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The fullerenes—precursors for 21st century materials

A. G. Avent, P. R. Birkett, C. Christides, J. D. Crane, A. D. Darwish,
P. B. Hitchcock, H. W. Kroto, M. F. Meidine, K. Prassides, R. Taylor, and
D. R. M. Walton.

School of Chemistry and Molecular Sciences, University of Sussex, Falmer,
Brighton, East Sussex, BN1 9QJ, United Kingdom.

Abstract: The fullerenes represent a new *molecular* form of carbon. Their remarkable physico-chemical properties make them desirable as components in new materials, and in order to exploit these properties it is necessary to understand the principles for the preparation of both pure buckminsterfullerene (C_{60}) derivatives of known addition number and pattern, and C_{60} containing materials of known composition and structure. C_{60} is brominated by Br_2 in a variety of solvents to give either $C_{60}Br_6$ or $C_{60}Br_8$, depending upon the particular solvent used. Crystals of $C_{60}Br_6.Br_2.CCl_4$, $C_{60}Br_6.xBr_2$ ($x \approx 2$), and $C_{60}Br_8.xBr_2$ ($x \approx 2$) are obtained from CCl_4, C_6H_6, and CS_2 respectively. Reaction of C_{60} with ICl yields $C_{60}Cl_6$, which has the same addition pattern as $C_{60}Br_6$. Cocrystallisation of C_{60} and I_2 from $C_6H_5CH_3$ solution yields the intercalate $C_{60}.I_2.C_6H_5CH_3$ which contains discrete C_{60} and I_2 molecules. Slow evaporation of C_6H_6 solutions of C_{60} gives crystals of the solvate $C_{60}.4C_6H_6$. Mixing of saturated C_6H_6 solutions of C_{60} and $(\eta^5\text{-}C_5H_5)_2Fe$ gives a dark red solution from which black crystals of $C_{60}.2[(\eta^5\text{-}C_5H_5)_2Fe]$ are deposited. In a similar manner cocrystallisation of C_{60} and $(\eta^5\text{-}C_5H_5)_4Fe_4(CO)_4$ from C_6H_6 solution yields black crystals of the intercalate $C_{60}.(\eta^5\text{-}C_5H_5)_4Fe_4(CO)_4.3C_6H_6$.

INTRODUCTION

Synthesis

In 1985 the Rice/Sussex group discovered and named the first fullerene, the all-carbon molecule buckminsterfullerene (C_{60}) (1), the background of which has been amply reviewed (2,3). Its remarkable stability is a consequence of its structure; a closed hollow cage of sixty equivalent carbon atoms arranged as a truncated icosahedron (or soccer ball); twelve pentagons and twenty hexagons joined together so that no two pentagons share an edge.

In 1990 Krätschmer *et al.* succeeded in isolating macroscopic amounts of soluble fullerene mixtures by solvent extraction of the sooty deposit produced by the arc-vaporisation of graphite (4). These mixtures were composed mostly of C_{60} but also contained significant amounts of C_{70} (the next possible fullerene without edge-sharing pentagons) and traces of other higher fullerenes (C_{76}, C_{78}, *etc.*). In a parallel and independent study at Sussex, Taylor *et al.* succeeded in chromatographically separating pure C_{60} and C_{70} from such mixtures and characterised them by ^{13}C NMR (5). Subsequently the structures of some of the higher fullerenes have been deduced by similar methods (6,7,8,9), although to date only C_{60}, and to a much lesser extent C_{70}, are available in experimentally useful quantities to the synthetic chemist.

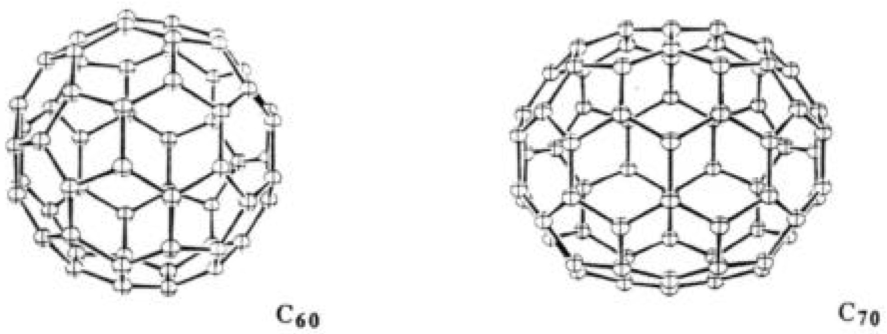

Fig. 1 Cage structures of I_h-C_{60} and D_{5h}-C_{70}.

