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Tetrahedron Letters 47 (2006) 7413–7415
Tetrahedron Letters

Synthesis of a short-chain fullerene dimer

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Received 18 July 2006; revised 7 August 2006; accepted 17 August 2006

Abstract—The synthesis of a short-chain fullerene dimer via bifunctional cycloaddition is demonstrated. A mono-functionalised C_{60} species is isolated, and has the potential for further organic functionalisation.

Multi-fullerene systems, in which the carbon cages are covalently linked, are of great interest as they provide simple models of polymeric or coalesced fullerenes and, if linked by optically or electrochemically active chains, may possess novel electronic properties.[1] The photophysical properties of numerous C_{60}-based dimer molecules, including those linked by thiophenes,[2] tetrathiafulvenes[3] and π-conjugated oligomers,[4] have been studied and, in some cases, such molecules are investigated as components in photovoltaic devices.[5] Fullerene dimers can be prepared by either dimerisation of fullerene cages or fullerene derivatives or through bifunctional cycloadditions. Only a limited number of short-chain dimers have so far been reported and all involve direct modification of the fullerene cages. These systems, prepared by either solution chemistry or solid-state high speed vibration milling (HSVM)[6] include the directly bonded C_{120},[7,8] oxygen bridged $C_{120}O$,[9,10] and $C_{120}O_2$,[11] carbon bridged C_{121}[12] and the more unusual germanium[13] and silicon bridged[14] dimers. In 1993, Belik et al. reported the reaction of C_{60} with *o*-quinodimethane as a route to stable C_{60} derivatives,[15] and this cycloaddition strategy has been employed many times in preparing fullerene dimers with controlled cage separation.[16] In all cases an aromatic core is covalently linked to fullerene cages through cyclohexene rings. Herein, we report a related synthesis in which a tetrabromoalkene undergoes cycloaddition to two fullerene cages to produce a short-chain fullerene dimer.

The starting material 2,3-bis-(bromomethyl)-1,4-dibromo-2-butene was synthesised by the bromination of 2,3-dimethylbutadiene followed by a twofold *N*-bromosuccinimide (NBS) bromination[17] using azobisisobutyronitrile (AIBN) as an initiator.[18] This was then reacted with C_{60} by iodine-induced elimination of the bromine groups in the presence of 18-crown-6.[19] Since this step is normally carried out in dimethylformamide, and fullerenes have a poor solubility in this solvent, the synthesis had to be transferred to toluene using 18-crown-6 as a phase transfer catalyst. This gave both the monofunctionalised C_{60} **1**[20] in 75% yield and a symmetrical C_{60} dimer **2**[21] in 12% yield (Scheme 1). A successful separation of the reaction mixture was achieved by HPLC, with the monomer eluting after 6.23 min and the dimer after 19.68 min (Buckyprep-M 20×250 mm, toluene, 18 ml min^{-1}). In addition, unreacted C_{60} (13%) eluted after 7.03 min.

MALDI mass spectrometric analysis of the monomer and dimer gave peaks at *m*/*z* 959.9 and 1521.1, respectively, corresponding to the molecular ions of the two species (Fig. 1).

UV–vis absorption spectra of C_{60}, monomer **1** and dimer **2** revealed that the main C_{60} features are retained in both functionalised species, although in the monomer the relative intensities of the main absorption peaks were altered. The shoulder observed at 435 nm is highly characteristic of 1,2-addition across a 6:6 bond in C_{60} (Fig. 2).[22]

The monomer was characterised by ^1H and ^{13}C NMR spectroscopy, and the dimer by ^1H NMR only due to its poor solubility. The ^1H NMR spectrum of monomer **1** revealed two doublets at $\delta = 4.19$ and 4.56 ppm corresponding to the CH_2 and CH_2Br proton environments, respectively. The ^{13}C NMR spectrum showed a total

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Keywords: Fullerenes; Dimers; Cycloadditions.

