

Carbon allotropes of dumbbell structure: C₁₂₁ and C₁₂₂

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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

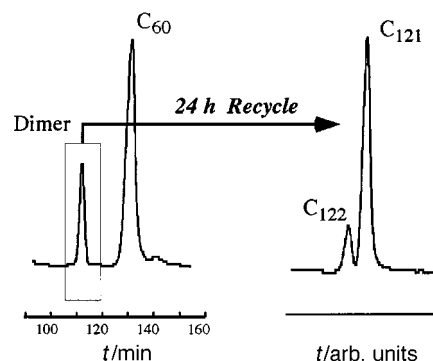


Fig. 1 GPC experiments for the separation of C₁₂₁.

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).

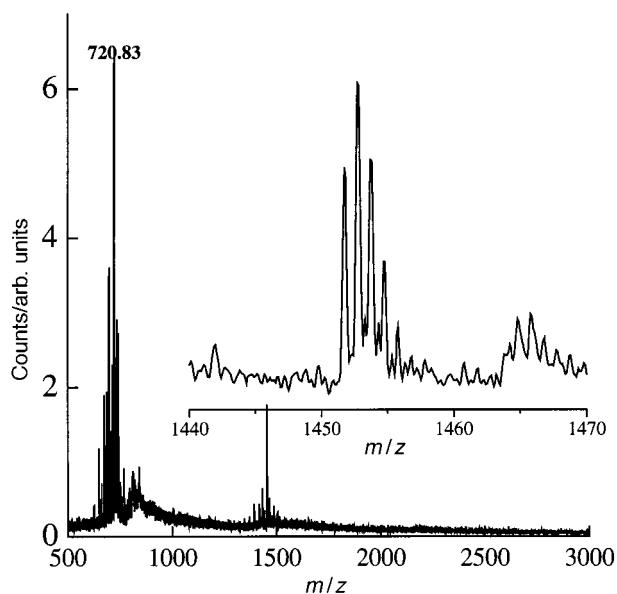
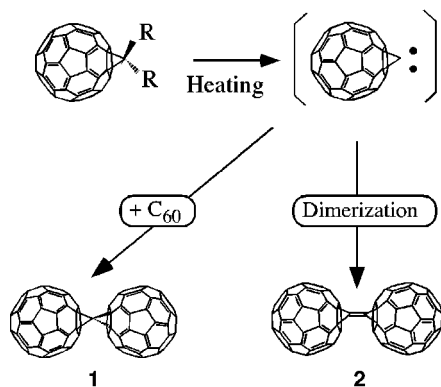


Fig. 2 LDI-TOF MS of C₁₂₁; inset is a detail of the dimer peak, reflector mode, negative ionization.



Scheme 1

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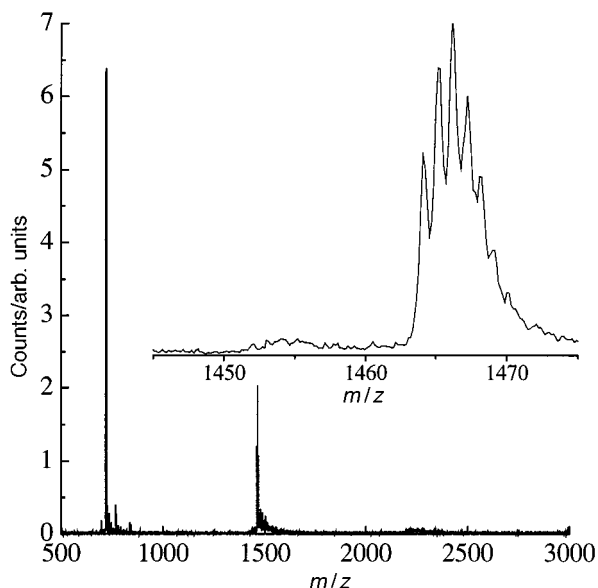


Fig. 3 LDI-TOF MS of C_{122} ; inset is a detail of the dimer peak, linear mode, negative ionization.

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 $1017\text{--}1025\text{ cm}^{-1}$.

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

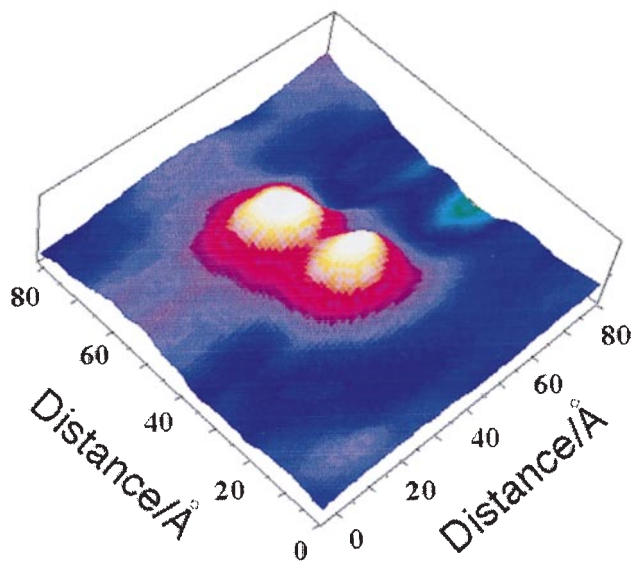


Fig. 4 An STM image of C_{122} deposited on graphite (sample voltage -0.5 V , current 0.5 nA , 80 K , ultra-high vacuum).

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.

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Notes and references

‡ With GPC Jaigel 1H40-2H40 preparative columns, the elution volumes of C_{60} and $C_{60}\text{CBr}_2$ 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, $[\text{MH}^+] = 1672.91\text{ amu}$. 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: $\lambda_{\text{max}}/\text{nm}$ 430 and 700.

|| Selected data for **1**: $\nu_{\text{max}}(\text{KBr})/\text{cm}^{-1}$ 1462, 1359, 1260, 1190, 1083, 1022, 801, 763, 736, 573, 525, 416. For **2**: $\nu_{\text{max}}(\text{KBr})/\text{cm}^{-1}$ 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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