Structure and properties

In contrast to the infinite structures of diamond and graphite, the fullerenes represent a pure *molecular* form of the element. They are closed hollow cages comprising exactly twelve pentagons and any number (n) of hexagons ($n \neq 1$) in which each carbon atom is approximately sp^2-hybridised. All the isolable fullerenes known to date also obey the Isolated Pentagon Rule; *i.e.*, no two pentagons share an edge. The first IPR-fullerene is the archetypal fullerene I_h-C_{60} (n = 20), more commonly refered to simply as C_{60}. The second possible member of the IPR-fullerene family is D_{5h}-C_{70} (Fig. 1), which is indeed the second most abundant fullerene.

Besides having a strong aesthetic appeal, the high symmetry of the C_{60} molecule has important consequences for its chemistry. Although all sixty carbon atoms are chemically equivalent, the structure contains two distinct bond types; the *inter*-pentagonal "double" bonds being short, typically ≈ 1.39 Å, whereas the *intra*-pentagonal "single" bonds are long, typically ≈ 1.44 Å (10,11). In pure C_{60} the near spherical molecules pack in a face-centred cubic (fcc) arrangement (Fig. 2). This structure contains large interstitial cavities which account for nearly 27% of the unit cell volume, and results in C_{60} being less than half as dense (1.65 g cm^{-3}) as diamond (3.51 g cm^{-3}).

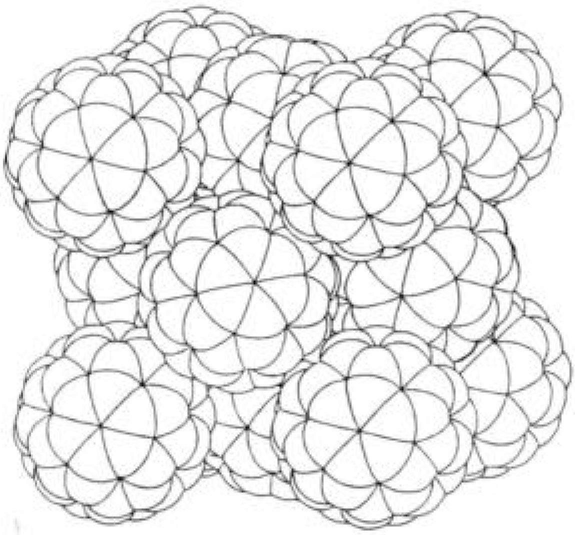

Fig. 2 Space filling representation of the face-centred cubic packing of pure C_{60}.

The electronic structure of C_{60} results in it being a good electron acceptor and weak oxidant, as well as conferring on it interesting physical and photophysical properties. Six reversible one electron reductions have been observed in solution, which correspond to the filling of the low lying t_{1u} LUMO (12,13), and metal salts formally containing $[C_{60}]^{12-}$ (*e.g.*, Ba_6C_{60}) have been prepared in the solid state, which corresponds to the filling of both the t_{1u} level and the next available t_{1g} level (14). Some of the group 1 and group 2 metal salts of C_{60} (in which the metal ions occupy the interstices) display superconductivity at low temperature with transition temperatures (T_c) of 33 K for $RbCs_2C_{60}$ and 8.4 K for Ca_5C_{60} (15,16). In addition, solutions of C_{60} (and C_{70}) display optical limiting properties (17).

In general C_{60} is best described as a partly delocalised electron-deficient poly-alkene rather than a superaromatic molecule, and much of the reported chemistry to date is consistent with this description (18,19). Although C_{60} is a moderately reactive molecule the preparation and characterisation of pure derivatives of known composition is a daunting challenge. With sixty carbon atoms (or thirty double bonds) available for reaction the number of possible isomers of $C_{60}X_n$ is large except for a few special cases (n = 1, 59, 60). This scale of this problem is illustrated by the fact that $C_{60}X_2$ has 23 different isomers, and if chemically distinct addends are involved the situation necessarily becomes worse. It is obvious that in the general case the separation of complex product mixtures is a difficult and time consuming problem. The logical solution is to develop experimental conditions under which only one major product is formed, in which a specific number of groups have added on to the cage with a known addition pattern.

