The Mechanochemical Synthesis and Properties of the Fullerene Trimer C_{180}

Koichi Komatsu,* Koichi Fujiwara, and Yasujiro Murata
Institute for Chemical Research, Kyoto University, Uji, Kyoto 611-0011

(Received April 25, 2000; CL-000395)

A solid-state reaction of C_{60} with 4-aminopyridine as a catalyst under high-speed vibration milling conditions afforded fullerene trimer C_{180}, which was characterized by IR and UV–vis spectroscopies as well as the APCI mass spectroscopy of the cyanated derivative.

The all-carbon fullerene oligomers and polymers have attracted considerable interest of physicists and physical chemists. These materials have been prepared under photochemical[1] or high-pressure/high-temperature conditions,[2] or by the action of alkali metals.[3] However, the insolubility of these materials in any solvent has precluded their characterization particularly from the viewpoint of organic chemistry. On the other hand, we previously reported that the mechanochemical reaction of fullerene C_{60} with potassium salts such as KCN, KOAc, and K_2CO_3, with metals with high reducing power, or with solid aromatic amines, under the "high-speed vibration milling (HSVM)" conditions can successfully afford the fullerene dimer C_{120}.[4] Upon careful examination of the reaction, now we found that not only the dimer but the trimer of C_{60} could be synthesized for the first time under the similar reaction conditions.

When C_{60} (50 mg) was treated with 4-aminopyridine (7 mg) under HSVM conditions for 30 min, the analysis with HPLC using a Cosmosil "Buckyprep" column eluted with toluene showed a very small and broad peak at a retention time of about 29 min in addition to a peak for C_{60} at 7.4 min and a peak for the dimer C_{120} at 14.7 min. From the retention time, this small peak was assumed to be the trimer C_{180}.[5] By the use of a Cosmosil "5PBB" column of a preparative size, with an adsorption behavior different from "Buckyprep," eluted with *o*-dichlorobenzene (ODCB), this small peak was separated into two peaks, fraction A (retention time, 20.5 min) and fraction B (23.5 min). When reexamined with a "Buckyprep" column, fraction A was shown to be a mixture of at least three components with the retention time of 25.9, 28.5, and 31.3 min while fraction B gave a single peak at 27.6 min with C_{60} as a reference appearing at 7.4 min (Figure 1). Upon evaporation of the solvent, combined components in fractions A and B amounted to 4% yield as C_{180}.

This inferred C_{180} was a dark brown solid very hardly soluble in ODCB, and upon atmospheric pressure chemical ionization (APCI) mass spectrometry both fractions A and B gave only a fragmented peak of C_{60}. Upon APCI mass spectroscopy, the fullerene dimer C_{120} also exhibits only the fragmentation peak of C_{60}. However, after it was allowed to react with sodium cyanide in an ODCB–DMF solution and quenched with trifluoroacetic acid, the product clearly exhibited the molecular ion peak for the cyanated C_{120}, i.e., $C_{120}(CN)^-$. In the same way, when fraction B of inferred C_{180} was treated with sodium cyanide in solution and examined by APCI mass spectroscopy (negative-ion mode), the molecular ion peak for the cyanated C_{180}, i.e., $C_{180}(CN)^-$, was clearly observed. Thus, the actual formation of the trimer C_{180} was confirmed.

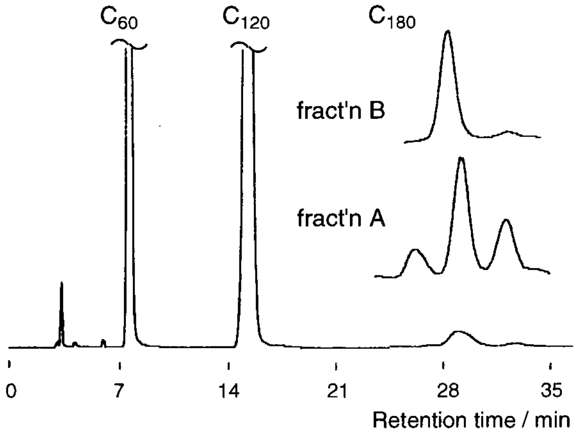

Figure 1. HPLC chart of a mixture of C_{60}, C_{120}, and C_{180}: column, Buckyprep; eluent, toluene; flow rate, 1 ml min^{-1}: inset are the chromatograms of fractions A and B.

