3216 *J. Am. Chem. Soc.* **2000,** *122,* 3216−3217

Communications to the Editor

A New Method for Separating the Isomeric C_{84} Fullerenes

Guan-Wu Wang, Martin Saunders,* Anthony Khong, and
R. James Cross

Department of Chemistry
Yale University, Box 208107
New Haven, Connecticut 06520-8107

Received December 6, 1999

In recent years, numerous studies of chemical reactions of the fullerenes C_{60} and C_{70} have been reported. However, reactions reported on the higher fullerenes from C_{76} through C_{84} have been few in number. A reason for the scarcity of results on the chemistry of these compounds is that they are only available as isomeric mixtures. Separation of these isomers has been extremely difficult. Shinohara and co-workers have applied HPLC with extensive recycling to separate the C_{84} isomers[1,2] and have very recently reported success in separating five minor isomers.[3] Recently, Diederich and co-workers have described procedures for separating C_{84} isomers.[4] They performed the Bingel reaction to form cyclopropane ester adducts of the C_{84} isomer mixture. The Bingel mono- and bis-adducts were separated by chromatography, and the added groups were subsequently removed using a "retro-Bingel" procedure. While this process has been successful in separating few isomers, it has the disadvantage of requiring that one perform a chemical reaction on the fullerene mixtures. After the chromatographic separation, a controlled-potential electrolytic reduction is necessary to remove the added groups and to recover the fullerenes.

In this paper, we present a new method for tackling this difficult separation problem. Hirsch et al. have shown[5] that Diels−Alder reaction of C_{60} with 9,10-dimethylanthracene (DMA) is reversible at room temperature. The rate of reversion to the starting materials is slow enough that chromatographic separation of the adducts can be achieved before the DMA comes off. The $C_{60}(DMA)_n$ mixture can be completely converted back to C_{60} by the addition of excess dimethyl acetylenedicarboxylate (ADCM).[5] We have now applied this readily reversible reaction to the separation of the C_{84} isomers. It was very convenient to monitor the progress of the separation using helium-3 NMR spectroscopy.

A mixture of higher fullerenes containing roughly 60% of C_{84} isomers, 40% of C_{76} and C_{78} isomers, with small amounts of other fullerenes such as C_{70}, C_{82}, and C_{86}[6] was labeled with ^{3}He using high temperature and high pressure. The ^{3}He NMR spectrum is shown in Figure 1.

Scheme 1

$$C_{84} + n\,DMA \rightleftharpoons C_{84}(DMA)_n \xrightarrow{ADCM} C_{84}$$

Table 1. Chemical Shifts and Their Difference and Ratios of $^3He_2@C_n$ and $^3He@C_n$

	δ_{He}, δ_{He2} (ppm)	$\delta_{He2} - \delta_{He}$ (Hz)	$^3He_2@C_n/^3He@C_n$ (%)
C_{84} isomer **1**	−7.502, −7.539	−14.5	19.2
C_{84} isomer **2**	−8.404, −8.369	13.3	19.9
C_{84} isomer **4**	−9.605, −9.647	−15.6	23.2
C_{78}-$C_{2v'}$	−11.914, −11.821	35.0	10.0
C_{78}-C_{2v}	−16.888, −16.766	46.5	10.3
C_{76}-D_2	−18.703, −18.565	53.3	8.1

About one equivalent of DMA was added to the labeled crude fullerene mixture, and the reaction was allowed to proceed overnight. The reaction mixture was separated on a silica gel column. Four fairly distinct bands were seen and collected. The first fraction was eluted using hexane. Fractions 2 and 3 were then collected using 1:1 hexane/toluene as the eluent, and the fourth fraction was eluted with toluene.[7] These four fractions were treated with excess ADCM for 4 days. The ADCM reacts with DMA dissociated from the adducts. The fullerenes are thus regenerated (Scheme 1).

The ^{3}He NMR spectra of these fractions showed that the ratios of the C_{84} isomers in each fraction were changed dramatically by this procedure. It was also evident that C_{76} and C_{78} isomers reacted to give adducts which appeared not to dissociate during this procedure.[8] We therefore ran each of the four fractions through a Cosmosil *PYE* HPLC column and accumulated those peaks corresponding to C_{84} isomers.[9] The ^{3}He NMR spectra of these mixtures were retaken. Figure 2a and 2b show the ^{3}He spectra of fractions 1 and 3, respectively. ^{3}He NMR spectra of fractions 2−4 are similar. We can clearly see that the main isomer (D_2) at −8.96 ppm is strongly enriched in fraction 1 compared with that in the original fullerene mixture and other fractions. The peaks at −10.01, −11.11, −13.05,[10] −14.15 ppm are completely missing, implying that these isomers bind to DMA much more tightly and that the main isomer at −8.96 ppm is the most loosely bound one. It is likely that we can eventually separate this isomer in pure form simply by repeating the reaction of fraction 1 with DMA followed by column chromatography.