The challenge of C_{60} chemistry is not solely concerned with the preparation of covalently functionalised derivatives. The synthesis and study of multicomponent molecular systems containing discrete C_{60} molecules is also an important avenue of research. In such systems the nature of the intermolecular (especially *inter*-C_{60}) contacts, and their effect on the bulk properties, is of particular interest. These *inter*-C_{60} contacts may be in all three dimensions, as in the fcc packing of pure C_{60}, or be restricted to two dimensions in close-packed layers or one dimensional structures. This structural anisotropy combined with the presence of non-covalent intermolecular interactions may lead to interesting bulk properties; *e.g.*, magnetism, electrical conduction, and photophysical properties.

HALOGENATED FULLERENES

$C_{60}Br_6$ and $C_{60}Br_8$

Reaction of C_{60} with Br_2 in CCl_4 and C_6H_6 solutions yields deep red crystals of formulation $C_{60}Br_6.Br_2.CCl_4$ and $C_{60}Br_6.xBr_2$ respectively (20). These compounds both contain the $C_{60}Br_6$ molecule (Fig. 3), and as there are no statistically significant differences between the two determinations only the data for the latter structure are reported. The most striking feature of the molecule is that the six bromine atoms are found aggregated in one region of the cage, centred on a pentagonal face. The peripheral five bromines have similar stereochemistries with an average C-Br bond length of 1.96(3) Å and the functionalised carbon atoms are sp^3-hybridised with tetrahedral geometries. The central bromine atom, Br^*, is the odd one out. It destroys the fivefold symmetry of the molecule and has a longer C-Br distance of 2.03(2) Å. The six bromine atoms surround an isolated planar *cis*-butadiene fragment with two double bonds of length 1.36(3) and 1.31(4) Å and a central single bond of length 1.47(3) Å. The portion of the C_{60} cage remote from the region of addition is unperturbed compared with C_{60} itself, with *inter*- and *intra*-pentagonal bonds averaging 1.38(3) and 1.45(3) Å respectively.

Reaction of C_{60} with Br_2 in CS_2 solution yields black crystals of formulation $C_{60}Br_8.xBr_2$ (x = 2) (20). As found for $C_{60}Br_6$, the bromine atoms in $C_{60}Br_8$ are gregarious and are all located in one region on the surface of the cage (Fig. 3). In $C_{60}Br_8$ however, the bromines are neither arranged around a pentagonal face nor are any two bound to adjacent carbon atoms. The arrangement of the eight bromine atoms in $C_{60}Br_8$ corresponds to one third of the structure of $C_{60}Br_{24}$ (21), the product obtained by reacting C_{60} with neat Br_2. This arrangement is noteworthy as it represents the maximum number of groups which can be bound to C_{60} so that no two are bound to adjacent carbon atoms, thus minimising unfavourable steric

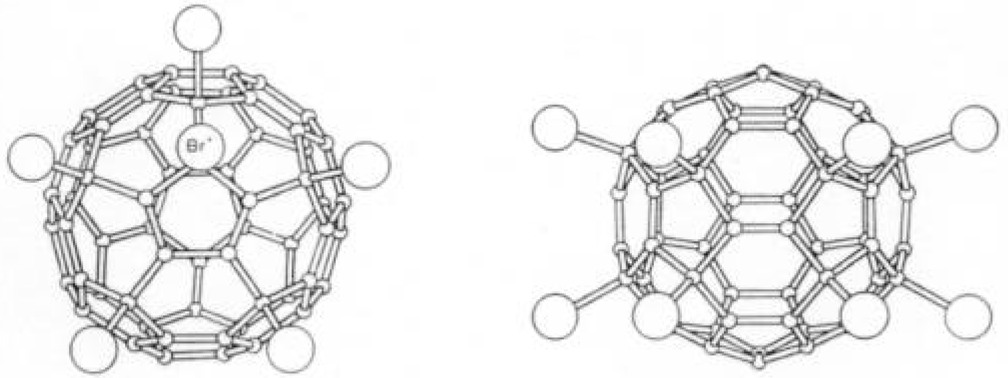

Fig. 3 The molecular structures of $C_{60}Br_6$ and $C_{60}Br_8$.

