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The structure of buckminsterfullerene compounds☆

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Abstract

The fullerenes represent a new *molecular* form of carbon which has remarkable physico-chemical properties, making them desirable as components in new materials. An understanding of 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, is necessary for the development of fullerene chemistry. 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 $C_{60}Br_6 \cdot Br_2 \cdot CCl_4$, $C_{60}Br_6 \cdot xBr_2$ ($x \approx 2$), and $C_{60}Br_8 \cdot xBr_2$ ($x \approx 2$) are obtained from CCl_4, C_6H_6, and CS_2 respectively. Reaction of C_{60} with ICl in C_6H_6 yields $C_{60}Cl_6$, which is isostructural with $C_{60}Br_6$. Reaction of $C_{60}Cl_6$ under Friedel–Crafts conditions with C_6H_6 results in the formation of $C_{60}Ph_5Cl$ which is converted into $C_{60}Ph_5H$ by reaction with PPh_3 in C_6H_6. C_{60} undergoes a cycloaddition with C_5H_6 yielding $C_{60}C_5H_6$ which is stabilised with respect to the retro Diels–Alder reaction by either hydrogenation or bromination of the pendant C_5H_6 moiety to give $C_{60}C_5H_8$ and $C_{60}C_5H_6Br_2$ respectively. Cocrystallisation of C_{60} and I_2 from $C_6H_5CH_3$ solution yields the solvated intercalate $C_{60} \cdot I_2 \cdot C_6H_5CH_3$ which contains discrete C_{60}, I_2 and $C_6H_5CH_3$ molecules. Slow evaporation of C_6H_6 solutions of C_{60} gives crystals of $C_{60} \cdot 4C_6H_6$. 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 $C_{60} \cdot 2[(\eta^5\text{-}C_5H_5)_2Fe]$ 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 $C_{60} \cdot (\eta^5\text{-}C_5H_5)_4Fe_4(CO)_4 \cdot 3C_6H_6$.

1. Introduction

1.1. Synthesis

The first fullerene, the all-carbon molecule buckminsterfullerene (C_{60}) [1] was discovered in 1985 by the Rice/Sussex group; the subject has been amply reviewed [2,3]. C_{60} is remarkably stable as a consequence of its structure; sixty equivalent carbon atoms arranged as a closed hollow cage in the form of a truncated icosahedron (or soccer ball); twelve pentagons and twenty hexagons joined together so that no two pentagons share an edge.

Macroscopic amounts of soluble fullerenes were isolated by solvent extraction of the sooty deposit produced by the arc vaporisation of graphite in 1991 by Krätschmer et al. [4]. The mixture was 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

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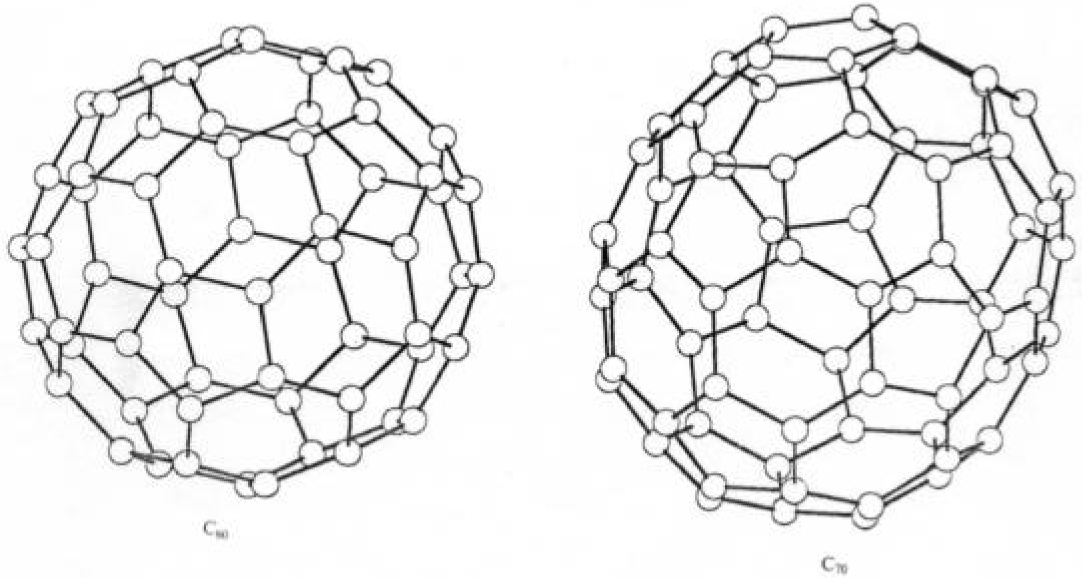