The UV–visible spectra of fractions A and B are quite similar and that of fraction B is shown in Figure 2. Both of them exhibit absorptions typical for 1,2-disubstituted 1,2-dihydro[60]fullerenes, i.e., the UV absorption at 330 nm, a slight shoulder at around 433 nm, and a long-wavelength absorption tailing to 703 nm. The IR spectrum of C_{180} fraction B (Figure 3) was found to be quite similar to the spectrum of C_{120}.[4]

Upon irradiation of room light, HPLC analysis indicated that the ODCB solutions of both fractions A and B of the trimer C_{180} very slowly undergo a decrease in its concentration with concomitant increase of C_{60} and C_{120}. Thus, the trimer C_{180} undergoes slow dissociation into C_{60} and C_{120} with a half-life of about 3 days under irradiation of room light (ca. 100 luxes).

The saturated concentration of either fraction A or B is too low (5×10^{-5} M or 0.1 mg mL^{-1} in ODCB) to allow the ^{13}C NMR measurement, and we can deduce the structure only based on theoretical calculations. The structures for the stable

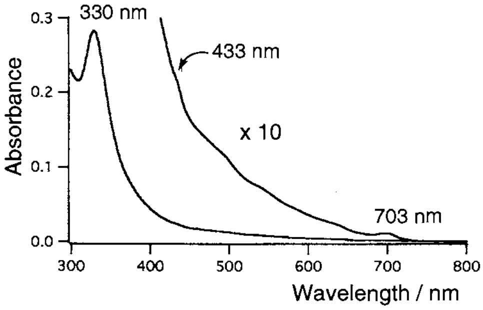

Figure 2. UV-vis spectrum of C_{180} (fraction B) in ODCB.

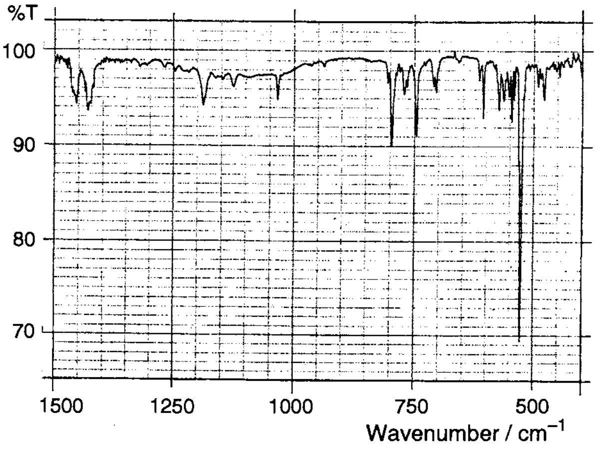

Figure 3. IR spectrum (KBr) of C_{180} (fraction B).

isomers of C_{180} calculated by PM3 are shown in Figure 4 together with their heat of formations. Among the isomers with the extended structure, the "e" isomer was found to be the most stable and the stability decreases in the order, "trans-4" (+0.28 kcal mol^{-1} in $\Delta\Delta H_f$ relative to the "e" isomer), "trans-3" (+0.44 kcal mol^{-1}), and “trans-1” (+0.51 kcal mol^{-1}). On the other hand, among the isomers with the cyclic structure, only the "cis-2 / cis-2 / cis-2" isomer was found to be significantly more stable (–29.4 kcal mol^{-1} in $\Delta\Delta H_f$ relative to the "e" isomer) while all others were less stable than the extended "e" isomer as a reference. Based on the appearance of the HPLC chart shown above, we suppose that fraction B, which exhibits only a single HPLC peak both on a “Buckyprep” column and on a "5PBB" column, could be assigned to an isomer with a totally different structural characteristic such as the one with a cyclic structure (“cis-2 / cis-2 / cis-2”) while fraction A with at least three components would be a mixture of isomers with extended structures (e.g., “e”, “trans-4”, and “trans-3”).