interactions between bulky groups. In $C_{60}Br_8$ the average C-Br bond length is 1.97(5) Å and the pattern of the bromines leaves three isolated double bonds; an inner one of length 1.27(15) Å and two equivalent outer ones of length 1.30(15) Å. The non-functionalised region of the cage is not significantly perturbed with averaged *inter*- and *intra*-pentagonal bond distances of 1.40(5) and 1.44(3) Å respectively.

$C_{60}Cl_6$

C_{60} reacts quantitatively with ICl in dry C_6H_6 to yield $C_{60}Cl_6$ (22). Although this molecule has not been characterised by single crystal *X*-ray diffraction its IR spectrum is similar to that of $C_{60}Br_6$ and its ^{13}C NMR spectrum ($CCl_4/CDCl_3$) is consistent with the same pattern of addition as $C_{60}Br_6$ (Fig. 4). A thirty-two line spectrum is observed due to the plane of symmetry through the molecule; twenty-eight sp^2-hybridised carbon signals (including two at half intensity) and four sp^3-hybridised carbon signals (including two at half intensity). Unlike $C_{60}Br_6$ and $C_{60}Br_8$ this compound is soluble in organic solvents and has potential as a precursor for many other C_{60} derivatives.

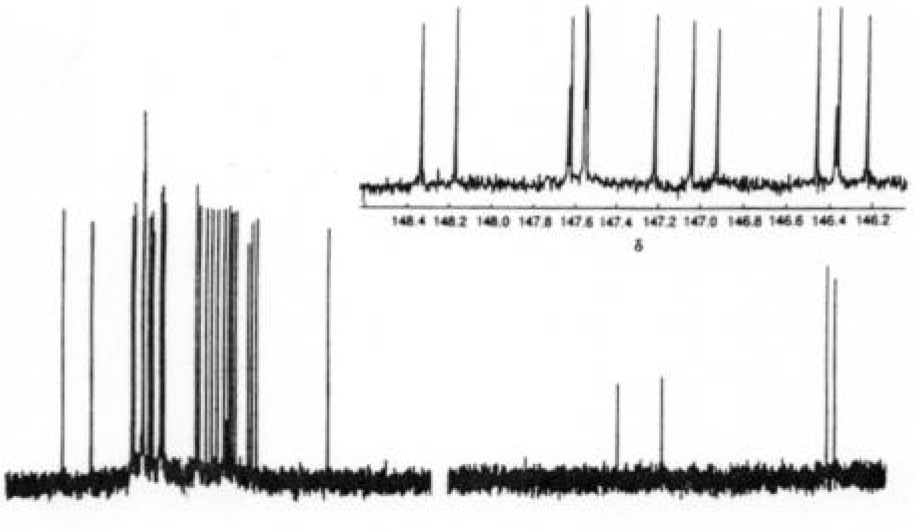

Fig. 4 The ^{13}C NMR spectrum of $C_{60}Cl_6$.

$C_{60}.I_2.C_6H_5CH_3$

Unlike Br_2, I_2 does not appear to react with C_{60} to form isolable addition products $C_{60}I_n$, but is reported to form the intercalate $C_{60}(I_2)_2$ (23). Solutions of C_{60} and I_2 in $C_6H_5CH_3$ do not form this compound however, but deposit black crystals of $C_{60}.I_2.C_6H_5CH_3$ (24). This compound crystallises in an orthorhombic space group and unfortunately the C_{60} molecule is disordered, with two orientations related by a mirror plane. The I_2 molecule lies on this mirror plane and has a normal bond length of 2.685(2) Å. A consequence of this disorder, combined with the presence of the heavy iodine atoms, is that the alternation in C-C bond lengths for the C_{60} cage is not observed; all C-C bond distances are found to be 1.43(3) Å and the average centre-to-carbon distance is 3.53 Å.

