$C_{120}OS$: the first sulfur-containing dimeric [60]fullerene derivative

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$C_{120}OS$ has been synthesised by thermal reaction of $C_{120}O$ and sulfur, isolated by HPLC, and characterised by MALDI-TOF-MS, LT-FAB-MS, XPS, Raman, UV-VIS, IR and ^{13}C-NMR spectroscopy; all data are consistent with a molecule of C_s symmetry with the fullerene cages linked by furan- and thiophene-like bridging units.

Following thermal reactions of the $C_{60}/C_{60}O/C_{60}O_2$ system in the solid state, various dimeric fullerene derivatives, *e.g.* $C_{120}O$,[1,2] $C_{120}O_2$ [3,4] and C_{119},[5] have been isolated and characterised. Since ethers and thioethers exhibit similar chemical behavior, we reasoned that it should be possible to synthesise sulfur analogues of the mono- and dimeric [60]fullerene oxides. Several efforts to prepare them in toluene or *o*-dichlorobenzene (ODCB) solutions using typical sulfur-transferring reagents such as Lawesson's reagent,[6] titanocene pentasulfide[7] or sulfur activated with $AlCl_3$, failed. Therefore, we performed the thermolysis of a 1:1 (wt%) mixture of solid $C_{120}O$[1,2] and elemental sulfur for 24 h at 230 °C under Ar at atmospheric pressure. The result was the well-known decay of $C_{120}O$ into C_{60} (*ca.* 5–10% with respect to the total amount of fullerene) as well as the production of $C_{120}OS$ (up to 70%). $C_{120}OS$ was also produced by direct heating of $C_{60}/C_{60}O$ mixtures with sulfur, but with lower yields. The product mixtures were dissolved in ODCB and analysed by high-performance liquid chromatography (HPLC)† and matrix-assisted laser desorption/ionisation time-of-flight mass spectrometry (MALDI-TOF-MS). $C_{120}OS$, purified by two-stage HPLC, is a stable, dark brown solid, and its solubility in ODCB is *ca.* 1 mg ml^{-1}

As in the case of the oxides of [60]fullerene dimers,[1,3,4] negative-ion matrix-assisted laser desorption/ionisation time-of-flight mass spectrometry (MALDI-TOF-MS) was used to detect the molecular anion radical, M⁻•, of $C_{120}OS$ (M_r 1489.38) at *m/z* 1489 (Fig. 1).‡ The fragment ions at *m/z* 720, 736 and 752, respectively, can be assigned to C_{60}, $C_{60}O$ and $C_{60}S$. Unfortunately, the observed molecular weight is also consistent with the formula $C_{120}O_3$, and the weak signal at *m/z*

752 may be interpreted as $C_{60}O_2$. The low abundance of ^{34}S (4.2%) and the experimental error in the measurement of the isotopic pattern did not allow us to distinguish between $C_{120}O_3$, $C_{120}OS$ or even C_{124}. Therefore, high-resolution negative-ion low-temperature fast-atom bombardment mass spectrometry (HR-LT-FAB-MS)[8,9] was used to obtain exact masses for $C_{120}OS$ isotopomers, confirming $C_{120}OS$ as the molecular formula.§ The results were: $^{12}C_{120}OS$, *m/z* 1487.9748 (calc. 1487.9670, error +5.2 ppm); $^{12}C_{119}^{13}COS$, *m/z* 1488.9764 (calc. 1488.9703, +4.1 ppm); $^{12}C_{118}^{13}C_2OS$, *m/z* 1489.9811 (calc. 1489.9737, +5.0 ppm).

Direct confirmation of the presence of sulfur in $C_{120}OS$ was obtained by X-ray photoelectron spectroscopy (XPS).¶ Sulfur was detected *via* the binding energies of 2p electrons which were measured as 163.2 eV ($S_{2p}^{3/2}$) and 164.4 eV ($S_{2p}^{1/2}$) and are consistent with a thioether moiety and not an S–O linkage (binding energy for sulfoxides: *ca.* 168 eV[10]).