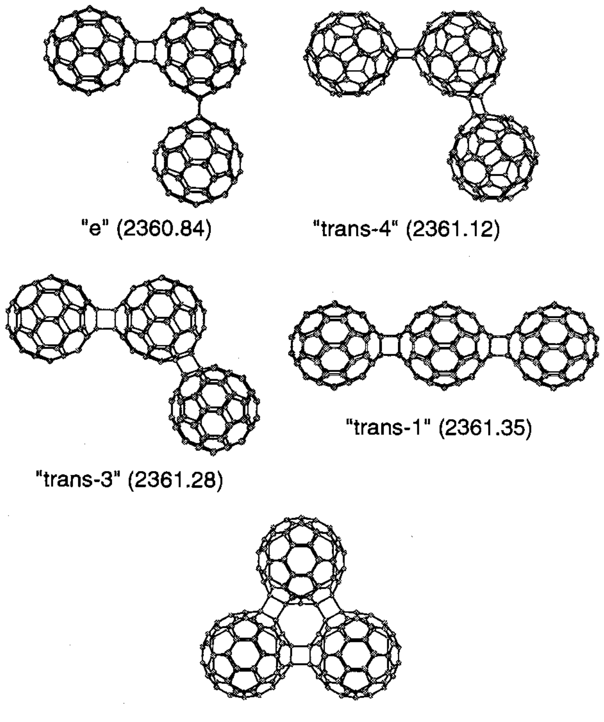

Figure 4. Structures of the stable isomers of C_{180} calculated by PM3: in the parentheses are given the values of heat of formation in kcal mol^{-1}.

The present work was supported by Japan Society for the Promotion of Science (RFTF97R11601). K. F. thanks JSPS Research Fellowship for Young Scientists.

References and Notes

1 a) A. M. Rao, P. Zhou, K-A. Wang, G. T. Hager, J. M. Holden, Y. Wang, W-T. Lee, X-X. Bi, P. C. Eklund, D. S. Cornett, M. A. Duncan, and I. J. Amster, *Science*, **259**, 955 (1993). b) Y. Wang, J. M. Holden, X-X. Bi, and P. C. Eklund, *Chem. Phys. Lett*., **217**, 413 (1994). c) Y-P. Sun, B. Ma, C. E. Bunker, and B. Liu, *J. Am. Chem. Soc*., **117**, 12705 (1995). d) B. Burger, J. Winter, and H. Kuzmany, *Z. Phys. B*, **101**, 227 (1996).

2 a) H. Yamawaki, M. Yoshida, Y. Kakudate, S. Usuba, H. Yokoi, S. Fujiwara, K. Aoki, R. Ruoff, R. Malhotra, and D. Lorents, *J. Phys. Chem*., **97**, 11161 (1993). b) Y. Iwasa, T. Arima, R. M. Fleming, T. Siegrist, O. Zhou, R. C. Haddon, L. J. Rothberg, K. B. Lyons, H. L. Carter, Jr., A. F. Hebard, R. Tycko, G. Dabbagh, J. J. Krajewski, G. A. Thomas, and T. Yagi, *Science*, **264**, 1570 (1994). c) M Núñez-Regueiro, L. Marques, J-L. Hodeau, O. Béthoux, and M. Perroux, *Phys. Rev. Lett*., **74**, 278 (1995). d) C. Goze, F. Rachdi, L. Hajji, M. Núñez-Regueiro, L. Marques, J-L. Hodeau, and M. Mehring, *Phys. Rev. B*, **54**, R3676 (1996). e) P-A. Persson, U. Edlund, P. Jacobsson, D. Johnels, A. Soldatov, and B. Sundqvist, *Chem. Phys. Lett*., **258**, 540 (1996).

3 a) S. Pekker, A. Jánossy, L. Mihaly, O. Chauvet, M. Carrard, and L. Forró, *Science*, **265**, 1077 (1994). b) P. W. Stephens, G. Bortel, G. Faigel, M. Tegze, A. Jánossy, S. Pekker, G. Oszlanyi, and L. Forró, *Nature*, **370**, 636 (1994). c) M. C. Martin, D. Koller, A. Rosenberg, C. Kendziora, and L. Mihaly, *Phys. Rev. B*, **51**, 3210 (1995).

4 a) G-W. Wang, K. Komatsu, Y. Murata, and M. Shiro, *Nature*, **387**, 583 (1997). b) K. Komatsu, G-W. Wang, Y. Murata, T. Tanaka, K. Fujiwara, K. Yamamoto, and M. Saunders, *J. Org. Chem*. **63**, 9358 (1998).

5 At present the precise mechanism of the reaction is not clear. However, it is supposed that the one-electron transfer from 4-aminopyridine to C_{60} is playing an important role: the produced C_{60} radical anion should be highly reactive in the solid state and would react with C_{60} or with C_{120} to give C_{120} or C_{180} respectively.