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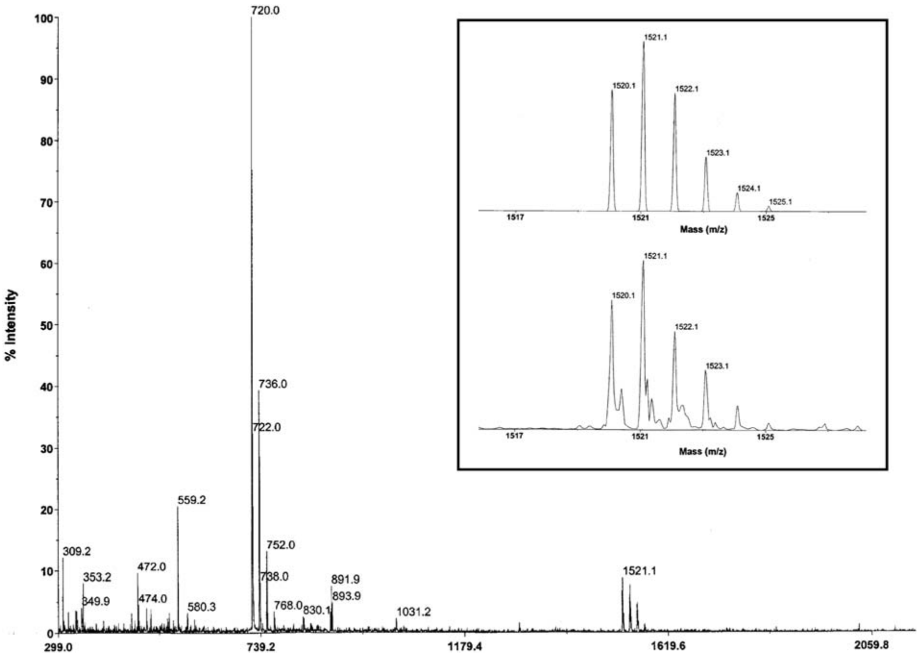
doi:10.1016/j.tetlet.2006.08.061



Scheme 1. Synthesis of novel fullerene monomer **1** and dimer **2** from reaction of 2,3-bis-(bromomethyl)-1,4-dibromo-2-butene with C_{60}. (a) KI, 18-crown-6, toluene, reflux.

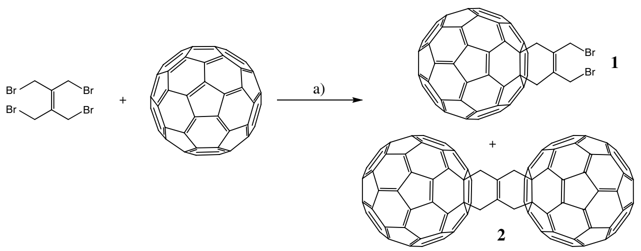


Figure 1. MALDI mass spectrum of dimer **2**. Inset: isotopic distribution pattern theoretically (above) and actual (below).

of 20 peaks, with three sp^3 carbon environments at $\delta = 30.1$, 44.5 and 65.0 ppm. These correspond to CH_2Br, CH_2 and C_{60} sp^3 carbon environments, respectively. The C_{2v} symmetry of the molecule arises due to rapid ring flipping of the cyclohexene unit, and was confirmed by the other 17 peaks found in the range $\delta = 135.5$–155.5 ppm. These all correspond to sp^2 carbon environments. The ^1H NMR spectrum of the dimer revealed two doublets at $\delta = 8.09$ and 8.40 ppm corresponding to the two different proton environments in the compound.

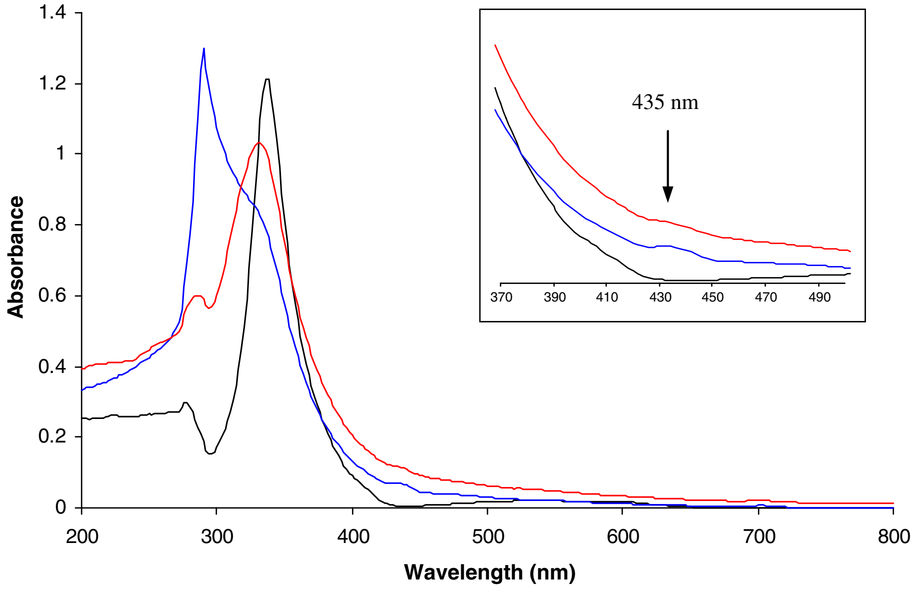


Figure 2. UV–vis spectrum (toluene, 273 K) of C_{60} (——), C_{60} monomer **1** (——) and C_{60} dimer **2** (——). Inset: enlargement of region between 370 nm and 500 nm showing the shoulder at 435 nm indicating 1,2-addition across the 6:6 bond in C_{60}.

