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The Supercritical Fluid Antisolvent Synthesis of $C_{60}(C_2H_x)$ ($x = 4$ or 6); The Crystal Structures of Two Materials Which Were Thought Unlikely to Exist**

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Synthetic routes to C_{60}(gas) intercalation compounds have reached the point where the intercalation of molecules larger than CO_2 has appeared impossible.[1] We report the synthesis of the intercalation compounds of C_{60} with C_2H_4 and C_2H_6, by using supercritical fluid (SCF) antisolvents to grow single crystals from C_{60} dissolved in 1,2-dichlorobenzene.

Interest in C_{60}(gas) intercalation compounds remains high. Their use as gas storage media has been suggested, with approximately 40 bar of intercalated gas able to held at atmospheric pressure, with the possibility of controlled release.[1,2] More recently, superconducting properties have been reported in these materials by hole and electron doping.[3,4]

The lattice compressibility studies of Morosin and coworkers led to the discovery of the intercalating behavior of He and Ne into C_{60}.[5] The field was expanded by Gadd et al., who introduced hot isostatic pressing (HIP, greater than 1.5 GPa and above 500 °C) to open thermally the fullerene lattice and facilitate diffusion.[1,2] In 1999, this work culminated in a review of all gas-intercalated species. There was no clear evidence for the intercalation of hydrocarbons larger than CH_4 because the forcing conditions of HIP appear to promote polymerization.[1] It was concluded that true intercalation of hydrocarbons larger than CH_4 was unlikely.

In contrast, fullerene(solvent) intercalation compounds are known for a wide range of hydrocarbon solvents.[6,7] These are related to the C_{60}(gas) materials, although they have several solvent molecules per C_{60} unit, with a complete rearrange-

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ment of the crystal lattice. They can be prepared by several routes; the evaporation of C_{60} solutions to dryness, conventional antisolvent precipitation, or vapor deposition.[7]

C_2H_4 and C_2H_6 are too large and thermally unstable to be intercalated by HIP and both are poor solvents for C_{60}. Herein we show that C_2H_4 (critical temperature, $T_c = 9\,°C$) and C_2H_6 ($T_c = 32.6\,°C$) can be intercalated into C_{60} by greatly extending a route which has already been used successfully to form $C_{60}(CO_2)$, with supercritical CO_2 as the antisolvent.[8]

The route involves a combination of traditional crystallization and supercritical antisolvent techniques (see Figure 1). Large crystals of $C_{60}(C_2H_4)$ and $C_{60}(C_2H_6)$ are produced despite using only very small quantities of C_{60} (typically 5 mg per experiment) and with relatively mild temperatures and pressures being applied (35 °C, 150 bar). Smaller crystallites can also be prepared by supercritical antisolvent procedures similar to those used for $C_{60}(CO_2)$.[8] The materials were analyzed by powder and single-crystal X-ray diffraction, which confirmed the formation of $C_{60}(C_2H_x)$ intercalated compounds that showed no noticeable change in gas content over six months. The single-crystal X-ray diffraction studies are, to the best of our knowledge, the first for any low-temperature phase of a C_{60}(gas) intercalation compound, the only similar studies relating to pure C_{60}.[9]

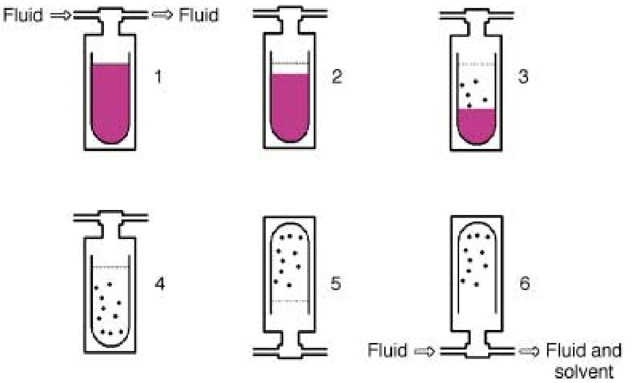

Figure 1. Schematic illustration of the supercritical technique for synthesizing (C_2H_x)–C_{60} intercalation compounds. 1) A solution of C_{60} in 1,2-$C_6H_4Cl_2$ is placed in a glass tube inside a high-pressure view-cell; by placing the tube away from the direct path of incoming gas, the cell can be pressurized to 150 bar with the appropriate supercritical fluid at 35 °C with minimal disturbance of the solution (C_2H_4, $T_c = 9\,°C$; C_2H_6, $T_c = 32.6\,°C$). 2) The cell is sealed and the fluid is allowed to diffuse into the solution. Gas is added periodically to maintain the pressure at 150 bar. 3) Crystallization takes place over a period of 3–5 days until the solution is completely colorless. 4) The view-cell is then turned upside down and flowing supercritical fluid is used to flush out the solvent and dry the crystals. 5 and 6) The dry crystals can then be recovered from the tube.

