Solvated C_{60} and C_{60}/C_{70} and the Low-resolution Single Crystal X-Ray Structure of C_{60}

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Novel, solvated C_{60}/C_{70} and C_{60} phases have been synthesized and single crystals exhibiting long-range order obtained; X-ray diffraction studies support the spheroidal hollow shape of underivatized C_{60}.

The molecular level characterization of carbon clusters is a topic of great current interest. The general spheroidal shape of C_{60} and C_{70} molecules[1] and rough C–C distances have been determined from microscopy,[2a,b] powder diffraction,[2c] EXAFS[3] and NMR data.[4] More accurate geometrical parameters have been obtained very recently for C_{60} from the structures of metallated fullerenes.[5] Derivatization results in a range of C–C bonds and is claimed to remove the possibility of a fluxional structure. Attempts to obtain single crystals suitable for X-ray crystallography from non-derivatized fullerenes have been hampered by rotational and long-range disorder in the crystal lattice.

We report here the synthesis of mixed C_{60}/C_{70} and pure C_{60} solvates and their low resolution single-crystal X-ray structures.[6] Unlike the solvent-free crystals obtained *via* sublimation[2c] or from aromatic solvents,[2d] the crystalline carbon clusters obtained from cyclohexane exhibit reasonably long-range order. Crude samples containing mixtures of C_{60} and C_{70} fullerene are produced and extracted from carbon soot according to known techniques.[2d,7] Pure C_{60} is obtained by chromatography.[8,9] The spectroscopic characteristics of the pure C_{60} are consistent with the literature.[9] Solids containing a mixture of C_{60} and C_{70} were washed with acetonitrile and dissolved in hot cyclohexane. Slow cooling of the supersaturated solutions yields mixed C_{60}/C_{70} cubic crystals suitable for X-ray diffraction studies.[9b] Crystals of solvated, pure C_{60} were obtained similarly. Both solvates lose their crystallinity when exposed to air owing to solvent loss.†

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† Orange–brown single crystals of C_{60}/C_{70}–C_6H_{12} are, at 20 ± 1 °C, cubic, space group *Fm*3*m* or *Fm*3*c*, with a = 28.216(9) Å; those of pure C_{60} with C_6H_{12} solvation have a = 28.144(15) Å. A total of 580 (C_{60}/C_{70}) and 572 (C_{60}) independent reflections having 2θ(Cu-Kα) < 94.9° (the equivalent of 0.4 limiting Cu-Kα spheres) were collected at 20 ± 1 °C on a computer-controlled Nicolet autodiffractometer using θ–2θ scans and nickel-filtered Cu-Kα radiation; only 105 (C_{60}/C_{70}) and 106 (C_{60}) data had $I > 3\sigma(I)$. This low yield of data was not unexpected since the C_{60} and/or C_{70} units are expected to have substantial disordering in the solid state even in the absence of cyclohexane molecules of crystallization which will almost certainly be disordered as well. Computer modelling studies of the packing of C_{60}/C_{70}, pure C_{60} and cyclohexane (CHEM-X package[10]) were performed using the theoretical atomic coordinates of C_{60} and C_{70}.[11]