The FTIR spectra of C_{60}, 2,3-bis-(bromomethyl)-1,4-dibromo-2-butene, the C_{60} monomer and the C_{60} dimer showed a number of interesting features. The C_{60} absorption band at 525 cm^{-1} was retained in both the monomer and dimer. Also observed in both products were the CH_2 stretching peaks at ~2970 cm^{-1} and CH_2 deformations at ~1250 cm^{-1} appearing in the products and the bromine-bearing reagent, but not in C_{60}.

A short-chain fullerene dimer prepared from readily available starting materials has been successfully synthesised and characterised. A monomer intermediate has been isolated and has the potential for functionalisation with a wide range of organic molecules or other fullerenes.

Acknowledgements

This research is a part of QIP IRC www.qipirc.org (GR/S82176/01). G.A.D.B. thanks EPSRC for a Professorial Research Fellowship (GR/S15808/01). We thank the EPSRC National Mass Spectrometry Service Centre, University of Wales, Swansea, for MALDI analysis.

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18. Synthesis of 2,3-bis-(bromomethyl)-1,4-dibromo-2-butene: 2,3-dimethylbutadiene (8.4 ml, 0.078 mol) was dissolved in carbon tetrachloride (CCl_4) (50 ml). Bromine (12 g, 0.075 mol) dissolved in CCl_4 (50 ml) was added dropwise over 3 h at 0 °C with stirring. After this time, NBS (26.7 g, 0.15 mol), AIBN (cat.) and CCl_4 (15 ml) were added. The reaction mixture was heated under reflux for 12 h. The resulting solution was filtered while hot to remove succinimide, with the liquid cooled to form crystals of the impure product. The crystals were filtered cold, and recrystallised from ethyl acetate to give the pure product (8.98 g, 30%). ^{1}H NMR (500 MHz, $CDCl_3$): $\delta = 4.15$ (s, 8H; CH_2). ^{13}C NMR (125.8 MHz, $CDCl_3$): $\delta = 137.1$, 27.82. FTIR (KBr disc) 2970 cm^{-1} (CH_2 stretch (w)), 1440 (CH_2 bend (s)), 1250 (C–H deformation (s)), 720 (CH_2 rocking (m)). EI MS *m*/*z*: 399.7321 M^- Calculated mass 399.7319.
19. Synthesis of monomer **1** and dimer **2**: C_{60} (474 mg, 0.658 mmol) and 2,3-bis-(bromomethyl)-1,4-dibromo-2-butene (148 mg, 0.329 mmol) were placed in a round-bottomed flask along with 18-crown-6 (750 mg, 2.84 mmol), KI (125 mg, 0.753 mmol) and toluene (125 ml). This was heated under reflux overnight in the absence of light with stirring under an atmosphere of nitrogen. The product mixture was allowed to cool, and then washed with 5% NaOH aqueous solution (125 ml) and H_2O (125 ml). The toluene layer was collected, and dried over magnesium sulfate. After filtration and solvent exchange for fresh toluene, the products were separated using HPLC, giving monomer **1** in 75% yield (443 mg) and dimer **2** produced in 12% yield (112 mg).
20. Monomer **1**: ^{1}H NMR (500 MHz, $CS_2/CDCl_3$ (3:1)) $\delta = 4.56$ (4H, d, $J = 5.9$ Hz), 4.19 (4H, d, $J = 5.9$ Hz). ^{13}C NMR (125.8 MHz, $CS_2/CDCl_3$ (3:1)) $\delta = 155.5$, 147.3, 146.3, 146.0, 145.5, 145.3, 145.2, 144.8, 144.4, 142.9, 142.3, 141.9, 141.8, 141.4, 140.0, 136.9, 135.5, 65.0, 44.5, 30.1, 29.5. FTIR (KBr disc) 2970 cm^{-1} (CH_2 stretch (w)), 1440 (CH_2 bend (s)), 1250 (C–H deformation (s)), 720 (CH_2 rocking (s)), 525 (C_{60} (s)). UV–vis λ (toluene)/nm 290 (ε/dm^3 mol^{-1} cm^{-1} 52,004), 330 Sh (33,662), 436 Sh (2775). MALDI *m*/*z*: 959.9 M^-.
21. Dimer **2**: ^{1}H NMR (500 MHz, $CS_2/CDCl_3$ (3:1)) $\delta = 8.40$ (4H, d, $J = 5.3$ Hz), 8.09 (4H, d, $J = 5.3$ Hz). FTIR (KBr disc) 2970 cm^{-1} (CH_2 stretch (w)), 1440 (CH_2 bend (s)), 1250 (C–H deformation (s)), 720 (CH_2 rocking (s)), 525 (C_{60} (s)). UV–vis λ (Toluene)/nm 286 (ε/dm^3 mol^{-1} cm^{-1} 24,135), 330 (41,399), 434 Sh (4,672). MALDI *m*/*z*: 1521.1 M^-.
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