The room-temperature X-ray powder pattern for $C_{60}(C_2H_4)$ (Figure 2) is similar to that of pure C_{60} apart from the emergence of a (200) peak, consistent with an fcc lattice with $a = 14.338(4)$ Å (compared with $a = 14.16(1)$ Å for pure C_{60}).[9] Thus, C_2H_4 demonstrates the largest known lattice expansion of C_{60} without a change in the crystal lattice type (for example, $a = 14.243(3)$ and 14.247(2) Å for $C_{60}(CO_2)$ and $C_{60}(Xe_{0.316})$, respectively).[8,10]

Single-crystal X-ray analysis at 290 K reveals a cubic F-centred lattice with $a = 14.28(3)$ Å and, on cooling, a phase change occurs leading to a primitive cubic lattice; this phase change is also observed for pure C_{60}. Differential scanning calorimetry (DSC) of $C_{60}(C_2H_4)$ suggests a transition temperature of 210.1 K, which is in good agreement with the change observed by X-ray diffraction (211(2) K); this is approximately 40 K lower than for pure C_{60} (249 K).[11] 210 K is one of the lowest transition temperatures reported for C_{60}(gas) compounds (compared with 241, 235, and 240.2 K for compounds with CH_4, CD_4, and Ar, respectively).[10,12] The 210 K transition is reversible and reproducible with no observable deterioration in crystal quality with repeated cycling.

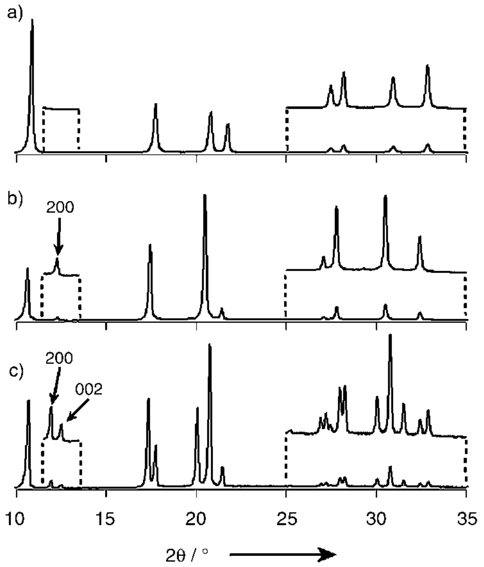

Figure 2. Powder X-ray diffraction patterns for C_{60} (a), (C_2H_4)–C_{60} (b), and (C_2H_6)–C_{60} (c) at room temperature.

Full structural refinements were carried out for data collected at 150, 90, and 30 K, with similar results for all three temperatures; all values are quoted for 150 K, further details are given below.[13] The low-temperature structure of $C_{60}(C_2H_4)$, space group $Pa\bar{3}$, is very similar to that of pure C_{60} with the C_2H_4 molecules occupying octahedral interstitial sites, as has been observed in other gas intercalation compounds.[10,12] Figures 3 and 4 show the molecular and packing structure. Neighboring C_{60} units have the same orientation as in pure C_{60}[9,14] such that, when viewed along the [110] direction, a bond fusing two hexagons of a neighboring unit is located above the center of a pentagonal face (C1−C5) which optimizes the alignment of an electron-rich region (the [6,6] bond) over an electron deficient one (the pentagonal face).[14] These are the shortest intermolecular contacts between C_{60} molecules (3.252 and 3.338 Å). The bonds in the C_{60} molecule, which were refined freely, fall into two distinct groups, with shorter [6,6] bonds ranging from 1.386(3) to 1.391(3) Å and longer bonds fusing pentagons and hexagons ([6,5] bonds) ranging from 1.442(3) to 1.454(3) Å. We see no indication of disorder within the C_{60} unit but the intercalated C_2H_4 molecule does exhibit disorder and was modeled over three orientations at this site. As the hydrogen atoms could not be located, the discussion of the orientation of the C_2H_4 moiety with respect to the C_{60} unit is limited; the