Figure 2c shows the ^{3}He NMR of fraction 3 after it was treated with DMA overnight. It is obvious from Figure 2b and Figure 2c that isomers **5**−**6** have much larger equilibrium constants, and the equilibrium constants for the other isomers are isomer **1** > isomer **4** > isomer **2** > isomer **3**. It seems that all of the DMA

---

[1] Dennis, T. J. S.; Kai, T.; Asato, K.; Tomiyama, T.; Shinohara, H. *Chem. Commun.* **1998**, 619−720.

[2] Tagmatarchis, N.; Avent, A. G.; Prassides, K.; Dennis, T. J. S.; Shinohara, H. *Chem. Commun*. **1999**, 1023−1024.

[3] Dennis, T. J. S.; Kai, T.; Asato, K.; Tomiyama, T.; Shinohara, H.; Yoshida, T.; Kobayashi, Y.; Ishiwatari, H.; Miyake, Y.; Kikuchi, K.; Achiba, Y. *J. Phys. Chem. A* **1999**, *103*, 8747−8752.

[4] Crassous, J.; Rivera, J.; Fender, N. S.; Shu, L.; Echegoyen, L.; Thilgen, C.; Herrmann, A.; Diederich, F. *Angew. Chem., Int. Ed. Engl*. **1999**, *38*, 1613−1617.

[5] Lamparth, I.; Maiche-Mössmer, C.; Hirsch, A. *Angew. Chem., Int. Ed. Engl*. **1995**, *34*, 1607−1609.

[6] The sample was purchased from MER Corporation.

[7] The first fraction was green and contained unreacted C_{84} isomers, along with unreacted DMA. Fractions 2−4 were brown and were DMA products of fullerenes.

[8] ^{3}He NMR showed that the peaks for $^3He@C_{76}$ and $^3He@C_{78}$ disappeared in each fraction and that numerous new peaks appeared due to their DMA adducts between −11 ppm and −21 ppm.

[9] The retention time of C_{84} isomers is 30.2 min on the 5μ *PYE* column (10 × 250 mm) with toluene as the eluent; rate, 2 mL/min. The fraction at 36.6 min, which was almost absent in fraction 1, was collected and combined with material from fractions 2−4. Two ^{3}He NMR peaks at −10.59 and −14.16 ppm were seen. A mass spectrum taken by Professor Chava Lifshitz at Hebrew University indicates that they are isomers of C_{86} and C_{84}, respectively.

[10] Fractions 1−4 (at 30.2 min) were combined and separated by HPLC again. The HPLC peak was cut into three fractions. The peak at −13.05 ppm was present only in the first fraction; therefore, it is most likely a C_{82} isomer, consistent with Shinohara and co-workers' work in ref 3.