The more important features of this structure are the intermolecular interactions (Fig. 5). The *inter*-C_{60} contacts are over all three dimensions and each C_{60} molecule has eight nearest neighbours with centre-to-centre distances less than 12.5 Å; two at 9.97 Å, two at 9.99 Å, and four at 10.22 Å, with the next nearest C_{60} at 13.47 Å. The C_{60} molecules are also π-stacked to the disordered $C_6H_5CH_3$ molecules with closest $C(C_{60})$-$C(C_6H_5CH_3)$ distances of 3.23 and 3.33 Å. The C_{60}-I_2 interaction is especially interesting as it is particularly short, 3.09 Å to the nearest carbon, compared to the sum of van der Waals radii of 3.68 Å and the closest $C(C_{60})$-$I(I_2)$ distances of 3.60 to 4.00 Å reported for $C_{60}(I_2)_2$ (23). The second iodine atom of the I_2 molecule interacts with a carbon atom of the disordered $C_6H_5CH_3$ molecule, also at a very short distance of 3.13 Å. This indicates that the polarisable I_2 molecule may be acting as the "filling" in a donor:acceptor "sandwich"; *i.e.*, between the electron rich $C_6H_5CH_3$ molecule and the electron deficient C_{60} molecule.

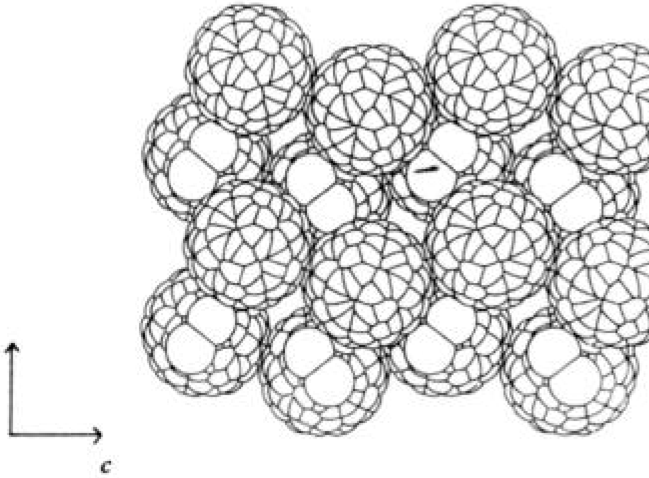

Fig. 5 Space-filling representations of the packing of the C_{60} and I_2 molecules in $C_{60}.I_2.C_6H_5CH_3$; view perpendicular to *bc* plane (both orientations of the disordered C_{60} molecules are included and the $C_6H_5CH_3$ molecules are omitted for clarity).

FULLERENE BASED MOLECULAR MATERIALS

$C_{60}.4C_6H_6$

Slow evaporation of a C_6H_6 solution of C_{60} gives black crystals of the solvate $C_{60}.4C_6H_6$ (25). At 173 K the C_{60} molecule shows no significant distortions from sphericity, with an average centre-to-carbon distance of 3.50(3) Å. Unfortunately the large atomic displacement parameters result in large variations in individual bond lengths and the average *inter*- and *intra*-pentagonal bond lengths are 1.32(9) and 1.48(13) Å. The *inter*-C_{60} contacts are over all three dimensions and each C_{60} molecule has six nearest neighbours with centre-to-centre distances less than 12.5 Å; two at 9.96 Å and four others at 10.01, 10.04, 10.10, and 10.28 Å. Of the four C_6H_6 molecules, three are π-stacked with a C_{60} molecule, and the fourth occupies an interstice between the other molecules.

$C_{60}.2(Cp_2Fe)$

Mixing of saturated C_6H_6 solutions of C_{60} and Cp_2Fe ($Cp = \eta^5\text{-}C_5H_5$) in the volume ratio 2:1 gives a deep red solution from which black plates of $C_{60}.2(Cp_2Fe)$ crystallise upon standing (11). The structure was determined at 143 and 296 K and was found to contain ordered C_{60} and Cp_2Fe molecules at both temperatures (Fig. 6); the structural data discussed in the text refer to the low temperature determination. In pure C_{60} the molecules are freely rotating at room temperature, and although this motion becomes restricted below 260 K it is only completely frozen out at about 90 K (26). This indicates that in $C_{60}.2(Cp_2Fe)$ there are significant intermolecular interactions capable of locking the C_{60} molecules into place.

