SHORT PAPER

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Supramolecular complex of C_{60} with tetrakis(*p*-iodophenyl)ethylene[†]

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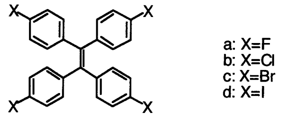
When complexed with tetrakis(*p*-halophenyl)ethylene, the C_{60} molecule arranges to form chiral inclusion crystals.

Keywords: tetrakis (p-halophenyl) ethylene, c_{60}, inclusion complex

The supramolecular organisation of C_{60} by inclusion crystallisation with host compounds has been of considerable interest in recent years due to their potential application to new materials with novel functions.[1] The linear [2+2] polymerisation of C_{60} molecules in the supramolecular complex has also been reported.[2] Here, we report the synthesis and crystal structure of the new C_{60} molecular complex with tetrakis(*p*-iodophenyl)ethylene **1d** in which C_{60} molecules are arranged in linear columns.

We recently reported that tetrakis(*p*-halophenyl)ethylenes **1a–1d** form stable inclusion complexes with various organic molecules through halogen–halogen and halogen–π interactions. The achiral host molecule **1** forms chiral crystals with achiral guest molecules in the solid state.[3] When complexed with tetrakis(*p*-halophenyl)ethylenes **1a–1d**, C_{60} selectively forms 1:2 inclusion crystals with **1d**. For example, when a solution of C_{60} (20 mg) and tetrakis(*p*-iodophenyl)ethylene **1d** (46 mg) in toluene (10 ml) was kept at room temperature for several days, an inclusion complex of C_{60}, **1d** a and toluene in a 1:2:3 ratio was obtained as black prisms (23 mg). Fullerene C_{70} does not form a crystalline complex with tetrakis(*p*-halophenyl)ethylenes **1a–1d**.



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The structure of the title complex, crystallising in the chiral space group $C222_1$, was determined by single crystal X-ray diffraction. Figure 1 shows the conformation of the host molecule. Steric strain is evident from deviations from 0 or 180° of the torsion angles involving the ethylenic bond C25–C26. Thus, the torsion angles C4–C25–C26–C16 and C10–C25–C26–C22 are –10(2) and –12(2)° respectively, indicating that the pivot atoms C4 and C22 of the phenyl groups lie above the mean plane including the double bond and its four bonded atoms, while the pivot atoms C10 and C16 lie below this plane. Inspection of the torsion angles describing the orientations of the iodophenyl substituents shows that the host molecule adopts approximately 222 symmetry.

The crystal structure is based on linear strands of guest fullerene molecules isolated from one another by intervening host and solvent molecules. In the [100] projection of the crystal structure shown in Fig. 2(a), linear arrays of guest C_{60} molecules are viewed along their stacking direction, the isolated arrays packing in a distorted hexagonal arrangement. Individual nearest neighbour C_{60} strands are separated by distances ranging from 15.6 to 18.4Å measured in the *bc*-plane. A single, representative strand of C_{60} molecules with surrounding host and solvent molecules is shown in Fig.2(b) in the [010] projection. The distance between the centres of two successive C_{60} molecules within a strand coincides with the crystal *a* axis (9.9993(2)Å at 297K). This distance is only 1% longer than that determined at 173K in the complex between C_{60} and *p*-bromocalix[4]arene propyl ether[1] which contains analogous isolated one-dimensional fullerene strands. In the latter complex, however, the calixarene molecules surrounding these strands pack with their dipole moments aligned unidirectionally. This polar host arrangement evidently induces an opposing dipole in the C_{60} molecules, which is responsible for their close spacing within a strand.[1] The interesting and contrasting feature of the present complex is that analogous guest strands occur in an environment of non-polar host **1d** molecules and toluene molecules.

