

Carbon allotropes of dumbbell structure: C₁₂₁ and C₁₂₂

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Received (in Cambridge, UK) 13th November 1998, Accepted 19th November 1998

The synthesis, isolation and preliminary characterization of all-carbon [60]fullerene dimers C₁₂₁ and C₁₂₂ are reported.

We here report data concerning the synthesis and preliminary characterization of all-carbon fullerene derivatives C₁₂₁ **1**, a new dumbbell-like dimer, and C₁₂₂ **2**. The existence of these molecules was first suggested by Osterodt and Vogtle,¹ and Strongin *et al.*² recently succeeded in the synthesis of C₁₂₂. C₁₂₁ and C₁₂₂ were previously detected in the mass spectra of C₆₀CBr₂,³ C₆₀CH₂¹ and C₆₀(CO₂Et)₂.⁴

Recently we succeeded in the synthesis, separation and characterization of **1** and **2**. The synthesis was based on the reaction described in Scheme 1. Typically, 50 mg of C₆₀CBr₂ and 250 mg of C₆₀ were mixed and gently ground. The powder was then heated in an argon atmosphere (flow 50 ml min⁻¹) up to 450 °C at a rate of 5 K min⁻¹ and subsequently cooled to room temperature. The resulting black powder was soluble in CS₂ and *o*-dichlorobenzene, giving a red–brown solution (the same product could be obtained by using C₆₀CHCO₂Et instead of C₆₀CBr₂, and a higher temperature, *i.e.* 550 °C). The product was a mixture of unreacted C₆₀ and other phases, as detected by gel permeation chromatography, GPC (toluene, 340 nm detection, 12 ml min⁻¹). The GPC peak at 1320 ml was collected[‡] and found to contain **1** and **2** as major and minor phases, respectively. The yield in **1** was about 10% and it increased slightly with an increase in the C₆₀/C₆₀CBr₂ ratio. The amount of **2** decreased when increasing the C₆₀/C₆₀CBr₂ ratio; the formation of **2** could be suppressed when using a large excess of C₆₀ (more than ten-fold) but in this case the separation of the dimer product from the mixture was more difficult. The separation between C₆₀, **1** and **2** was made by GPC in recycling mode. In Fig. 1 a GPC experiment for the mixture of **1** and **2** is shown. After 24 h the separation between the two peaks was large enough to allow the collection of pure samples of C₁₂₁ and

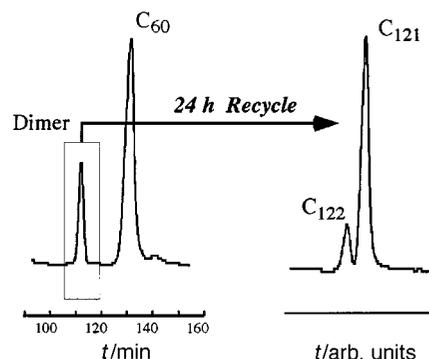


Fig. 1 GPC experiments for the separation of C₁₂₁.

C₁₂₂. The GPC elution volume for **1** was smaller than for C₆₀ or C₆₀CBr₂ and similar to that of **2**, indicating that their molecular volumes are roughly the same but higher than those of C₆₀ or C₆₀CBr₂. The laser desorption and ionization time of flight (LDI TOF) mass spectrum[§] of **1** is presented in Fig. 2. The peak at *m/z* 1452.9, with a characteristic isotopic pattern, was assigned to C₁₂₁ (negative ionization, calculated *m/z* 1453.3). A small C₁₂₂ peak was also observed in the mass spectrum of C₁₂₁. This is probably due to the association of C₆₁ clusters under the mass spectroscopy conditions, since the C₁₂₂ peak increased with the laser power. The LDI TOF mass spectrum of **2** presented an intense peak for C₁₂₂ (*m/z* 1465.4, calc. *m/z* 1465.3) but no C₁₂₁ peak, irrespective of the laser power (Fig. 3).

