$C_{120}O_2$: The first [60]fullerene dimer with cages bis-linked by furanoid bridges

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$C_{120}O_2$ has been prepared, characterised by MALDI–TOF MS, UV–VIS, FTIR, and shown by ^{13}C NMR spectroscopy to have C_{2v} symmetry, the [60]fullerene cages being linked by adjacent furanoid rings; thus the structure has a connecting bridge containing a four-membered ring, reminiscent of that conjectured for the [2 + 2] fullerene cycloadduct.

Recently, we described the preparation and characterisation of $C_{120}O$, the first dimeric fullerene derivative.[1] The structure was subsequently confirmed.[2] As part of our ongoing interest in fullerene oxides, and the search for C_{119} precursors,[3] we prepared and isolated $C_{120}O_2$ by thermolysis of $C_{120}O$.[4] Solid $C_{120}O$ was heated to 400 °C for 1 h at normal pressure in an Ar atmosphere. Under these conditions we observed (i) decay of $C_{120}O$ into C_{60} (up to 60% with respect to the initial $C_{120}O$), (ii) the formation of $C_{120}O_2$ (*ca.* 15%) together with oligomeric oxides $(C_{60})_nO_m$ (n = 3–5; m = 3–9), and (iii) an insoluble uncharacterised residue (*ca.* 10%).[4] $C_{120}O_2$, isolated from the obtained mixture by a two-stage HPLC separation,† is a brown solid, stable under ambient conditions and in solution (HPLC analysis).

The mass spectrum of $C_{120}O_2$ [matrix-assisted laser desorption/ionisation time-of-flight (MALDI–TOF) MS, negative mode of ionisation, matrix 9-nitroanthracene] shows (Fig. 1) the intense molecular ion peak at 1473.3 amu (calculated for $C_{120}O_2$, 1473.32 amu). Weak peaks at 720.2 and 736.6 amu indicate minor fragmentation of $C_{120}O_2$ into C_{60} and $C_{60}O$; a similarly weak peak at 1489.8 amu ($C_{120}O_3$) may indicate oxidation by the matrix under MALDI conditions.

Our initial attempts to obtain a ^{13}C NMR spectrum failed due to the low solubility of the substance in CS_2. To overcome this problem we produced enriched material with *ca.* 7% ^{13}C.‡ The ^{13}C NMR spectrum is shown in Fig. 2 and consists of two lines in the sp^3 region and 27 in the sp^2 region (with three coincident peaks).§ The number of lines, and their intensity distribution is consistent with a molecule of C_{2v} symmetry. The two groups of four equivalent sp^3-hybridised carbon atoms indicate that each [60]fullerene cage is bis-linked by adjacent furanoid rings. Thus, the connecting bridge contains a four-membered ring. The four half-intensity sp^2 peaks are due to the carbons on one of the σ_v planes.

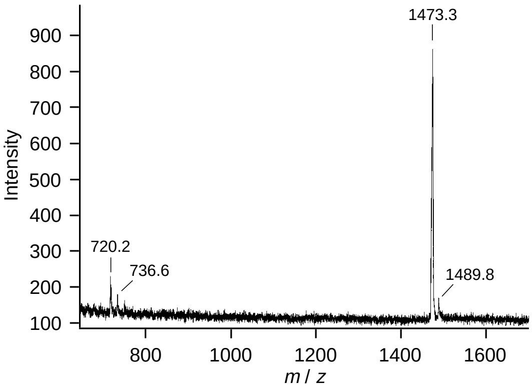

Fig. 1 MALDI–TOF mass spectrum of $C_{120}O_2$

The ^{13}C NMR data suggest two most likely structures, in both of which a four-membered ring is part of the linkage between the cages: in one, the two furanoid rings link the cages *via* 6,6 junctions as in the case of $C_{120}O$[1] **1**, whereas the other structure involves 6,5 junctions for this purpose **2** (Fig. 3). Whilst structure **2** has a four-membered ring exactly analogous to that conjectured for photopolymerised fullerenes,[5] **2** may be disputed on two grounds: (i) it contains unfavourable double bonds in pentagons[6] (calculated to destabilise by *ca.* 8.5 kcal mol^{-1} per double bond);[7] (ii) the structure is inappropriate to explain the position in the spectrum of the signals for the on-plane carbons. For structure **2** each on-plane pair is roughly equidistant from the addend, so that four lines in a similar region of the spectrum could be expected. By contrast, in structure **1** one of the pairs is adjacent to the addend site, and is *exo* to a pentagon containing two sp^3-hybridised carbons. These latter are less electron-withdrawing than sp^2-hybridised carbons and

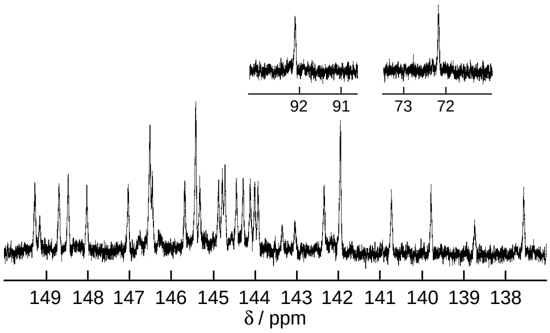

Fig. 2 ^{13}C NMR spectrum of $C_{120}O_2$

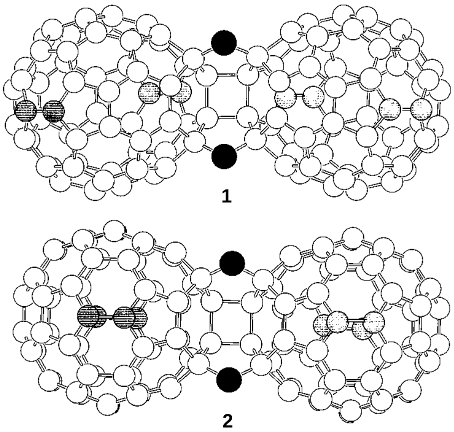

Fig. 3 Possible structures of $C_{120}O_2$ with C_{2v} symmetry: furan-ring linkage *via* 6,6 junctions **1** or *via* 6,5 junctions **2**. The oxygens are black, and the on-plane carbon pairs are hatched for clarity.

