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Novel Synthesis and Characterization of Five Isomers of $(C_{70})_2$ Fullerene Dimers

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There is considerable interest regarding all-carbon fullerene dimers.[1,2] The unique physical properties[2] of fullerene dimers provide intriguing possibilities as model compounds for nano- and polymer science[3] and offer potential access to novel molecular electronic devices. The simplest such fullerene dimer $(C_{60})_2$, has been prepared by solid-state[4−9] and by chemical[9] methods. Komatsu first reported[5] the generation of the $(C_{60})_2$ dimer via a mechanochemical reaction using a high-speed vibration milling (HSVM) technique.[4,5] The $(C_{60})_2$ dimer has also been synthesized by fast-pressure treatment,[10] by applying pressure to bis(ethylenedithio)-tetrafulvalene-doped-[60]fullerene,[7] as well as by light irradiation of [60]fullerene.[8] In addition, the pressure-induced formation of one $(C_{70})_2$ dimer isomer has recently been reported.[9] To date, however, all methods for the synthesis of $(C_{60})_2$ and $(C_{70})_2$ dimers require high temperatures or pressures as well as relatively sophisticated apparatus.

Our interest in this subject was stimulated by the possibility of generating dimers of endohedral metallofullerenes.[11] Herein, we report the novel synthesis, separation by high performance liquid chromatography (HPLC), and characterization of five isomers of $(C_{70})_2$ (see Figure 1) using a remarkably simple and effective dimerization method which has wide scope and requires no special apparatus.

For the synthesis of dimeric $(C_{70})_2$, [70]fullerene (42 mg, 0.005 mmol) and K_2CO_3 (14 mg, 0.10 mmol) were placed in a small (10 cm diameter) mortar and pestle, and the mixture was ground by hand for 15 min. The crude mixture was subjected to flash column chromatography, eluting with toluene to remove unreacted starting material followed by *o*-dichlorobenzene. This latter fraction was collected, diluted with toluene, and subjected to preparative HPLC using a 5PYE column (Nacalai Cosmosil 25 × 250 mm, toluene as eluent, 15 mL/min flow rate). A broad peak containing a mixture of isomers of $(C_{70})_2$ was observed at a retention time of 25−30 min, and in this manner, $(C_{70})_2$ was isolated in 8% yield.[12] This fraction was collected and subjected to recycling HPLC, under the same conditions described above, to finally separate five different isomers after one cycle on a 5PYE column (relative ratio of production for the five isomers of $(C_{70})_2$ is 0.8/1.0/0.5/0.5/0.2 (Figure 2).

This result is in sharp contrast with the previously reported dimerization reaction of [70]fullerene under high pressure (1 Gpa)/high temperature (200 °C) conditions which gave only one isomer of $(C_{70})_2$ as a single product.[9]

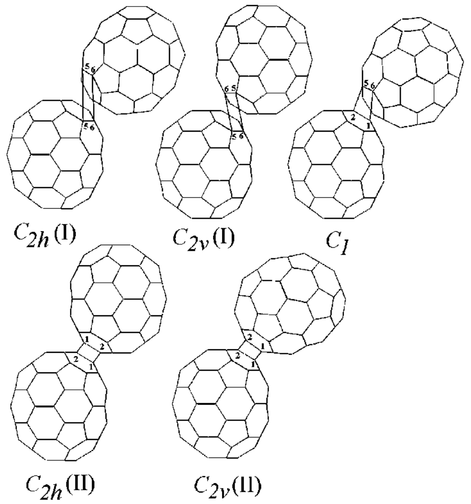

Figure 1. Molecular structures and symmetries of five $(C_{70})_2$ all-carbon dimers derived from a [2 + 2] addition between those C−C bonds that are near the poles and have the highest π-bond orders[18] and greater kinetic reactivity,[20] i.e., 1,2- and 5,6- bonds.