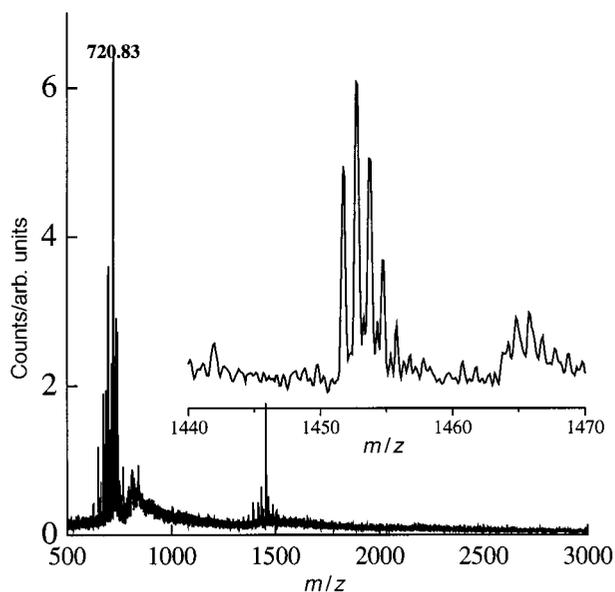
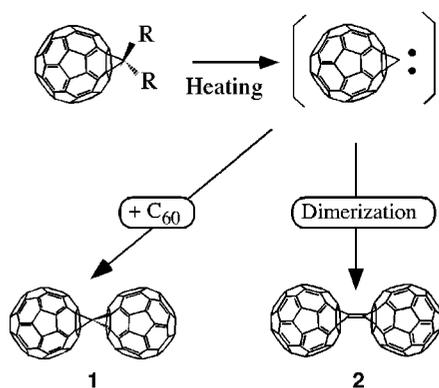


Fig. 2 LDI-TOF MS of C₁₂₁; inset is a detail of the dimer peak, reflector mode, negative ionization.



Scheme 1

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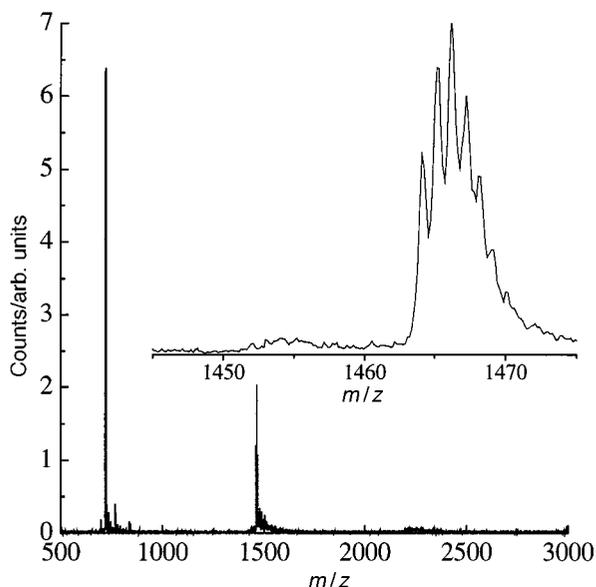


Fig. 3 LDI-TOF MS of C_{122} ; inset is a detail of the dimer peak, linear mode, negative ionization.

The UV-VIS spectra[¶] of **1** and **2** showed peaks at 430 and 700 nm, usually observed for 1,2-dihydrofullerenes. IR spectroscopy^{||} measurements revealed the presence of the C_{60} cage and some additional peaks due to the lower symmetry of **1** and **2** relative to C_{60} . In the spectra of **1**, a peak appearing at 1022.4 cm^{-1} was assigned to a cyclopropane skeletal stretch,⁵ expected at 1017–1025 cm^{-1} .

So far, we have been unable to obtain a ^{13}C NMR spectrum of **2**, either because of its low solubility or the presence of impurities or other isomers in the sample. The ^{13}C NMR spectrum^{**} of **1** was also rather difficult to obtain, due to the low C_{121} solubility and a low relaxation rate for the carbon nuclei. Sixteen low signal-to-noise lines were observed between δ 140–148 (16 lines expected in this region for a C_{2v} symmetry C_{121} molecule), in agreement with the high symmetry of this dimer. Three additional lines were sometimes observed in the cluster at δ 142, possibly related to either the presence of C_{122} or other impurities in the sample. A small upfield resonance at δ 67.7 could be assigned to the four sp^3 fullerene cyclopropane carbons. This value suggests a 6:6 closed connection to the fullerene core,^{††} in agreement with the proposed carbene attack mechanism (for an extensive discussion of ^{13}C NMR in fullerene derivatives, see ref. 6 and the references cited therein). The bridge between the two fullerenes could not be identified beyond doubt; its intensity should be eight times smaller than most of the fullerene cage carbons. We tentatively assign a δ 48.8 resonance to the carbon bridge.

We also performed scanning tunnelling microscopy (STM) measurements on samples of **1** and **2** deposited on graphite. Fig. 4 shows an image of **2**; the size of the dimer is in agreement with that expected. STM images of **1** were similar to that of **2**, also showing dumbbell-like structures.