Fig. 1. Cage structures of I_h-C_{60} and D_{5h}-C_{70}.

and independent study at Sussex, Taylor et al. [5] separated pure C_{60} and C_{70} from such mixtures by column chromatography and characterised them using ^{13}C NMR spectroscopy. The structures of some of the higher fullerenes have subsequently been deduced by similar methods [6–9], although to date only C_{60}, and to a much lesser extent C_{70}, are available in experimentally useful quantities to the synthetic chemist.

1.2. Structure and properties

The fullerenes represent a pure molecular form of carbon in contrast to the infinite structures of graphite and diamond. 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 (IPR); i.e., no two pentagons share an edge. The first IPR-fullerene is the archetypal fullerene I_h-C_{60} ($n = 20$), more commonly referred to simply as C_{60}. The second possible member of the IPR-fullerene family is D_{5h}-C_{70} (Fig. 1), which is the second most abundant fullerene.

The high symmetry of the C_{60} molecule has important consequences for its chemistry. All sixty carbon atoms are chemically equivalent; however, 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. 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 ($3.51\,g\,cm^{-3}$).

C_{60} is a good electron acceptor and weak oxidant due to its electronic structure which also confers upon it interesting physical and photophysical properties. Six reversible one electron reductions have been observed in solution, corresponding to the filling of the triply degenerate low lying t_{1u} LUMO [12,13]. 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

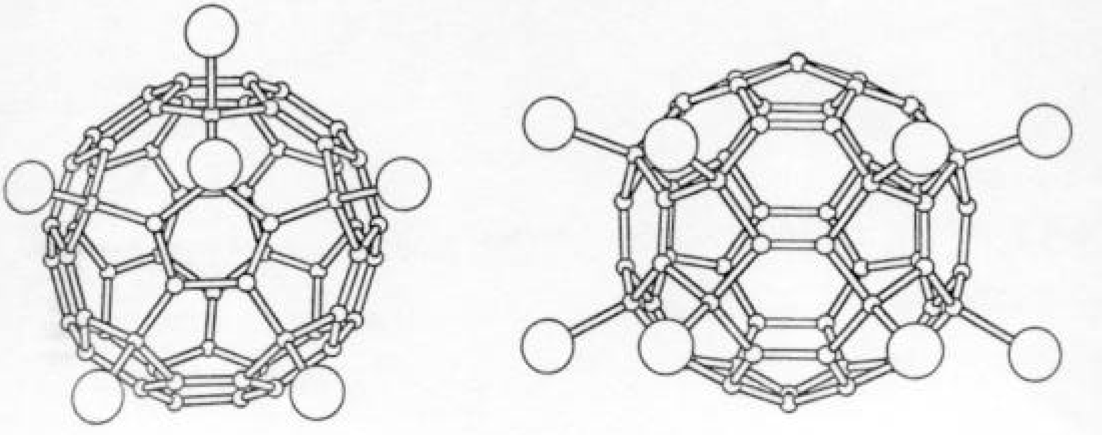


Fig. 2. The molecular structures of $C_{60}Br_6$ and $C_{60}Br_8$.

interstices) display superconductivity 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].

C_{60} is best described as a partly delocalised electron-deficient polyalkene rather than a superaromatic molecule, and much of the reported chemistry to date is consistent with this description [18,19]. Preparation and characterisation of pure derivatives of C_{60} is a daunting challenge. Sixty carbon atoms (or thirty double bonds) are available for reaction and therefore the number of possible isomers of $C_{60}X_n$ is large except for a few special cases ($n = 1, 59, 60$). The 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. In the general case the separation of complex product mixtures is a difficult and time consuming problem and therefore the logical solution is to develop experimental conditions under which only one major product is formed where a specific number of groups have added on to the cage in an established recognised pattern.