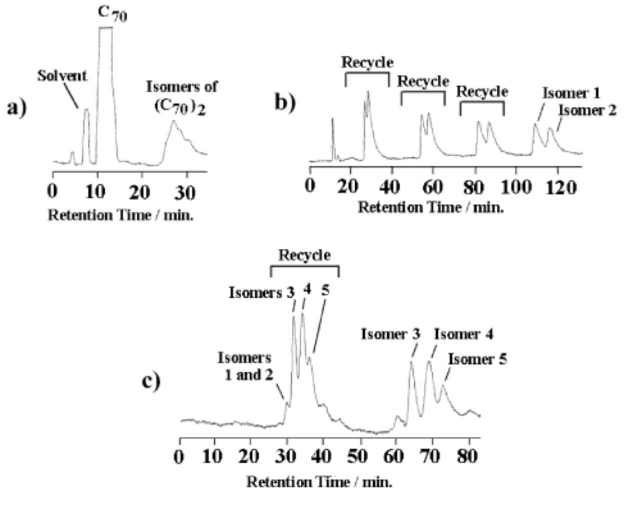

Figure 2. Multi-stage high performance liquid chromatography charts (a) for the separation of the mixture of $(C_{70})_2$ from starting material [70]-fullerene; (b) for the separation and isolation in pure form of the first two isomers of $(C_{70})_2$, after collecting half of the fraction collected in (a) and recycling the first half for three cycles; (c) for the separation and isolation in pure form of the remaining three isomers of $(C_{70})_2$, after recycling the second half of the fraction collected in (a) for one cycle.

Analysis of $(C_{70})_2$ by mass spectrometry using standard procedures (EI, FAB, MALDI-TOF) furnished only [70]fullerene fragment ions.[13] However, after treatment of the purified material with NaCN in an *o*-dichlorobenzene/*N*,*N*-dimethyl formamide mixture,[14] atmospheric pressure chemical ionization mass spectrometry (APCI-MS) afforded a peak at *m*/*z* 1706, which corresponds to the monocyanated adduct $[(C_{70})_2(CN)^-]$. The UV absorptions at 310, 400, and 460 nm for the five isomers of $(C_{70})_2$ suggest electronic structures similar to those of [70]fullerene (Supporting Information Figure 1S). The onsets of the spectra of all five $(C_{70})_2$ dimers were

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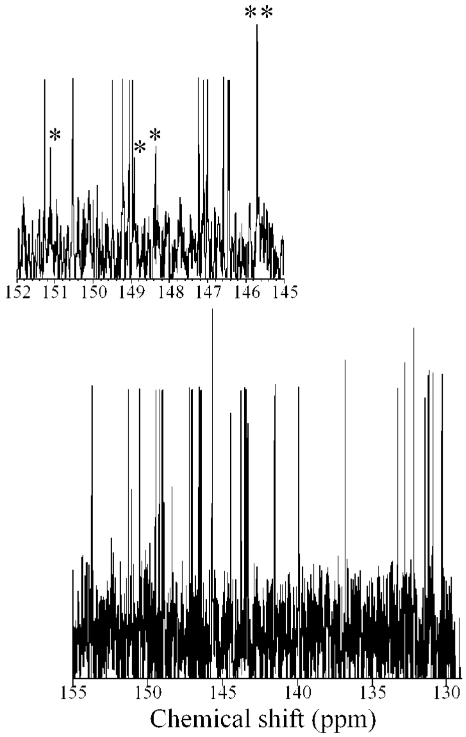

Figure 3. High-resolution ^{13}C NMR spectrum [600 MHz, in carbon disulfide solution, $Cr(acac)_3$ as relaxant and benzene-d_6 for the internal lock, 160 000 scans] of the purified second eluting isomer of $(C_{70})_2$. The inset shows the expanded region 152−145 ppm where * denotes half-intensity lines and ** denotes a half-intensity line coincidentally overlapped with a full one.

shifted to longer wavelengths, suggesting a smaller HOMO−LUMO energy gap compared to that of monomeric [70]fullerene.

The ^{13}C NMR spectrum of the second eluting isomer in carbon disulfide solution contained 32 full intensity and four half intensity lines in the fullerene sp^2 region (see Figure 3).[15] This is consistent with either C_{2h} (I) or C_{2v} (I) molecular symmetry of a [2 + 2] cyclobutane-bridged dimeric structure of $(C_{70})_2$ (Figure 1),[16] as both symmetries coincidentally display the same pattern of lines. In both of these molecular structures there is a plane of symmetry perpendicular to and bisecting the bridge plane of the dimeric structure, which gives 32 pairs of distinguishable sp^2 carbon atoms in each fullerene cage. Thus, from a total of 136 sp^2 atoms in the dimeric structure of $(C_{70})_2$, the remaining 8 sp^2-fullerene carbon atoms (which belong on the symmetry plane) form four distinguishable pairs and consequently give rise to the four half intensity lines, whereas the remaining 4 sp^3 bridging carbon atoms are also chemically equivalent.