The LDI TOF mass spectrum of C_{121} showed extensive fragmentation around m/z 1452 and 720 as well as the presence of both odd- and even-numbered carbon clusters. These peaks are likely to be the result of the addition/loss of C_2 units to/from C_{121} in the mass spectrometer. The even-numbered carbon clusters were produced by aggregation of C_{61} and subsequent loss/addition of C_2 units. Whether the detected odd-numbered carbon clusters are stable or only transient species in the mass spectrometer still remains an open question. However, these results suggest that either weakly bound or spirane-like clusters are formed under the mass spectrometry conditions without the coalescence of the fullerene spheres. The elimination of C_2 units in the mass spectra of fullerene derivatives does not seem to require the formation of closed clusters, since it takes place for both even- and odd-numbered carbon clusters. Further studies on the laser-induced decomposition of odd-numbered carbon

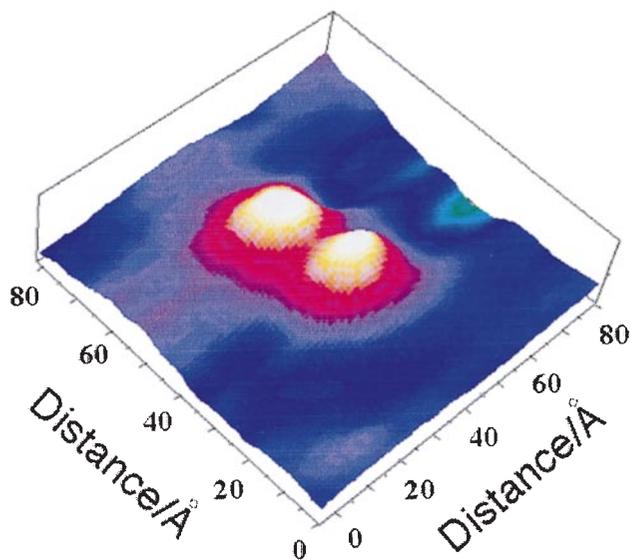


Fig. 4 An STM image of C_{122} deposited on graphite (sample voltage -0.5 V, current 0.5 nA, 80 K, ultra-high vacuum).

clusters should give an insight into the formation mechanism of fullerene molecules.

In conclusion, we succeeded in the synthesis and isolation of all-carbon fullerene dimers C_{121} and C_{122} . The dumbbell-like structure of these dimers is supported by ^{13}C NMR, IR, UV-VIS, mass and STM measurements.

We thank Professor K. Saigo, Dr M. Hayashi and Dr K. Kinbara, University of Tokyo, for help provided during this work. The authors acknowledge support from the Japan Science and Technology Corporation (JST-CREST).

Notes and references

‡ With GPC Jaigel 1H40-2H40 preparative columns, the elution volumes of C_{60} and $C_{60}CBr_2$ are 1580 and 1500 ml, respectively.

§ Maldi TOF mass spectroscopy was performed with a JMS Voyager Elite instrument (337 nm laser) in linear and reflector modes in both positive and negative ionization. Either dithranol or α -cyano 4-hydroxycinnamic acid was used as the matrix. The instrument calibration was performed with neurotensin, $[MH^+] = 1672.91$ amu. LDI TOF mass spectroscopy was performed with a PerSeptive Biosystems Voyager instrument.

¶ UV-VIS spectra of **1** and **2** were measured in CS_2 and *o*-dichlorobenzene: λ_{max}/nm 430 and 700.

|| Selected data for **1**: $\nu_{max}(KBr)/cm^{-1}$ 1462, 1359, 1260, 1190, 1083, 1022, 801, 763, 736, 573, 525, 416. For **2**: $\nu_{max}(KBr)/cm^{-1}$ 1380, 1321, 1180, 1186, 1015, 920, 785, 602, 585, 571, 531, 526, 418.

** Selected data for **1**: δ_c 147.88, 147.54, 146.7, 146.43, 146.09, 145.55, 145.49, 144.8, 142.85, 142.59, 142.51, 142.42, 142.31, 141.3, 140.85, 140.1, 67.7. ^{13}C NMR spectra were measured using a JEOL 270 instrument, 67.7 MHz in CS_2 and 1,2-dichlorobenzene- d_4 or benzene- d_4 for field/frequency lock.

†† *i.e.* at the connections between two hexagons on the fullerene core.

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