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Discovery of $C_{60}O_3$ Isomer Having C_{3v} Symmetry

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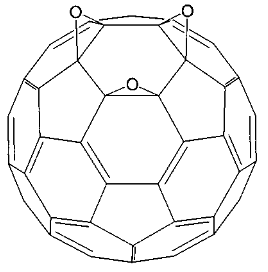
Abstract: A hitherto undetected type of $C_{60}O_3$ isomer was found in the reaction solution of C_{60} with *m*-chloroperoxybenzoic acid by means of a chromatographic technique using two different columns. Both electronic spectroscopy and atmospheric pressure chemical ionization (APCI) mass-spectroscopy examinations show its C_{3v} symmetry, in which three oxygen atoms are added onto one benzenoid ring of C_{60}.



$C_{60}O_3$ isomer with C_{3v} symmetry

Since the early stages of fullerene chemistry, epoxidated fullerenes, $C_{60}O_n$, have been of interest from the viewpoint of cluster science.[1] At the same time, studies of $C_{60}O_n$ have also been carried out in regard to its applications in medicine and photoelectronic devices.[2,3] In particular, the regioselectivity of $C_{60}O_n$ has attracted attention for the preparation of large carbon clusters. Beck et al.[4] and Deng et al.[5] used C_{60} oxides to produce fullerene polymers and showed that the addition of oxygen atoms to fullerene could make the fullerene cage reactive.

While the generation of $C_{60}O_n$ has been studied intensively,[1a,c,d,6] the precise structures and the properties of their isomers have scarcely been investigated. The mono-epoxide and one isomer of the di-epoxide have been isolated and their structures characterized.[1a,c] Beck et al. described $C_{60}O_3$ isomers using high-performance liquid chromatography (HPLC) and laser desorption ionization mass spectrometry (LDI-MS) analyses.[7] Fusco et al. characterized partially isolated $C_{60}O_3$ using electronic spectra, FTIR, and ^{13}C NMR spectra and suggested the presence of isomers with C_s and C_2 symmetries.[8] However, further investigation has been reported concerning neither their exact structures nor their properties.

Parallel to the experimental studies, the structures of epoxidated fullerenes were first studied theoretically on the basis of the thermodynamic stability of the ground-state molecules[9] and on the dynamic behavior of the molecules via following transition states.[10] Those results regarding the structures of $C_{60}O$ and $C_{60}O_2$ explained the experimental observation well. Recently, Manoharan has shown computationally that the multiple epoxidation of fullerene preferably proceeds at the adjacent double bonds of the existing epoxide group rather than at the farther ones.[11] He predicted that the multiple oxidation should occur on one benzenoid ring of C_{60} to form the $C_{60}O_3$ isomer with C_{3v} symmetry, though it had never been detected. Similarly, Feng et al. studied three isomers of $C_{60}O_3$ using the semiempirical quantum mechanical INDO method and predicted that the $C_{60}O_3$ isomer with C_{3v} symmetry as well as the other isomers with C_2 and C_s symmetries should be very stable.[12] They attributed the difficulty in obtaining the C_{3v} isomer to the steric hindrance in the reaction where the third oxygen atom approached the third 6−6 bond on the hexagon with two epoxy rings. On the contrary, using a modified extend Hückel method, Curry et al. have predicted that three isomers (C_{3v}, C_2, and C_s) of $C_{60}O_3$ should exist in equilibrium at room temperature.[13]

The $C_{60}O_3$ isomer with C_{3v} symmetry, a pomegranate-shaped fullerene, is of special interest because it will be the first fullerene derivative with C_{3v} symmetry with such a unique character as large intramolecular charge sepa-

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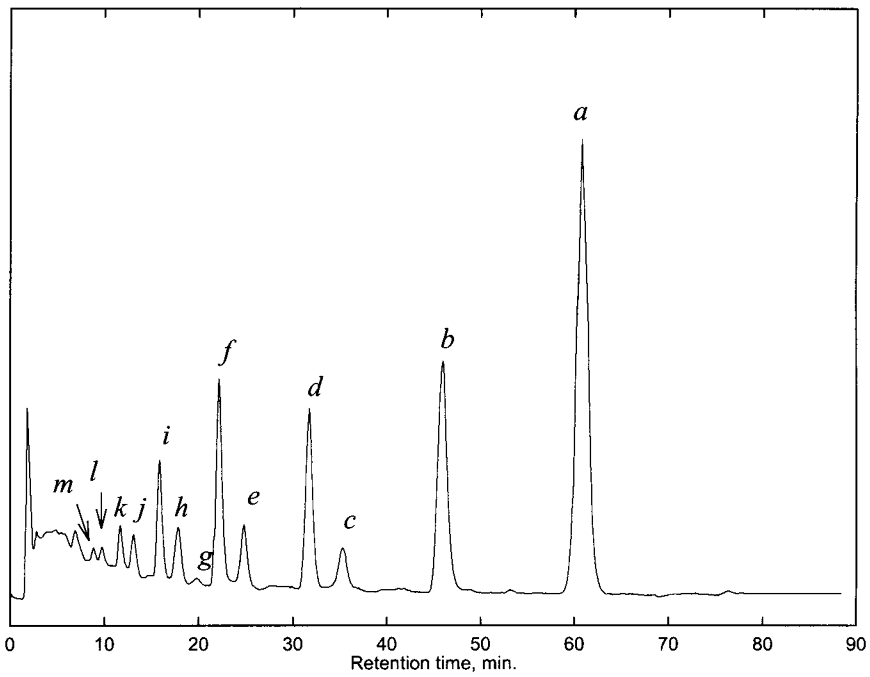

