Preparation and Single Crystal Structure Determination of the Solvated Intercalate C_{60}·I_2·Toluene

Paul R. Birkett, Christos Christides, Peter B. Hitchcock, Harold W. Kroto, Kosmas Prassides, Roger Taylor and David R. M. Walton
School of Chemistry and Molecular Sciences, University of Sussex, Brighton, Sussex, UK BN1 9QJ

C_{60} and I_2 cocrystallise from toluene as a solvated intercalate containing very close molecular contacts between the iodine and both the C_{60} and toluene molecules.

Single crystal structures of solvated C_{60} *viz.* C_{60}·$4C_6H_6$[1,2] and C_{60}·C_6H_6·CH_2I_2,[3] and C_{60} intercalates *viz.* C_{60}·2 ferrocene,[4] C_{60}·3(1,4-dihydroquinone),[5] C_{60}·2[bis(ethylenedithio)tetrathiofulvalene][6] and $C_{60}S_{16}$,[7] have been described. Solid C_{60} also intercalates with electron donors such as alkali metals to generate novel ionic materials of the form A_nC_{60} (n = 3, 4, 6 or 12) which for the composition n = 3 lead to high temperature superconductivity.[8] The non-superconducting intercalate C_{60}·$2I_2$ has also been described[9-12] and no charge-transfer interactions could be detected by ^{13}C NMR studies.[11] We now report the preparation and single crystal structure determination of a novel solvated intercalate which exhibits electron donor–acceptor interactions between C_{60}, iodine and toluene molecules.

Crystals of C_{60}·I_2·toluene were grown from a warm solution of C_{60} in toluene containing freshly sublimed iodine. Black rod-like crystals, similar in shape to those of C_{60}·$4C_6H_6$,[1,2] of a suitable size for single crystal X-ray crystallography were obtained within 3 h. Washing the crystals with pentane after initial decantation from the reaction solution resulted in leaching of iodine from the crystal lattice. Additionally, iodine sublimed from the crystals at room temperature during storage. Therefore, the crystals were collected for X-ray diffraction studies direct from the reaction solution without prior isolation. IR analysis of the solvated intercalate revealed only the expected signals for toluene and C_{60} without significant band perturbation. The presence of iodine within the crystal lattice was detected with starch-iodide paper.

X-Ray diffraction data,* collected at 143 K, showed the C_{60} molecules to be disordered and to lie on a crystallographic mirror plane (Fig. 1). A set of half occupancy positions corresponding to a complete C_{60} molecule was assigned, which together with its mirror image reflected the electron density. During the refinement, loose constraints were applied to the C_{60} molecule such that all atoms were equidistant from the centre of the molecule, all intra-pentagonal bonds were the same length and all inter-pentagonal bonds were the same length. The free variables refined to 3.53, 1.43 and 1.43 Å respectively. The apparent lack of difference between the two types of bonds in the C_{60} molecule was probably an artefact due to disorder within the crystals and the presence of heavy iodine atoms. The toluene molecules are disordered across the mirror plane, whereas the iodine atoms (comprising iodine molecules) lie on the mirror plane. The crystal packing system was orthorhombic with a unit cell volume of 3545.7 Å^3. Taking the van der Waals radius of C_{60} to be 5 Å then the free volume available for accommodating both intercalate, iodine and solvate, toluene, per unit cell amounts to 42.7%. This result contrasts with the 26.9% free volume per unit cell in simple cubic C_{60} at 140 K taking the unit cell dimensions to be 14.0622(2) Å.[13]

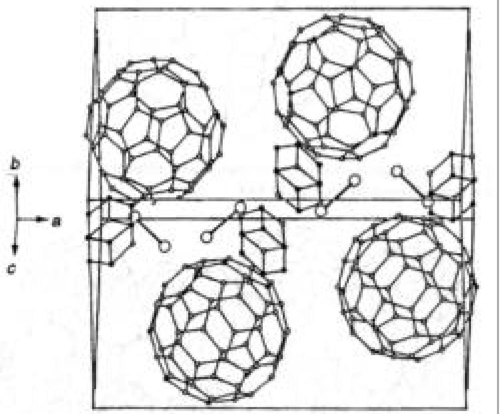

Fig. 1 Crystal packing of the solvated intercalate C_{60}·I_2·toluene showing only one of the two C_{60} orientations. Shaded carbon atoms in the disordered toluene molecules represent one of the two orientations found.