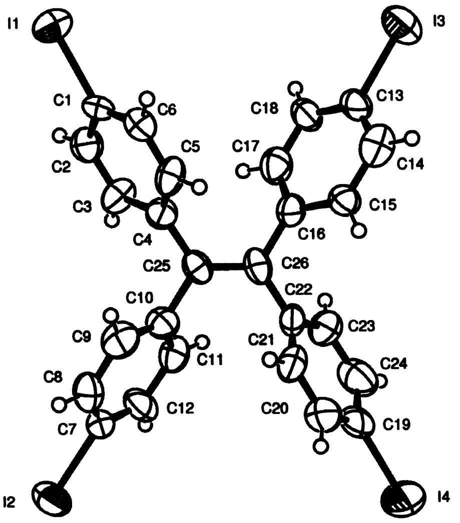

Fig.1 Conformation of the host molecule **1d**. The C–I distance range is 2.09(2)–2.11(2)Å and the ethylenic bond length C25–C26 is 1.38(2)Å. Atoms are drawn with 50% probability ellipsoids.

Figure 2(a) shows that the packing of the host and solvent molecules provides each C_{60} strand with a non-uniform environment. Each of two host molecules related by the C_2-axis parallel to *b* at z = $^1/_4$ presents a pair of iodophenyl rings to the C_{60} column. One iodophenyl ring of a pair faces one C_{60} molecule while the other ring faces a second C_{60} molecule translated one unit cell along *a*. The remaining neighbours of the column include both ordered and disordered toluene molecules and iodine atoms from adjacent host molecules. Due to the limited conformational flexibility of the host molecule, the

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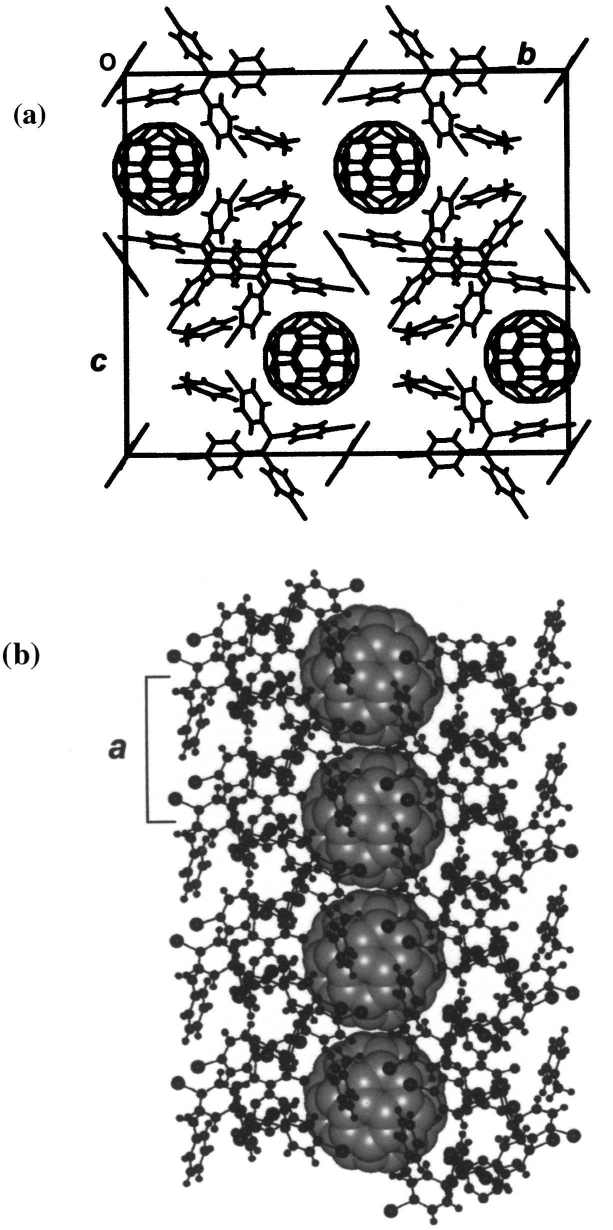