Figure 1. High-performance liquid chromatogram (Develosil C30 RPFULLERENE column, toluene/acetonitrile = 30:70, 335 nm detection) for the *m*-CPBA oxidation products of C_{60}. The mass numbers for peaks *a* to *m* were measured using LC-APCI-MS.

ration.[7] In this paper, we isolated three $C_{60}O_3$ isomers from the standard epoxidation, i.e., *m*-CPBA epoxidation under toluene reflux conditions, mixtures of C_{60}, and investigated their structures by means of HPLC using two different columns: electronic spectrum measurement and atmospheric pressure chemical ionization (APCI) mass-spectroscopy.

Figure 1 shows a chromatogram for the crude *m*-CPBA oxidation products of C_{60} in the reversed-phase HPLC analysis using a Develosil C30 RPFULLERENE column. Thirteen clearly separated peaks from *a* to *m* are present between 9 and 65 min. The mass numbers corresponding to each peak were determined by LC-APCI-MS. Unreacted C_{60} and the known $C_{60}O$ gave rise to peaks *a* and *b* in Figure 1. Peaks *c* and *d* are for isomers of $C_{60}O_2$, and peaks *e* and *f* are for $C_{60}O_3$, which correspond to peaks 5 and 6 in ref 8. The other peaks at shorter elution times are for higher oxides, i.e., $C_{60}O_4$ (*g*−*i*) and $C_{60}O_5$ (*j*, *k*). We could not assign the mass number of peaks *l* and *m*, but these peaks are likely to correspond to $C_{60}O_6$ and higher oxides, respectively. We have previously reported that we could observe up to $C_{60}O_{12}$ by LDI-MS analysis.[6e]

First, we separated the peak *f* carefully using HPLC with an RPFULLERENE column and examined the purity of the peak. Surprisingly, the peak-purity technique using an electronic spectrum[14] revealed that peak *f* was not pure but consisted of plural components. We further found that the HPLC with a Cosmosil Bucky Prep column could separate the peak *f* into two components. Figure 2 shows the chromatograms of the isolated fraction for peak *f* (in Figure 1) in the HPLC separation using the Develosil C30 RPFULLERENE column (a) and with the Cosmosil Bucky Prep column (b). Both peaks I and II in Figure 2b gave APCI mass signals at *m*/*z* 768 (M^-) and were shown to be pure by the above peak-purity technique. Under our experimental conditions, peaks I and II in Figure 2b and *e* in Figure 1 were present at a ratio of approximately 1:1:1. The molar yields of I, II, and *e* were 1.06, 1.20, and 1.25%, respectively, on the basis of the consumption of C_{60}. After the fraction were dried, three compounds of peaks I, II, and *e* were isolated as a brownish powder with low solubility in toluene and exposed to air for at least one week without light. No ^{13}C NMR data are available due to the poor solubility of all

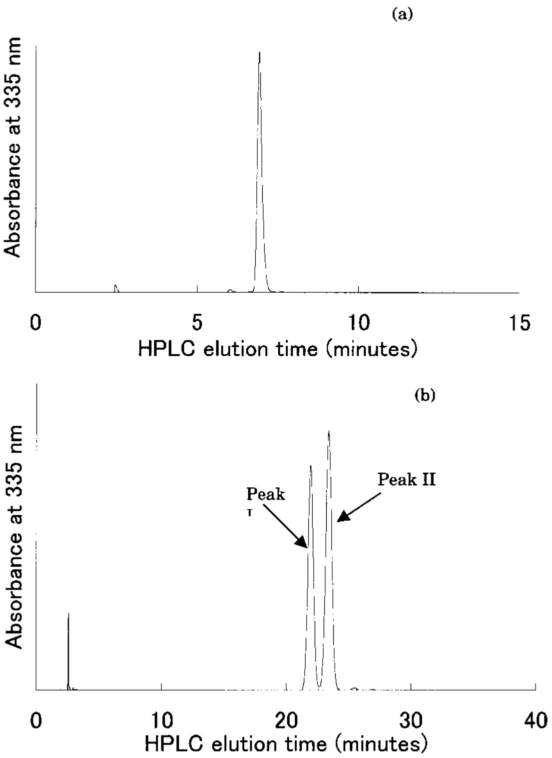

Figure 2. Chromatograms of isolated peak *f* (in Figure 1) in HPLC separation using a Develosil C30 RPFULLERENE column (toluene/methanol = 60:40) (a) and Cosmosil Bucky Prep column (toluene/methanol = 80:20) (b).