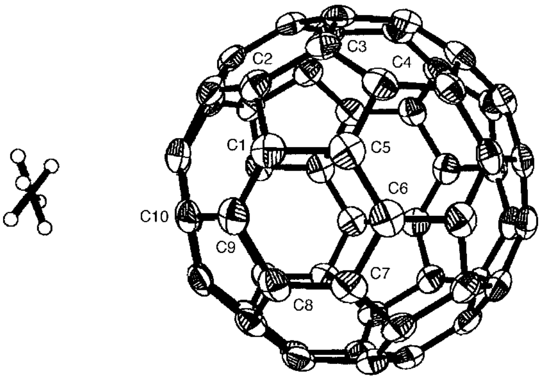

Figure 3. The molecular structure of (C_2H_4)–C_{60}, with the three orientations of ethene displayed. Ellipsoids are drawn at the 50 % probability level; ethene carbon atoms drawn as spheres of arbitrary radius.

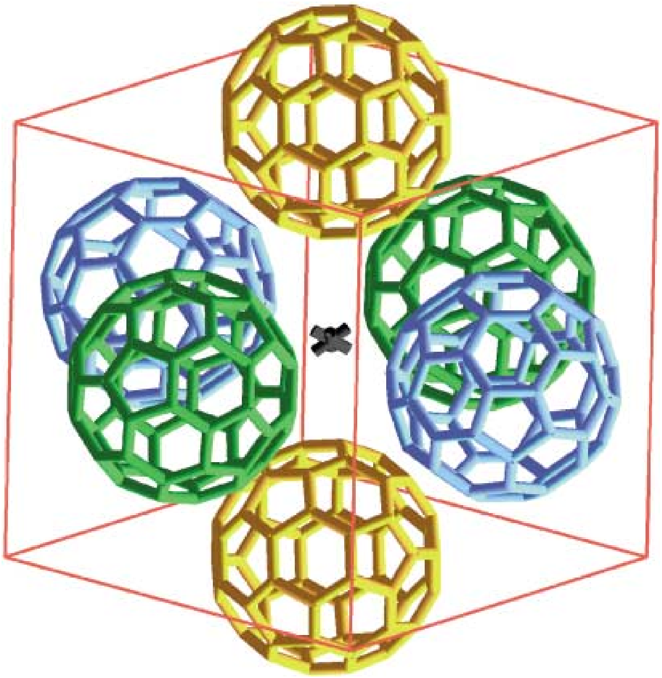

Figure 4. An illustration of the octahedral nature of the interstitial site occupied by the intercalated ethene molecule.

shortest C···C contact between the C_{60} and C_2H_4 units is 3.266 Å (to C10).

By contrast, $C_{60}(C_2H_6)$ differs from previous $C_{60}(\text{gas})_X$ ($x \geq 1$) intercalation compounds, as it has a body-centered tetragonal cell at room temperature; $a = 9.970(1)$, $c = 14.772(2)$ Å. This is the first reported instance of a new room-temperature phase occurring in such intercalation compounds. A phase transition occurs on cooling, but at a relatively high temperature (~268 (DSC) and 269(2) K (X-ray diffraction)).

As with $C_{60}(CO_2)$, the DSC results for $C_{60}(C_2H_6)$ suggest that a second transition occurs over a wide temperature range in addition to the sharp feature at about 268 K. Below 268 K, the crystals appear to have a primitive tetragonal lattice, similar to $C_{60}(CO_2)$, where $a \approx a_{\text{cubic}}/\sqrt{2}$.[15] Repeated efforts to solve and refine the structure in a number of tetragonal space groups were not successful as tetragonal symmetry constrains the mirror plane of C_{60} molecules to lie in the *ab* plane. As these problems could be caused by disorder, so data were collected at 30 K in an attempt to "freeze out" any motion of C_{60}. However, the same problems with the higher symmetry models occurred. This observation is similar to the neutron powder diffraction study of $C_{60}(CO_2)$ (5–293 K), where a reduction of the symmetry from tetragonal to monoclinic led to a satisfactory model.[15] This same model with C_{60} in the monoclinic space group $P2_1/n$ was used as our starting point, which led to a far more satisfactory result with both C_{60} and C_2H_6 units being well-ordered (Figure 5). While the agreement factors are still high, the model is chemically reasonable. Indeed, all models for $C_{60}(C_2H_6)$ are consistent regarding the alignment of the C_2H_6 molecules, which are located in the octahedral interstitial sites within the C_{60} lattice. The major difference between $C_{60}(C_2H_6)$ and $C_{60}(CO_2)$ is that the C_2H_6 molecules are almost exactly aligned with the *c* axis (Figure 5) while the CO_2 molecules lie at an angle of 21° to the *bc* plane and approximately 5° from the *ac* plane. This orientation is consistent with the expansion of the cell in the *c*-direction ($c = 14.829(2)$ Å, 150 K) when compared with pure C_{60} (14.061(5) Å).[9]