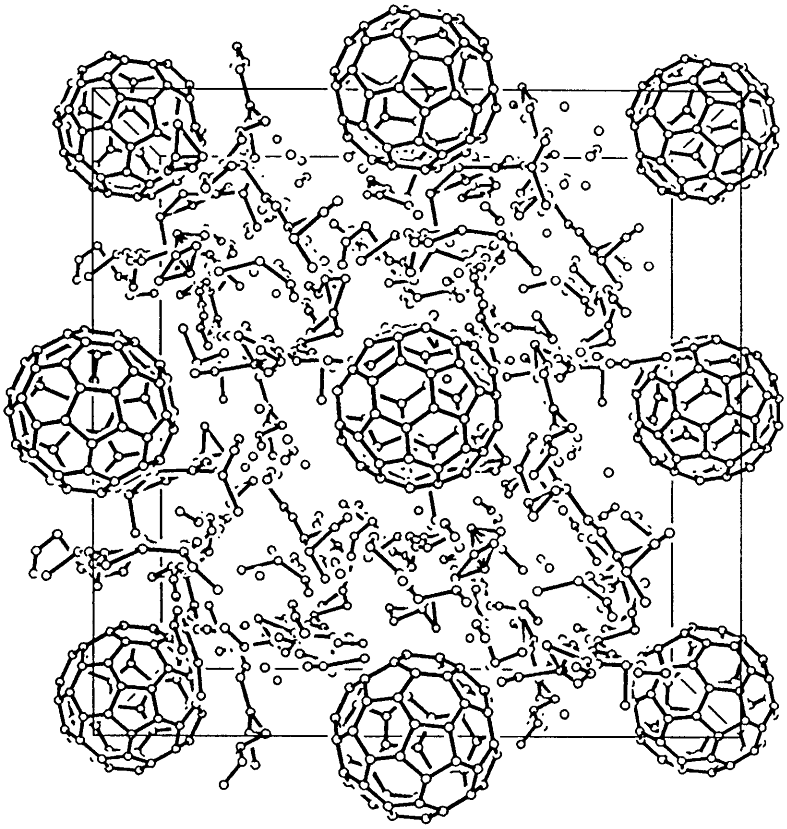

Fig. 1 Packing diagram for the C_{60} structure. Well defined C_{60} are located at (0,0,0), $(\frac{1}{2},\frac{1}{2},\frac{1}{2})$. Disordered C_{60} and solvent molecules are also shown at $(\frac{1}{4},\frac{1}{4},\frac{1}{4})$ and $(\frac{3}{4},\frac{1}{4},\frac{1}{4})$.

In the determination of the structure of the cyclohexane solvate of cocrystallized C_{60} and C_{70}, various preferred packing models predicted for idealized C_{60} and/or C_{70} molecules[11] in a face-centred cubic (fcc) lattice with a = 28.2 Å were checked using 105 independent reflections having $I > 3\sigma(I)$ with rigid-body refinement techniques for a noncentrosymmetric face-centred triclinic lattice. Of the models predicted to have the most favourable packing arrangement for spherical C_{60} and ellipsoidal C_{70} units, one with similarly oriented C_{60} units at (0,0,0) and $(\frac{1}{2},0,0)$ and severely (translationally and/or rotationally) disordered C_{60}, C_{70} and/or cyclohexane molecules at or near $(\frac{1}{4},\frac{1}{4},\frac{1}{4})$ and $(\frac{3}{4},\frac{1}{4},\frac{1}{4})$ was most consistent with the intensity distribution for the X-ray data.‡ This model, which was essentially that of a primitive cubic lattice with a = 14.1 Å and similarly oriented C_{60} moieties at the lattice points and disordered carbon atoms (due to severely disordered additional C_{60}, C_{70} and/or cyclohexane molecules) between C_{60} molecules at quasi-body-centred sites, was also the only one which gave a non-divergent least-squares refinement. An NaCl-type structure with a = 28.2 Å and idealized rigid-body C_{60} molecules at (0,0,0) and $(\frac{1}{2},0,0)$ could be refined, but the substitution of idealized rigid-body C_{70} units at one or both of these sites dramatically increased the R value and caused the refinement to diverge as did all attempts to refine additional C_{60} and/or C_{70} units at reasonable positions in the 28.2 Å unit cell, including positions at or near $(\frac{1}{4},\frac{1}{4},\frac{1}{4})$ and $(\frac{3}{4},\frac{1}{4},\frac{1}{4})$. This behaviour could be explained by having these additional fullerene molecules severely (translationally) disordered or by having these additional sites occupied by a mixture of C_{60}, C_{70} and cyclohexane molecules. Indeed, a difference Fourier map based on the partial NaCl-type C_{60} structure contained diffuse electron density in the regions between C_{60} units.