The C_{60} molecule displays no significant distortions from sphericity with an average centre-to-carbon distance of 3.537(7) Å and the distinction between the two C-C bond types is well defined, with average *inter*- and *intra*-pentagonal distances of 1.387(6) and 1.450(6) Å. The study of space-filling models shows that the Cp_2Fe molecules efficiently fill the space left between the C_{60} molecules. The C_{60} molecules are arranged in close packed layers stacked directly above one another and separated by layers of Cp_2Fe molecules. The nearest neighbour centre-to-centre distances within these layers are 9,899(3), 10.366(4), and 10.396(3) Å. The closest centre-to-centre *inter*-C_{60} distance between layers is 11.342(3) Å. One Cp ring of the Cp_2Fe is parallel to a pentagonal face of the C_{60} at a distance of 3.3 Å, a value typical of π-stacking interactions between planar aromatic molecules, and in addition is slipped sideways by 0.8 Å, presumably due to crystal packing forces. Since the C_{60} molecule lies on an inversion centre the structure consists of separate, but interlaced, π-stacked $Cp_2Fe{:}C_{60}{:}Cp_2Fe$ sandwiches.

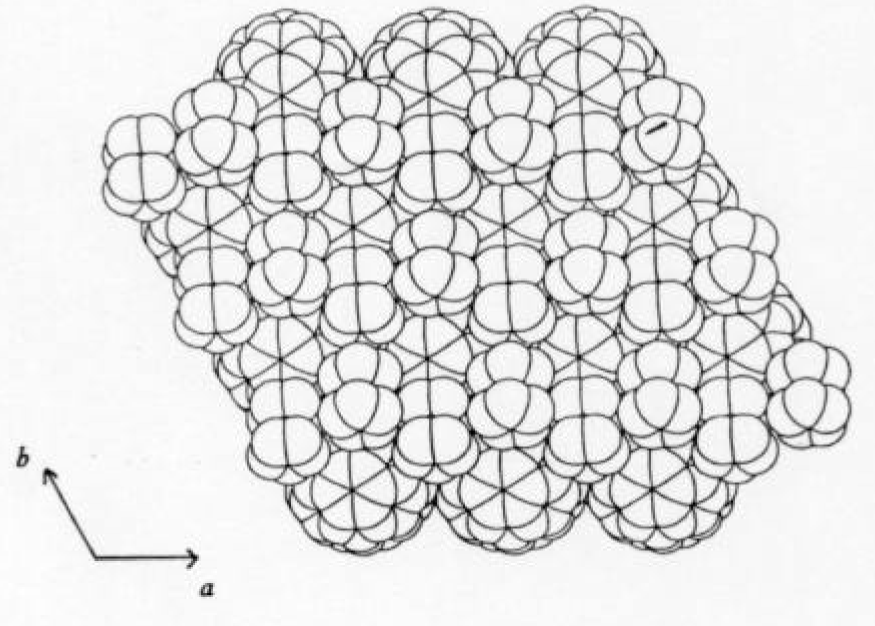

Fig. 6 Space-filling representation of the structure of $C_{60}.2(Cp_2Fe)$; view perpendicular to the *ab* plane showing how the Cp_2Fe molecules are arranged on the close-packed layer of C_{60} molecules.

$C_{60}.Cp_4Fe_4(CO)_4.3C_6H_6$

Crystallisation of C_{60} from a saturated C_6H_6 solution of $Cp_4Fe_4(CO)_4$ ($Cp = \eta^5\text{-}C_5H_5$) yields black needles of the lattice structure $C_{60}.Cp_4Fe_4(CO)_4$ as the solvate $C_{60}.Cp_4Fe_4(CO)_4.3C_6H_6$ (27). At the temperature of the crystal structure determination (173 K) all the molecules are ordered and possess no crystallographically imposed symmetry (Fig. 7). The C_{60} molecule shows no deviations from sphericity with an average centre-to-carbon distance of 3.52(2) Å and average *inter*- and *intra*-pentagonal bond lengths of 1.36(5) and 1.46(5) Å respectively.