Because of the low solubility of $C_{120}OS$ in ODCB, a sample was prepared for NMR studies with enrichment to *ca.* 7% ^{13}C.[4] The 125 MHz ^{13}C-NMR spectrum exhibited in the sp³ region four signals with equal integrals and in the sp² region 54 resolved signals for 56 distinguishable sp² carbons, *i.e.* two pairs of carbons were coincident, giving two peaks with integral 2.‖ This spectrum is consistent with a dimer structure having two-fold symmetry and no carbon atom lying on a symmetry element. The four distinguishable sp³ sites (eight carbon atoms) led us to a plausible structure which is homologous with the B isomer of $C_{120}O_2$.[3,4,11] The replacement of an oxygen atom in one of the furanoid bridges in C_{2v} $C_{120}O_2$(B) with sulfur results in a structure of C_s symmetry, denoted here as *syn*-**1** (stereo image in Fig. 2).** A total of six possible C_s isomers with *syn* or *anti* bridges (O, S atoms on the same or opposite sides of the cyclobutane bridging unit) were modeled with HyperChem 4.5 using the semi-empirical AM1 and PM3 methods. The *syn*-**1**
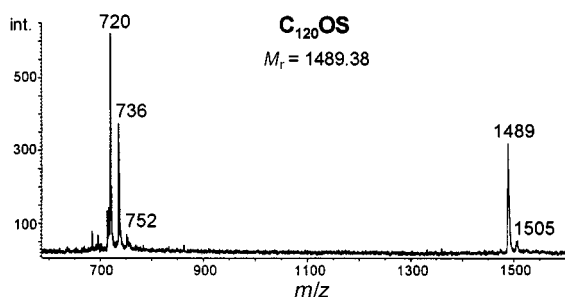

Fig. 1 The MALDI-TOF mass spectrum of $C_{120}OS$ in a 9-nitroanthracene matrix (negative-ion reflector mode) shows the molecular anion radical M⁻• at *m/z* 1489 and fragment ions at *m/z* 720, 736 and 752.
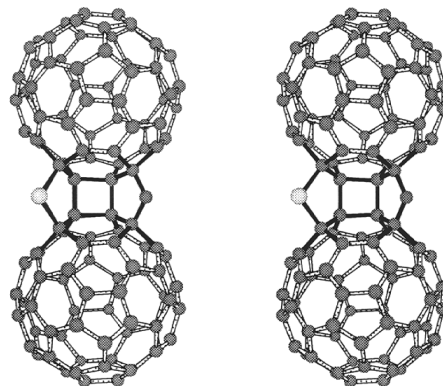

Fig. 2 Stereo pair for the lowest-energy structure of $C_{120}OS$ with C_s symmetry (denoted *syn*-**1**); furan, cyclobutane and thiophene bridges are attached to the 6,6, 5,6 and 6,6 junctions, respectively.
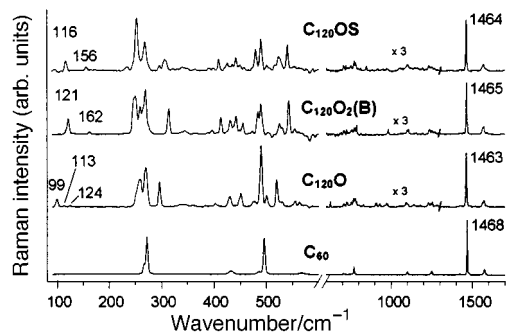
Fig. 3 FT-Raman spectra of solid C_{60}, $C_{120}O$, $C_{120}O_2$(B) and $C_{120}OS$. The region below 200 cm^{-1} is associated with 'rigid-body' cage–cage vibrations.

structure, with 6,6-5,6-6,6 junctions in each cage for the furan–cyclobutane–thiophene bridges (so-called *hph* junctions[11]), has the lowest energy and no double bonds within the pentagons. The next low-energy structure, *syn*-**2** with *php* junctions is 64 kcal mol^{-1} higher in energy. The *syn*-**1** structure can be readily formed from $C_{120}O$, which has 6,6 (*h*) furan junctions, by addition of a sulfur atom to the 6,6 junction next to the C–C bridging bond in one cage (in our nomenclature the so-called *cis*-**1** *anti* junction[4]) followed by the formation of C–S–C and C–C inter-cage bonds to the corresponding *cis*-1 6,6 junction in the opposite fullerene cage.

It has been shown that low-frequency vibrational modes in fullerene dimers are very sensitive to the details of the bridging structure.[4,12] The Raman spectra of C_{60}, $C_{120}O$, $C_{120}O_2$ and $C_{120}OS$ have been obtained under comparable conditions in the solid state (Fig. 3).†† The Raman spectra of $C_{120}OS$ and $C_{120}O_2$(B) are very similar in the range 100–600 cm^{-1}, but differ significantly from the spectrum of $C_{120}O$. In particular, two cage–cage vibrations were observed at 116 and 156 cm^{-1} for $C_{120}OS$ and at 121 and 162 cm^{-1} for $C_{120}O_2$(B), while three bands were found at 99, 113 and 124 cm^{-1} for $C_{120}O$. These results imply that $C_{120}OS$ and $C_{120}O_2$(B) have very similar bridging units and provide strong support for the NMR-consistent structure of $C_{120}OS$ with C_s symmetry (Fig. 2). The C–S–C bridge in $C_{120}OS$ has longer bonds and weaker force constants compared to the C–O–C bridge, and this is expected to result in lower cage–cage vibration frequencies in $C_{120}OS$ compared with $C_{120}O_2$(B), in agreement with the observed spectra.