The electronic perturbation of the carbons remote from the cyclobutane bridge is not significantly affected in the dimeric material $(C_{70})_2$, and consequently their chemical shifts have values similar to those of the corresponding carbons of the monomeric units of [70]fullerene. In fact, this is the case for the two carbons that belong on the symmetry plane and that are in the opposite site remote from the bridge having chemical shifts 151.11 and 145.69 ppm, respectively.[17] The remaining two sp^2 carbons near the cyclobutane bridge appear at 148.91 and 148.35 ppm.

The D_{5h} symmetrical [70]fullerene molecule has a total of eight nonequivalent C−C bonds, but only two of these (those near the poles which have the highest π-bond orders,[18] that is, cf. Figure 1, bonds 1,2- and 5,6-) are almost exclusively the ones involved in cycloadditions.[19,20] Thus, five [2 + 2] addition isomers can possibly be formed, in agreement with the experimentally observed results.[9] Under the same conditions used for the synthesis of $(C_{70})_2$, [60]fullerene was dimerized to $(C_{60})_2$ in 15% overall yield. Furthermore, when an equimolar mixture of [60]fullerene and [70]fullerene was ground in a mortar and pestle in the presence of K_2CO_3 for 15 min, two cross-dimer isomers of $[(C_{60})(C_{70})]$ were isolated in addition to $(C_{60})_2$ after HPLC purification and separation of the crude reaction mixture.[21,22] The presence of K_2CO_3 appears to be crucial to facilitate the reaction. No reaction was observed in the absence of K_2CO_3, and moreover, other reagents such as 4-aminopyridine[5] were ineffective.

In summary, we have successfully prepared and separated five [2 + 2] structural isomers of $(C_{70})_2$ using a simple dimerization methodology. This new procedure is simple, able to be performed in any laboratory, and offers a practical method for fullerene dimer synthesis. We are currently exploring the scope of these transformations to dimerizing endohedral metallofullerenes and producing novel carbon materials with intriguing electronic properties.

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Supporting Information Available: UV−vis−NIR electronic absorption spectra of the five HPLC-purified isomeric dimers $(C_{70})_2$. This material is available free of charge via the Internet at http://pubs.acs.org.

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(12) 60% unreacted [70]fullerene was recovered after column chromatography and HPLC separation.
(13) Upon exposure to light, the fullerene dimer $(C_{70})_2$ slowly dissociated to [70]fullerene. However, when protected from light, the dimer is stable for at least several months.
(14) Komatsu, K.; Murata, Y.; Fujiwara, K. *Chem. Commun.* **2000**, 1583.
(15) Chemical shifts in δ: 153.75, 151.26, 151.11 (half line), 150.52, 149.49, 149.22, 149.05, 148.97, 148.91 (half line), 148.35 (half line), 147.23, 147.10, 147.00, 146.58, 146.46, 146.45, 146.43, 145.69 (full and half line coincidentally overlapped), 144.45, 143.77, 143.52, 143.44, 143.37, 143.27, 141.50, 136.80, 133.30, 132.77, 132.19, 131.44, 131.25, 131.19, 131.16, 130.91, 130.33. The sp^3 carbons were unable to be resolved, most likely due to their very long T_1 relaxation time.
(16) The isomers with molecular symmetries C_{2v} (II), C_{2h} (II) and C_1 would give 33, 33, and 136 sp^2 fullurene signals of equal intensity, respectively.
(17) The chemical shifts of the corresponding sp^2 carbon atoms in [70]fullerene are 150.33 and 147.03 ppm respectively: Ajie, H.; Alvarez, M.; Anz, S. J.; Beck, R. D.; Diederich, F.; Fostiropoulos, K.; Huffman, D. R.; Kraetschmer, W.; Rubin, Y.; Schriver, K. E.; Sensharma, D.; Whetten, R. L. *J. Phys. Chem.* **1990**, *94*, 8630.
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(22) No $(C_{70})_2$ was observed after HPLC purification and separation of the crude reaction mixture.

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