The structure can be described as a three dimensional $C_{60}.Cp_4Fe_4(CO)_4$ host lattice with the guest C_6H_6 molecules occupying the interstitial cavities. The only *inter*-C_{60} contacts with centre-to-centre distances less than 12.5 Å occur within the double-columnar stacks parallel to the *a* axis; 9.94 (along *a* axis) and 9.91 Å, with the next nearest neighbour at 14.38 Å. The geometry of these contacts are similar to those found in the close-packed layers in $C_{60}.2(Cp_2Fe)$. Each stack is isolated from its neighbours by six co-parallel stacks of $Cp_4Fe_4(CO)_4$ molecules, which also act as *inter*-C_{60} bridges through C_{60}-Cp π-stacking interactions. Three of the four Cp rings are involved in π-stacking and the $Cp_4Fe_4(CO)_4$ molecule lies in an isoceles triangle of C_{60} molecules with closest $C(C_{60})$-C(Cp) contacts of 3.30(2), 3.35(2), and 3.36(2) Å for each ring.

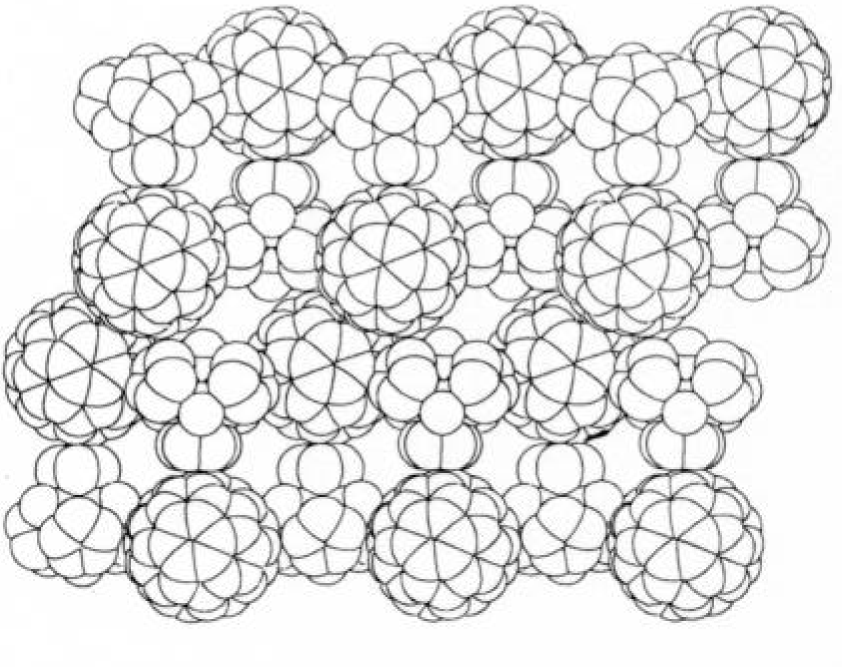

Fig.7 Space-filling representations of the $C_{60}.Cp_4Fe_4(CO)_4$ host lattice structure; view perpendicular to *bc* plane (C_6H_6 molecules omitted for clarity). The double-columnar stacks of C_{60} molecules are perpendicular to the plane of the paper (along *a* axis).

CONCLUSION

We have successfully used single crystal *X*-ray diffraction and ^{13}C NMR spectroscopy to determine the structures of a range of pure C_{60} containing compounds. The characterisation of the halogenated derivatives $C_{60}Br_6$, $C_{60}Br_8$, and $C_{60}Cl_6$ represents an important advance in fullerene chemistry. They could potentially exist as a mixture of a large number of isomers, but the structure of a single favoured pattern of addition has been established in each case. Molecular materials containing discrete C_{60} molecules have also been prepared and characterised. In $C_{60}.I_2.C_6H_5CH_3$, $C_{60}.4C_6H_6$, $C_{60}.2(Cp_2Fe)$, and $C_{60}.Cp_4Fe_4(CO)_4.3C_6H_6$ the structures are stabilised by favourable intermolecular interactions; *i.e.*, through the electron-deficient nature of C_{60} favouring association with electron-rich molecules. Furthermore it has been demonstrated that the geometry and number of *inter*-C_{60} contacts can be controlled, with the characterisation of three, two and one dimensional arrangements.

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