this will therefore induce a dipole in the adjacent double bond, resulting in one carbon (in the pentagon) appearing well upfield, the other carbon correspondingly downfield, as observed. The other on-plane pair is remote from the addend and so should appear at a similar position in the spectrum, also as observed. Lastly, in assigning the structure, we discounted the possibility (i) that all sp^3-hybridised carbons are located in one pentagon, implying a substantially larger number of double bonds in pentagons than in **2**; the structure should also have strong repulsive p-orbital interactions from the adjacent oxygens, and (ii) of the locations of the C–C and the C–O–C connections being reversed; this would produce severe strain because the cages would come into almost direct contact.

The UV–VIS spectrum (cyclohexane) resembles that for $C_{120}O$, showing peaks at 224, 256 and 318 nm, and a rather weak band at 422 nm. The FT–IR spectra [KBr for middle IR (MIR), Fig. 4(*a*); polyethylene for far IR (FIR), Fig. 4(*b*)] of $C_{120}O_2$ are compared to that of $C_{120}O$. The ^{13}C NMR data suggest that the furanoid bridges in $C_{120}O_2$ and $C_{120}O$ are rather similar and this similarity is also reflected in the IR spectra of both compounds. In the MIR, where the intra-cage vibrations occur, these similarities are especially striking [Fig. 4(*a*)]. However, the inter-cage vibrations of both dimers observable in the FIR show characteristic shifts. $C_{120}O$ exhibits one strong absorption band at 207 cm^{-1} and a weak band at 124 cm^{-1} (very close to 118 cm^{-1} Raman band of photopolymerized [60]fullerene),[5] both of which are probably responsible for the inter-cage stretching modes. The corresponding FIR features of $C_{120}O_2$ occur at *ca.* 260 (line pair) and 161 cm^{-1}, and thus are shifted (approximately by a factor of 1.28) in frequency compared to $C_{120}O$. Such a shift indicates the more rigid bridge construction in $C_{120}O_2$, thus confirming the NMR data.

In conclusion, we note that $C_{120}O_2$ is the first characterised compound having a four-membered ring as part of the linkage between the two fullerene cages.

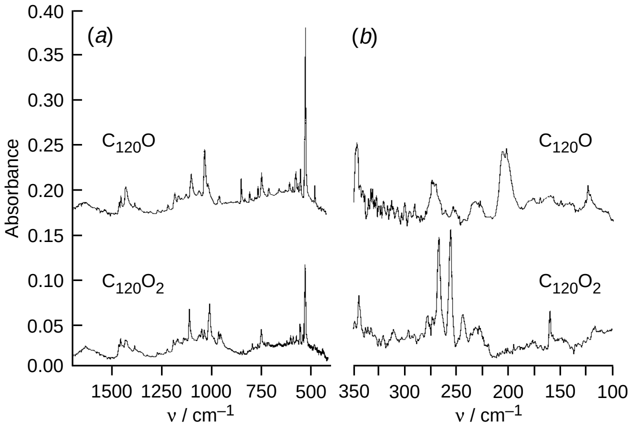

Fig. 4 (*a*) MIR (KBr, 1 mg of sample) and (*b*) FIR (polyethylene, 20 mg of sample) spectra of $C_{120}O_2$ compared to that of $C_{120}O$. The spectra of $C_{120}O$ are shifted for clarity.

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Footnotes

† $C_{120}O_2$ was first separated from C_{60} and higher mass species using a 250 × 4.6 mm Cosmosil 5PBB column, *o*-dichlorobenzene eluent, flow rate 1.0 ml min^{-1}, 150 bar, detection at 340 nm. Final purification was carried out with a 250 × 4.6 mm Cosmosil Buckyprep column, toluene eluent, flow rate 1.0 ml min^{-1}, 60 bar, detection at 340 nm. Under these conditions, $C_{120}O_2$ eluted at 18.1 min (*cf.* 7.8 min for C_{60} and 15.8 min for $C_{120}O$).

‡ ^{13}C-enriched C_{60} was obtained by the standard procedure[8] using graphite rods hollowed out and packed with a mixture of ^{13}C enriched powder and regular graphite; the enriched C_{60} was used as starting material for $C_{120}O$ preparation (ref. 1).

§ The ^{13}C NMR spectrum [125.76 MHz, CS_2–$CDCl_3$ 98 : 2, *ca.* 35 mmol dm^{-1} $Cr(acac)_3$, 60 h, 36 000 scans] exhibits peaks at δ 149.28 (4 C), 149.16 (2 C), 148.70 (4 C), 148.48 (4 C), 148.03 (4 C), 147.04 (4 C), 146.53 (8 C), 146.47 (4 C), 145.69 (4 C), 145.43 (8 C), 145.33 (4 C), 144.88 (4 C), 144.79 (4 C), 144.73 (4 C), 144.46 (4 C), 144.29 (4 C), 144.13 (4 C), 144.02 (4 C), 143.94 (4 C), 143.36 (2 C), 143.06 (2 C), 142.35 (4 C), 141.96 (8 C), 140.73 (4 C), 139.79 (4 C), 138.74 (2 C), 137.58 (4 C), 92.11 (4 C), 72.19 (4 C).

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