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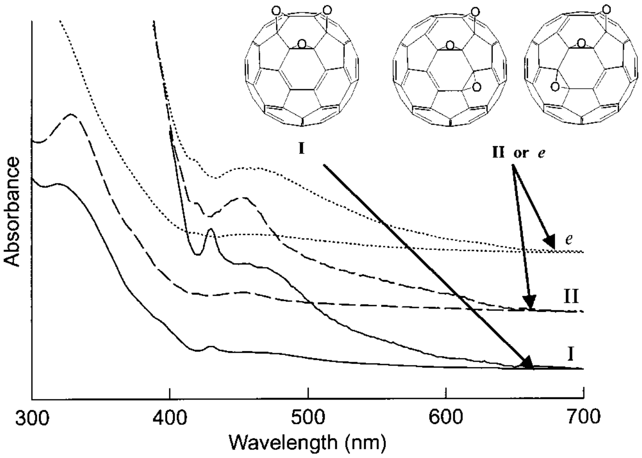

Figure 3. The UV−visible absorption spectra of $C_{60}O_3$ isomers corresponding to peaks I (solid line), II (broken line), and *e* (dotted line).

the compounds examined. The visible absorption spectra of peaks I and II in toluene were significantly different in shape as shown in Figure 3. The spectrum of peak II presented broad bands at 420 and 460 nm. Since the electronic spectra for the peaks II and *e* are broad and similar, no assignment was attempted. These peaks may be for the $C_{60}O_3$ isomers with C_s and C_2 symmetries as suggested by Feng et al.[12] Peak I at shorter elution times is shown Figure 2b and has a sharp absorption band at 435 nm and a broad band at 470 nm. Most importantly, the C_{3v} isomer, where three oxygen atoms are added onto one benzenoid ring of C_{60}, is predicted to have a sharp peak at 435 nm and a broad band between 467 and 489 nm. According to the report by Feng et al.,[12] the sharp peak in the absorption of the C_{3v} isomer observed at 435 nm is assigned to eight types of electronic transition from the occupied molecular orbitals (MOs) to the unoccupied MOs. On the other hand, any absorption bands for the C_2 and C_s isomers are assigned to three or four types of electronic transitions. Therefore, the C_{3v} isomer is expected to show a sharp peak at 435 nm, which is not observed in other isomers. The features of peak I in our experimental spectrum agreed well with such calculated values. Consequently, the compound isolated as peak I is the $C_{60}O_3$ isomer with C_{3v} symmetry.

In conclusion, we succeeded in the complete isolation of three $C_{60}O_3$ isomers from a C_{60} oxide mixture formed by the oxidization of C_{60} with *m*-CPBA by means of HPLC separation using two different columns. Contrary to the previous report by Fusco et al.,[8] the yields of the three $C_{60}O_3$ isomers were similar. An electronic spectrum of one $C_{60}O_3$ isomer shows its structure having C_{3v} symmetry. This is the first evidence for any fullerene derivative with C_{3v} symmetry. We are currently preparing ^{13}C NMR measurements of isolated $C_{60}O_3$ isomers starting from C_{60} enriched in ^{13}C to 15%. Studies regarding the photochemical and electrochemical properties of $C_{60}O_3$ isomers are now in progress.

Experimental Section

Fullerene C_{60} (purity > 99.98%, Matsubo) and *m*-chloroperoxybenzoic acid (*m*-CPBA, Tokyo Kasei) employed in this study were purchased and used without further treatment. Toluene solution (100 mL) containing 1×10^{-3} mol/dm^3 of C_{60} and 1×10^{-1} mol/dm^3 of *m*-CPBA was heated under reflux for 30 min without light. The crude reaction solution was washed twice with 50 mL of methanol to remove *m*-CPBA and was then separated by flash column chromatography on silica gel (FC40, Wako). The products were isolated using a HPLC apparatus equipped with a reversed-phase Develosil C30 RPFULLERENE 250 × 20 mm column (Nomura Chemical) or a Cosmosil Bucky Prep 250 × 10 mm column (nacalai tesque). The detection wavelength was set at 335 nm, and a mixture of methanol/toluene (35:65 v/v) was used as an eluent for both columns with flow rates ranging from 4 to 10 mL/min.

The mass number was determined using HPLC coupled with atmospheric pressure chemical ionization mass spectrometry (LC-APCI-MS, Agilent). In LC-APCI-MS analysis, the sample solution was eluted using methanol and toluene at flow rates of 1 mL/min. The negative ions of the substances were observed under a scan mode ranging between 600 and 1500 amu.

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