Consequently, it was decided to employ a 'heavy-atom' approach for locating additional electron density. Thus, the centre of one C_{60} molecule (treated as a 'heavy atom') was fixed at the origin of the unit cell and the centre of the second ('heavy atom') C_{60} was initially placed at $(\frac{1}{2},0,0)$ but its position allowed to vary. Each C_{60} unit was allowed to rotate freely but only the second was also allowed to translate; carbon atoms for each individual C_{60} unit were assigned a common, but variable, isotropic thermal parameter. The *ca.* 30 highest peaks revealed in subsequent difference Fourier maps were included in the next refinement cycle as carbon atoms with fixed positions and a common variable isotropic thermal parameter. This refinement–difference Fourier procedure was repeated until the difference Fourier maps

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‡ It is noteworthy for this structure that 92 of the 106 independent reflections having $I > 3\sigma(I)$ had all indices even and, of the 14 'observed' reflections with all indices odd, only 2 had $I > 17\sigma(I)$. The presence of the strong (1,3,5) reflection in the initial alignment set was the only preliminary indication that the correct unit cell utilized a face-centred lattice with a = 28.2 Å rather than a primitive lattice with a = *ca.* 14.1 Å. A 28.2 Å NaCl-type structure with spherically disordered or nearly identically oriented C_{60} units (*i.e.*, equivalent entities) at the lattice points of the two interpenetrating face-centred lattices would appear to be primitive with a = 14.1 Å. Inequivalency in these C_{60} entities introduced by slight translations of their centres of gravity off the above positions and/or their different rotational orientations would enhance the all-odd intensities and (correctly) indicate a face-centred lattice with a = 28.2 Å. The same enhancement would be obtained if additionally severely disordered C_{60} units and/or cyclohexane molecules at or near $(\frac{1}{4},\frac{1}{4},\frac{1}{4})$ and $(\frac{3}{4},\frac{1}{4},\frac{1}{4})$ would be present in the 28.2 Å unit cell.

Atomic coordinates, bond lengths and angles, and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre for C_{60}. See Notice to Authors, Issue No. 1.

were flat (±0.04 e Å^{-3}) and contained no additional peaks which were not within van der Waals distance of the C_{60} units.

The structural model at this point contained (*i*) two rigid-body idealized full-occupancy C_{60} units with common isotropic thermal parameters for the carbon atoms of 9(2) and 16(2) Å^2, respectively, (*ii*) 217 disordered carbon atoms with fixed positions, common variable occupancy factor of 0.55(3) and a common variable isotropic thermal parameter of 26(2) Å^2; none of these disordered atoms (or those related by symmetry) were within 2.92 Å of positions $(\frac{1}{4},\frac{1}{4},\frac{1}{4})$ and $(\frac{3}{4},\frac{1}{4},\frac{1}{4})$. The final model which was based on the following 14 variables: an overall scale factor [8.6(2)], three rotational parameters for each C_{60}, three translational parameters for the second C_{60}, a common variable occupancy factor for the disordered additional carbon atoms, and three common isotropic thermal parameters (one each for the two C_{60} units and one for the disordered additional carbon atoms) gave *R* (unweighted, based on *F*) = 0.139 for 105 independent reflections having 2θ(Cu-K$\bar{\alpha}$) < *ca.* 60° and $I > 3\sigma(I)$. The centre of gravity for the second C_{60} unit refined to [0.499(4),0.032(4),0.008(3)], a position quite close to the 'ideal' $(\frac{1}{2},0,0)$ site in the cubic space group.

In the determination of the structure of the cyclohexane solvate of pure C_{60}, similar procedures with the F_0 data from the cyclohexane solvate of *pure* C_{60} gave *R* (unweighted) = 0.109 for the same 14 variables with 106 reflections having $I > 3\sigma(I)$ and a structural model containing two rigid-body idealized fully-occupancy C_{60} units and 232 disordered carbon atoms with fixed positions, a common variable occupancy factor of 0.76(3) and a common variable isotropic thermal parameter of 27(1) Å^2. None of these disordered atoms or those related by symmetry were within 2.87 Å of positions $(\frac{1}{4},\frac{1}{4},\frac{1}{4})$ or $(\frac{3}{4},\frac{1}{4},\frac{1}{4})$ in the unit cell. As with the C_{60}/C_{70} data, the centre of gravity for the first C_{60} molecule was fixed at the origin of the unit cell. The common isotropic thermal parameter for its carbon atoms refined to a value of 3(1) Å^2. The centre of gravity for the second full-occupancy C_{60} molecule refined to [0.504(3),0.038(3),0.005(2)] while its common isotropic thermal parameter refined to 9(1) Å^2. The overall scale factor was 4.6(1).