The FTIR spectrum of $C_{120}OS$ (KBr micropellet) is also quite similar to that of $C_{120}O_2$(B) with bands at 1646, 1459, 1424, 1257, 1189, 1102, 1006, 965, 884, 790, 764, 549, 526 and 471 cm^{-1}. Finally, the UV-VIS spectrum of $C_{120}OS$ in n-hexane resembles that of $C_{120}O_2$(B) with peaks at 222, 274, 284 and 312 nm and weak bands at 422, 430, 464 and 486 nm.

In conclusion, $C_{120}OS$ is the first sulfur-containing dimeric [60]fullerene derivative to be synthesised and characterised by spectroscopic methods. All data are consistent with the lowest-energy modeled structure in which two fullerene cages are linked *via* furan and thiophene bridging rings with a *cis*-**1** configuration of 6,6 junctions. This structure is homologous to the lowest-energy dimeric oxide $C_{120}O_2$(B).

Notes and references

† $C_{120}OS$ was separated from C_{60} and $C_{120}O$ using a 250 × 4.6 mm Cosmosil Buckyprep column (elution with 9 : 1 toluene–n-hexane, flow rate 1 ml min^{-1}, detection at 340 nm). Elution times for C_{60}, $C_{120}O$ and $C_{120}OS$ were 8.9, 16.1 and 19.2 min, respectively.

‡ MALDI-TOF mass spectra were acquired in the negative-ion reflector mode with a Bruker Biflex instrument (Bruker-Franzen Analytik, Bremen, Germany) using 10 mg ml^{-1} 9-nitroanthracene in acetone as matrix.

§ Negative-ion LT-FAB-MS was performed with a JMS-700 instrument (JEOL, Tokyo, Japan). Solid $C_{120}OS$ was dissolved in 3 μl 1-chloro-naphthalene containing 10% 3-nitrobenzyl alcohol and then cooled in liquid nitrogen.[8] High-resolution measurements were made with narrow scans of the accelerating voltage. Internal mass calibration was achieved using [(H$_2$SO$_4$)$_n$HSO$_4$]$^-$ cluster ions generated from concentrated sulfuric acid. This technique was found to yield hydride adduct formation of about one third of the total molecular ion intensity superimposing the isotopic peaks and shifting the *m/z* values systematically to the high mass side (*ca.* 3 ppm).[9]

¶ XPS was obtained with an LH-12 XP spectrometer (Leybold Heraeus, Hanau, Germany). A polycrystalline gold target was placed in a concen-trated solution of $C_{120}OS$ for 40 h under argon atmosphere, rinsed with ODCB and toluene and finally dried under an argon gas flow.

‖ ^{13}C-NMR measurements were performed at 125.76 MHz with a Bruker AM-500 spectrometer using standard Fourier transform techniques and a 5 mm ^{1}H/^{13}C dual probehead (Bruker Analytik GmbH, Rheinstetten, Germany). The sample contained *ca.* 0.3 mg $C_{120}OS$ (7% ^{13}C) in 0.28 ml ODCB-d$_4$ (saturated solution) with *ca.* 17 mM Cr(acac)$_3$ added. Parameters: temperature 20 °C, rf pulse width 5.9 μs (70° flip angle), repetition time 2.0 s, 151200 transients in 84 h). Chemical shifts for sp^2 carbons (except where noted each resonance represents two carbons): δ (ppm rel. TMS) 152.10, 149.24, 149.09, 148.65, 148.35, 148.21, 147.90, 147.63, 147.29, 146.93, 146.82, 146.54, 146.45, 146.28, 146.09, 145.81, 145.75, 145.60, 145.33, 145.27, 145.15, 145.08, 145.04, 144.97, 144.94, 144.74, 144.72, 144.61, 144.60, 144.50 (4C), 144.39, 144.37, 144.34, 144.23, 144.05, 143.89, 143.76, 143.74, 143.65, 142.93 (4C), 142.47, 142.37, 142.19, 142.18, 141.93, 141.85, 141.17, 141.15, 140.50, 139.83, 138.55, 138.06, 137.38, 134.31; sp^3: 92.40, 80.24, 72.44, 67.38.

** Theoretically, there are putative $C_{120}O_3$ structures with C_s symmetry, *e.g.* four epoxy derivatives of $C_{120}O_2$(B), but these would exhibit 5 or 6 sp^3 carbon signals and an sp^2 pattern inconsistent with the observed spec-trum.

†† Bruker FRA 106 spectrometer (Bruker Optik GmbH, Karlsruhe, Germany) using Nd:YAG laser excitation at 1064 nm (resolution 2 cm^{-1}).

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Communication 8/09831J