Fig.2 (a) Packing diagram viewed along [100], parallel to the linear columns of C_{60} molecules, and (b) a single column of C_{60} molecules with surrounding host and solvent molecules viewed approximately parallel to [010].

iodophenyl rings are not involved in strong π–π interactions with the fullerene molecules. Accurate interaction distances cannot be quoted due to guest disorder, but using the idealised C_{60} co-ordinates, host–guest aromatic ring centroid–centroid distances in the range 4.2–4.6Å were found. This differs significantly from the host–guest interaction occurring in the C_{60}-triptycene inclusion complex[1] in which the concave faces of two host molecules engage in very efficient ‘capping’ of a single C_{60} molecule. The present structure is further stabilised by iodine–π interactions, the strongest of these involving the solvent molecules. Host atom I1 is at 3.73 Å from the centroid of the ordered toluene molecule. The disordered solvent molecule is approached by two diad-related I3 atoms (one from either side) with I-centroid distance 4.00 Å.

In summary, non-polar host **1d** molecules form chiral inclusion crystals with C_{60} molecules together with toluene molecules by π–π and iodine–π interactions in which C_{60} molecules are arranged in linear columns.

Experimental

Preparation of inclusion crystal: When a solution of C_{60} (20 mg) and tetrakis(*p*-iodophenyl)ethylene **1d** (46 mg) in toluene (10 ml) was kept at room temperature for several days, an inclusion complex of C_{60}, **1d** and toluene in 1:2:3 ratio was obtained as black prisms (23 mg). Anal. Calc. For $C_{133}H_{56}I_8$: C, 59.85; H, 2.11. Found: C, 59.92; H, 2.24.

Crystal data for $C_{60}{\cdot}2(C_{26}H_{16}I_4){\cdot}3(C_7H_8)$, M = 2669.98, Calcd.: %C 59.85, %H 2.12, Found: %C 59.92, %H 2.24, black prism, orthorhombic, space group $C222_1$ (no.20), $a = 9.9993(2)$, $b = 33.6614(7)$, $c = 29.3134(7)$Å, Z = 4, V = 9866.6(4)Å^3, $D_c = 1.797$ g cm^{-3}, $D_m = 1.79(1)$ g/cm^3 (by flotation in CH_2I_2/PhCl mixture), $\mu = 2.57$ mm^{-1}, Nonius Kappa CCD diffractometer, Mo–Kα radiation, $\lambda = 0.71073$ Å, T = 297(2)K, $\theta_{max} = 24.7°$, 16095 reflections collected (98.0% completeness), 8016 unique reflections ($R_{int} = 0.043$). The structure was solved by direct methods (SHELXS97) and expanded by difference electron density syntheses. The asymmetric unit comprises one host molecule **1d**, half of a C_{60} molecule and 1.5 toluene molecules. The fullerene was located on the C_2-axis parallel to *b* (Wyckoff position (b)) and was severely disordered. It was modelled by an idealised half-molecule placed on the C_2-axis. Optimization of its orientation was attempted but the refinement was fairly insensitive to this process and significant difference electron density peaks remained. An ordered toluene molecule was located in the general eightfold position. A second toluene molecule was rotationally disordered on the C_2-axis parallel to *a* (Wyckoff position (a)). Refinement on F^2 with SHELXL97 involved thermally anisotropic host non-hydrogen atoms and isotropic refinement of those of the guest and solvent molecules. Hydrogen atoms were added to the host and the ordered solvent molecule in idealized positions in a riding model. No H atoms were added to the disordered toluene molecule. Refinement converged at $R_1 = 0.081$, $wR_2 = 0.250$, S = 1.015 for 325 parameters. The correct absolute structure was indicated by the Flack parameter, $\chi = -0.03(7)$. The maximum residual electron density of 1.02 eÅ^{-3} was found on the surface of the disordered fullerene molecule.

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