Each C_{60} molecule is in contact with an iodine molecule so that the C–I–I angle is 168.5°. In addition, the iodine molecule has another contact with the disordered toluene molecule at an angle of 177.5°, whilst the angle between the contacting iodine and the plane of the aromatic ring of the toluene is 102.0°. The toluene molecule interacts with another C_{60} molecule at an angle of 179.1° within the same region of the C_{60} surface as its iodine contact (Fig. 2). The overall result is a complex network of repeating interwoven stacking units of C_{60}·I_2·toluene (Fig. 3) forming a staggered 'herring bone' chain of iodine molecules within the crystal lattice. Additionally, a similar series of C_{60} molecules are located along the crystallographic *a* axis.

The nearest C_{60} C–I contact distance is 3.09 Å, considerably shorter than the sum of the van der Waals radii of 3.68 Å,[14] with the iodine in contact with the C_{60} molecule at the midpoint of two specific mirror image carbon atoms. The nearest C_{60} C–I contact distances calculated for the intercalate C_{60}·$2I_2$ ranged from 3.60 to 4.00 Å,[8] whilst the C–I contact distances reported for the solvate C_{60}·C_6H_6·CH_2I_2 were 3.29 and 3.54 Å.[3] The I–toluene interaction distance is also short, *viz.* 3.13 Å. The iodine molecule is in contact with the disordered toluene molecule at one of the two 'common' aromatic ring carbon atoms (see Fig. 1) that are present in both mirror images. This result is in contrast to the complexes of aromatic hydrocarbons with molecular halogens *e.g.* C_6H_6·Br_2 where the contact is between the centre of the aromatic ring and the axial halogen molecule.[15]

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* Crystal structure determination details, atomic coordinates, bond angles and lengths, and temperature factors have been deposited at the Cambridge Crystallographic Data Centre. For details of the CCDC deposition scheme, see 'Instructions for Authors,' *J. Chem. Soc., Perkin Trans. 2*, 1993, issue 1.

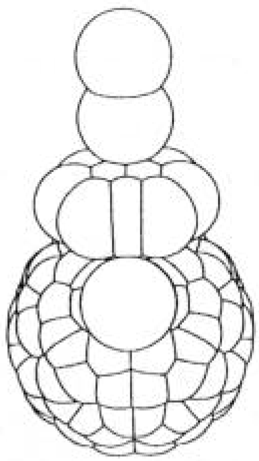

Fig. 2 Interaction positions of iodine and toluene molecules within the same domain of the C_{60} surface

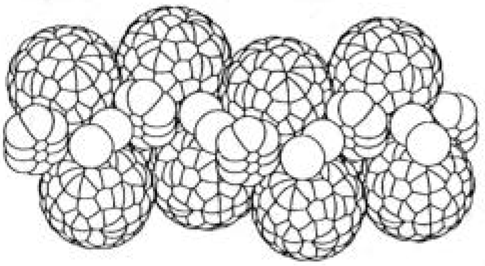

Fig. 3 Repeating units of C_{60}·I_2-toluene leading to a staggered network of both C_{60} and iodine molecules within the crystal lattice

The closest C_{60}–C_{60} centre-to-centre separation in the C_{60} chain along the *a* axis is 9.93 Å, almost identical to the C_{60}–C_{60} centre-to-centre distance in simple cubic C_{60} at 140 K [9.9435(1) Å].[13] The C_{60}–C_{60} centre-to-centre distance is 10.20 Å in the *ab* plane. The nearest C–C contact distance between the toluene and C_{60} molecules is 3.226 Å, whilst the carbon atom of the toluene molecule that contacts the iodine molecule has a nearest carbon contact distance of 3.334 Å to C_{60}. The C_{60} to toluene interaction is 'relatively' weak because toluene behaves as an electron donor towards the best electron acceptor available, *viz.* iodine. The electron affinity of iodine is 3.06 eV,[16] in contrast to C_{60} (2.65 eV).[17] In effect the iodine molecule is situated in an electron acceptor–donor sandwich between the C_{60} and toluene molecules respectively. The bond length of molecular iodine within the crystal structure is 2.685(2) Å which is close to the value of 2.715 Å observed for elemental iodine.[18] The calculated bond length of molecular iodine in the intercalate C_{60}·$2I_2$ was 2.53 Å.[8] There are no contacts between iodine molecules with the nearest intermolecular I–I distance found to be 8.28 Å. Further studies are in progress in order to establish whether any significant charge-transfer between the component molecules exists or not.

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