10.1021/ja994270x CCC: $19.00

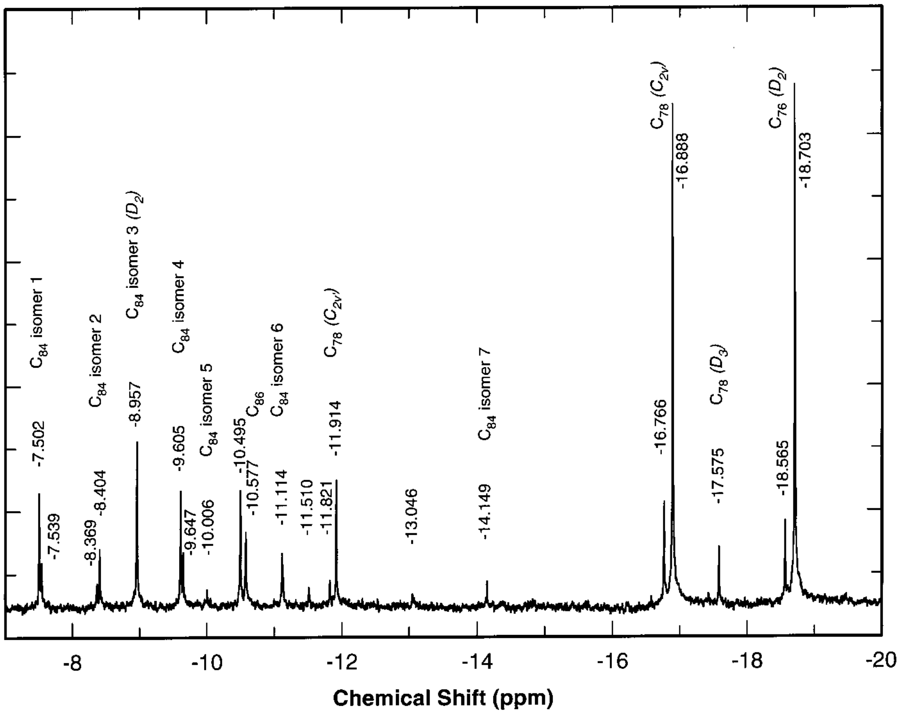

Figure 1. ^{3}He NMR of crude fullerene mixture

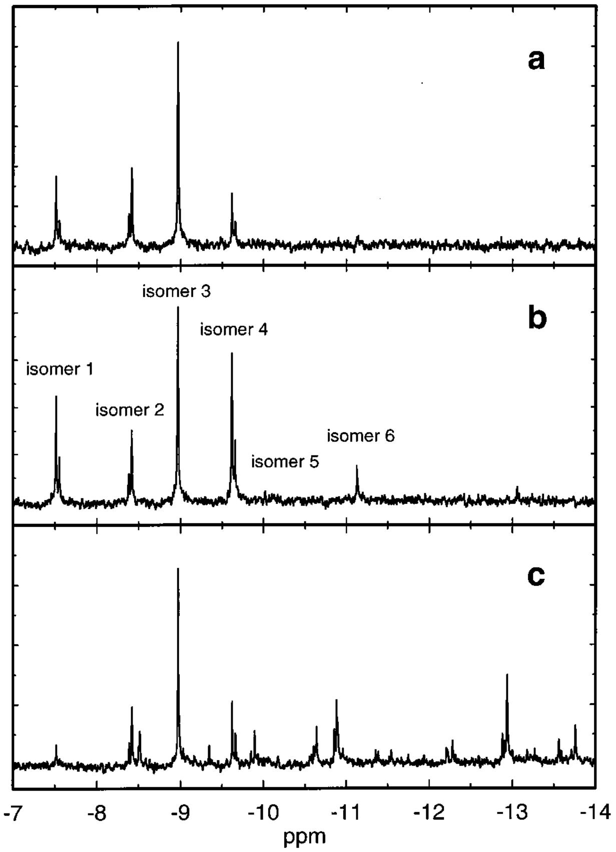

Figure 2. (a) ^{3}He NMR of fraction 1; (b) ^{3}He NMR of fraction 3; (c) ^{3}He NMR of fraction 3 after addition of DMA

adducts of $^3He@C_{84}$ are shifted upfield relative to those of $^3He@C_{84}$, similarly to those of $^3He@C_{60}$. In contrast, adducts of $^3He@C_{70}$ are shifted downfield. After one pass through the HPLC column, all fractions are completely free of C_{76} and C_{78}. This method can therefore easily remove these other fullerenes from C_{84} isomers since the retention times of DMA adducts of other fullerenes are considerably shorter than that of C_{84}.

A striking feature of our ^{3}He NMR spectra is that most of the large peaks of $^3He@C_{84}$ isomers have smaller peaks close to them. We were initially puzzled by these peaks.[11] However, in a strongly ^{3}He-labeled sample of C_{70}, we saw a small peak (about 5% of the intensity of the main peak) separated by just 7 Hz from $^3He@C_{70}$. We attributed this peak to $^3He_2@C_{70}$. This supposition was confirmed by mass spectrometry and by study of a Bingel monoadduct which had a much larger chemical shift difference between the peaks.[12] These observations parallel those in our present study. We have found that the ratio of intensities of the main and satellite peaks for each isomer remains unchanged on going from the initial crude mixture to all of the separated fractions. We therefore conclude that these smaller peaks are due to $^3He_2@C_{84}$ species. Table 1 lists the chemical shifts and their differences and the ratios of $^3He_2@C_{84}$ peak intensity versus those of the corresponding $^3He@C_{84}$ isomers, as well as those for C_{78} and C_{76}. Note that isomer **1** and isomer **4** of $^3He@C_{84}$ have upfield satellites, unlike those of fullerenes C_{70}, C_{76}, and C_{78}, and isomer **2** of C_{84}. The other isomers of C_{84} did not show satellite peaks. We assume that the $^3He_2@C_{84}$ that is present in these isomers has about the same chemical shift as the $^3He@C_{84}$. Interestingly, for all C_{84} isomers, the ratio of $^3He_2@C_{84}/^3He@C_{84}$ is about 20%, while for C_{76} and C_{78} isomers, these ratios are 8 and 10%, respectively. Because of the larger volume inside, it would be expected that there would be more $^3He_2@C_n$ in the larger fullerenes.

On the basis of our current interpretation of the ^{3}He NMR data, we conclude that it should be possible to conveniently separate the isomers of C_{84} in this way. Allowing for the peaks now assigned to be dihelium species, we feel that we have observed seven different isomers of C_{84}.

JA994270X

---

[11] Saunders, M.; Jiménez-Vázquez, H. A.; Cross, R. J.; Billups, W. E.; Gesenberg, C.; Gonzalez, A.; Luo, W.; Haddon, R. C.; Diederich, F.; Herrmann, A. *J. Am. Chem. Soc.* **1995**, *117*, 9305−9308.

[12] Khong, A.; Jiménez-Vázquez, H. A.; Saunders: M.; Cross, R. J.; Laskin, J.; Peres, T.; Lifshitz, C.; Strongin, R.; Smith, A. B., III. *J. Am. Chem. Soc.* **1998**, *120*, 6380−6383.