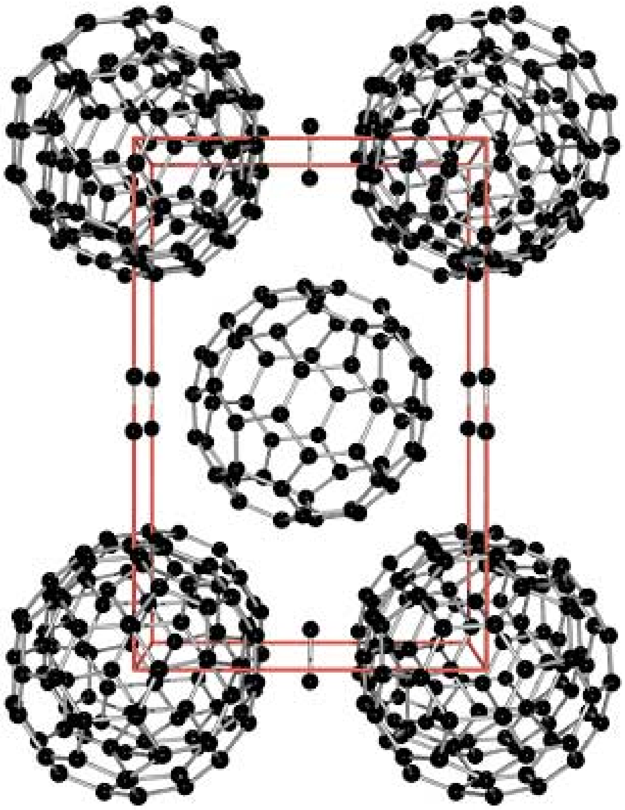

Figure 5. Packing diagram of (C_2H_6)–C_{60} viewed along the [100] direction, which shows the alignment of the ethane molecules with the *c* axis.

In this paper, we have described a new route to previously inaccessible C_{60}(gas) intercalation compounds, which yields single crystals of sufficient quality for X-ray diffraction studies. There are encouraging indications that our technique can be extended to larger hydrocarbons (for example, propene and propane). The same approach could also be applicable to other fullerenes. It has the distinct advantage over other routes to gas intercalation compounds in that it can be used with very small quantities of reagents, and all of the material is easily recovered at the end of the process. It is also likely that this technique could provide a simple method for crystallization of endohedral C_{60} compounds which have previously required large molecules as cocrystallites.[16]

Experimental Section

Safety Warning: Experiments with supercritical fluids are performed at high pressure and should only be carried out with appropriate equipment.

C_{60} (SES Research Inc, Houston, TX, 99.5%) was dissolved in 1,2-dichlorobenzene (Aldrich, 99.0%) to give a purple solution, which was filtered through a 0.45 µm filter prior to use.[17–19] C_2H_4 and C_2H_6 were used as supplied (Air Products and Chemicals, Inc., 99.5%). A Gilson 303 HPLC pump with a chilled 10SC pump head was used to generate pressure, controlled with a Jasco 880-81 back-pressure regulator. Powder X-ray diffraction patterns of all the new materials were taken at room temperature (Philips XPERT Θ-2Θ diffractometer, $Cu_{K\alpha}$ radiation, $\lambda = 1.5405$ Å). Diffraction patterns were collected over a 2θ range of 5–60°, and indexed using the DICVOL91 program.[20] DSC analysis was performed using a power-compensated Perkin Elmer DSC-7 under argon, with empty Al pans used as a reference prior to collection of the data. The material was initially cooled to −90 °C and held at that temperature for 5 min before heating to 20 °C at a rate of $10\,°C\,min^{-1}$. The sample was then cooled to −90 °C at a rate of $200\,°C\,min^{-1}$ and held at that temperature for 10 min prior to heating again from −90 to 20 °C at a rate of $10\,°C\,min^{-1}$ to record the data.

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