C_{86}-2 (C_s)	C_{88}-1 (C_s)	C_{88}-2 (C_2)	C_{88}-3 (C_2)
1	131.055	132.192	131.126	128.401	130.096
2	134.379	132.827	132.726	129.171	130.712
3	134.554	132.828	133.304	131.680	133.600
4	134.555	134.320	133.957	131.941	133.763
5	135.844	134.744	135.065	132.274	133.892
6	136.460	135.198	135.593	132.799	134.317
7	136.619	135.444	135.682	133.131	134.331
8	136.702	135.895*	135.842	133.478	134.558
9	137.689	135.999	135.985	133.479	135.206
10	138.172	136.746	136.426	134.844	136.039
11	138.653	136.841*	136.490	135.100	137.462
12	138.996	137.517*	136.967	136.429	137.482
13	139.676	137.817	137.084	136.766	138.849
14	140.031	138.395	137.085	137.278	139.006
15	140.184	139.234	138.675	137.682	139.350
16	140.203	139.331	139.512	138.473	140.180
17	140.260	139.536	139.767	138.935	140.277
18	140.306	139.894	139.984	138.937	140.737
19	140.746	140.751*	140.215	139.218	140.770
20	140.936	140.773	140.476	139.581	140.870
21	140.973	140.967	140.616	139.965	141.135
22	141.160	141.608	140.042*	140.158	141.268
23	141.365	141.655	140.044	140.724	141.290
24	141.368	141.714	141.330	140.995	141.365
25	141.368	142.506	141.430*	141.207	141.474
26	141.421	142.542	141.554	141.426	141.630
27	141.638	142.753	141.630	142.669	141.630
28	141.638	142.907	141.920	142.763	142.252
29	141.679	144.159	141.920	143.369	142.833
30	141.730	144.275	142.252	143.492	142.985
31	143.148	144.496	142.255	143.760	143.153
32	143.399	144.622	142.763	143.907	143.378
33	143.625	145.438	143.299	144.294	143.828
34	143.647	145.476*	143.643	145.032	144.251
35	143.804	145.614	143.885	145.327	145.381
36	143.991	145.960*	144.320	145.938	145.977
37	144.706	146.169	144.367	146.170	147.152
38	145.571	146.369	144.568	146.377	147.569
39	145.732	146.415	145.037	146.410	147.789
41	147.073	146.829	146.280	146.959	148.350
42	147.520	146.899	146.823	147.530	148.469
43	151.340	147.121	147.208	150.540	148.900
44		147.145	147.940	150.847	149.517
45		150.008	152.623*		
46		150.179	153.842*		

^{13}C NMR spectra for the C_{88} three isomers were measured in CS_2 solution at room temperature. The spectrum of C_{88}-1 was found to consist of 42 equal intensity lines followed by four weak lines with a half intensity. The numbers of full lines and half lines of C_{88}-1 strongly indicates the presence of C_s symmetry for the cage structure. On the other hand, the NMR spectra of both C_{88}-2 and C_{88}-3 were found to consist of 44 lines with an equal intensity. These results unambiguiously suggest that the structures of C_{88}-2 and C_{88}-3 are associated with a cage structure of C_2 symmetry. The chemical shifts of these three isomers are summarized in Table 1.

According to very recent calculations on possible all 35 IPR isomers of C_{88} by slanina et al.[10], only three isomers, C_2 (7), C_s(17) and C_2(33) were found to be energetically stable in comparison with other remaining 32 isomers. Very interestingly, both numbers of isomers and molecular symmetries predicted by the theoretical calculations are well consistent with the present ^{13}C NMR observations. Therefore, as the most plausible candidates for stable three isomers of C_{88}, we here propose the structures of C_s(17) for C_{88}-1 and C_2(7) or C_2(33) for C_{88}-2 and C_{88} -3 isomers.

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