Since none of the partial occupancy disordered carbon atoms (or those related by symmetry) in either structure were within 2.9 Å of $(\frac{1}{4},\frac{1}{4},\frac{1}{4})$ and $(\frac{3}{4},\frac{1}{4},\frac{1}{4})$, they define spherical holes of *ca.* 6 Å diameter around these positions. These positions are believed to be at or near the centres of gravity of additional (presumably severely disordered) C_{60} or C_{70} units, in agreement with the crystallographic packing model. This result is also consistent with the calculated 7 Å value of the inner diameter of the C_{60} and/or the length of the shorter axis of the ellipsoidal C_{70} molecules. Importantly, a C_{60} and C_{70} molecule centred on these sites would have to be rotationally disordered in the cubic lattice since the crystallographic site symmetry is inconsistent with the molecular point symmetry of either species. NMR experiments also demonstrate that C_{60} rotates in the solid state.[12] For both structures the centre of gravity of the second C_{60} refined close to the ideal value irrespective of the presence or absence of additional C_{70}. This result is also in agreement with the modelling studies. The closest C_{60} non-bonding contacts in either the C_{60} or C_{60}/C_{70} NaCl-type structure are *ca.* 12.2 Å, a value significantly larger than the 10.7 Å van der Waals diameter of C_{60}. Placing C_{60} centres of gravity at positions in the unit cell not near $(\frac{1}{4},\frac{1}{4},\frac{1}{4})$ or $(\frac{3}{4},\frac{1}{4},\frac{1}{4})$ results in nonbonded C_{60} contacts *smaller* than their van der Waals diameter. In the structural diagram presented in Fig. 1, the void spaces between C_{60} molecules located only at (0,0,0) and $(\frac{1}{2},0,0)$ appear as 7.1 Å diameter cylindrical channels running along the unit cell axes. These channels intersect at the $(\frac{1}{4},\frac{1}{4},\frac{1}{4})$ and $(\frac{3}{4},\frac{1}{4},\frac{1}{4})$ points where additional severely disordered fullerene molecules are presumably present. Away from these intersections, the channels presumably may contain additional disordered cyclohexane molecules in both structures since the van der Waals diameter for a spherically disordered cyclohexane is *ca.* 7 Å. While the exact role of cyclohexane in increasing the long-range structural order is not totally understood,§ the possibility of obtaining non-close-packed structures derived from C_{60} is demonstrated. It is expected that other solvents may yield other phases.

In conclusion, we have demonstrated that crystalline forms of solvated fullerenes can be obtained. Single crystals of C_{60}/C_{70} and C_{60} exhibiting reasonably long-range order allowed us to demonstrate the hollow convex shape of C_{60} *via* X-ray techniques.¶ The formation of well-defined crystalline phases composed of C_{60} and C_{70} not in direct van der Waals contact suggests the possibility that other crystalline fullerene-containing composite materials could be obtained.

Dr J. Millar is acknowledged for the NMR spectrum of crystalline C_{60}/C_{70}, and Drs M. Newton and K. Raghavachari for providing the calculated coordinates of C_{60} and C_{70}, respectively.

Received, 28th May 1991; Com. 1/02502C

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§ One referee correctly suggested that the solvent may increase the long-range structural order by stabilizing the quasi body-centred cubic array of fullerene molecules.

¶ A refinement of the C–C bond lengths of two independent C_{60} in pure, solvated C_{60} crystals yielded values comparable with those obtained *via* other techniques and/or from derivatized C_{60}; reported at the 201 ACS Meeting, Atlanta, 1991; S. M. Gorun, M. A. Greaney, V. W. Day, C. S. Day, R. M. Upton and C. E. Briant, ACS Symposium Series *Large Carbon Clusters*, ed. G. Hammond and V. Kuck, 1991, in the press.