In addition to the preparation of covalently functionalised derivatives of C_{60}, the synthesis and study of multicomponent molecular systems containing discrete C_{60} molecules is also an important avenue of research. The nature of the intermolecular (especially inter-C_{60}) contacts and their effect on the bulk properties within such systems 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 may 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.

2. Halogenated fullerenes

2.1. $C_{60}Br_6$ 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 $C_{60}Br_6 \cdot Br_2 \cdot CCl_4$ and $C_{60}Br_6 \cdot xBr_2$ respectively [20]. These compounds both contain the $C_{60}Br_6$ molecule (Fig. 2), 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 to be aggregated in one region of the cage, centred on a pentagonal face. The five peripheral bromines are identically situated 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 $C_{60}Br_8 \cdot xBr_2$ ($x \approx 2$) [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. 2). 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 $C_{60}Br_{24}$ [20,21], 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 bromines are bonded to adjacent carbon atoms, thus minimising unfavourable steric interactions between these bulky atoms. 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.

2.2. $C_{60}Cl_6$

C_{60} reacts quantitatively with ICl in dry C_6H_6 to yield $C_{60}Cl_6$ [22]. This molecule has not been characterised by single crystal X-ray diffraction. However, 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. 3). Twenty-eight sp^2-hybridised carbon signals (including two at half intensity) and four sp^3-hybridised carbon signals (including two at half intensity) are observed. However, unlike $C_{60}Br_6$ and $C_{60}Br_8$ this compound is both stable and soluble in organic solvents; thus it is a valuable precursor for further C_{60} derivatives.

2.3. $C_{60}Ph_5Cl$ and $C_{60}Ph_5H$

Reaction of $C_{60}Cl_6$ with C_6H_6 and $FeCl_3$ results in formation of $C_{60}Ph_5Cl$ in good yield [23]. The five peripheral chlorines of $C_{60}Cl_6$ are replaced by phenyl moieties whilst the central chlorine remains unreacted (Fig. 4). The ^{13}C NMR spectrum (CS_2, $CDCl_3$ lock) is similar to that of $C_{60}Cl_6$ with 28 sp^2-hybridised carbon signals (two of half intensity) and four sp^3-hybridised carbon signals (two of half intensity) corresponding to the cage carbon atoms. In addition there are a further twelve signals which correspond to the carbon atoms of the five phenyl groups. Unlike $C_{60}Br_6$, $C_{60}Br_8$ and $C_{60}Cl_6$ which readily eliminate halogen under mass spectrometry conditions yielding C_{60}, $C_{60}Ph_5Cl$ is more stable allowing its molecular ion to be recorded, the first observed for a chloro-C_{60} derivative.

Reaction of $C_{60}Ph_5Cl$ with PPh_3 in wet C_6H_6 results in the formation of $C_{60}Ph_5H$, the central chlorine being replaced by a hydrogen atom (Fig. 4). Again, the ^{13}C NMR spectrum (CS_2, $CDCl_3$ lock) is similar to that of $C_{60}Cl_6$ and $C_{60}Ph_5Cl$. The ^1H NMR spectrum (CS_2, $CDCl_3$ lock) exhibits a complex series of multiplets in the aromatic region and an additional sharp singlet, compared to the spectrum obtained for $C_{60}Ph_5Cl$, due to the cage proton at δ 5.2 ppm. This class of phenylated C_{60} compound is particularly interesting due to the potential electron acceptor/donor properties of the molecule. The phenyl groups and central pentagon around which they are aggregated are electron rich and will behave as an electron donor region, whilst the remainder of the cage should behave in the same manner as unreacted C_{60}, i.e. as an electron acceptor.

2.4. $C_{60} \cdot I_2 \cdot C_6H_5CH_3$

Unlike Br_2 and Cl_2, I_2 does not appear to react with C_{60} to form isolable addition products $C_{60}I_n$, but does form the intercalate $C_{60}(I_2)_2$ [24]. Solutions of C_{60} and I_2 in $C_6H_5CH_3$ do not form this compound, however, but deposit black crystals of

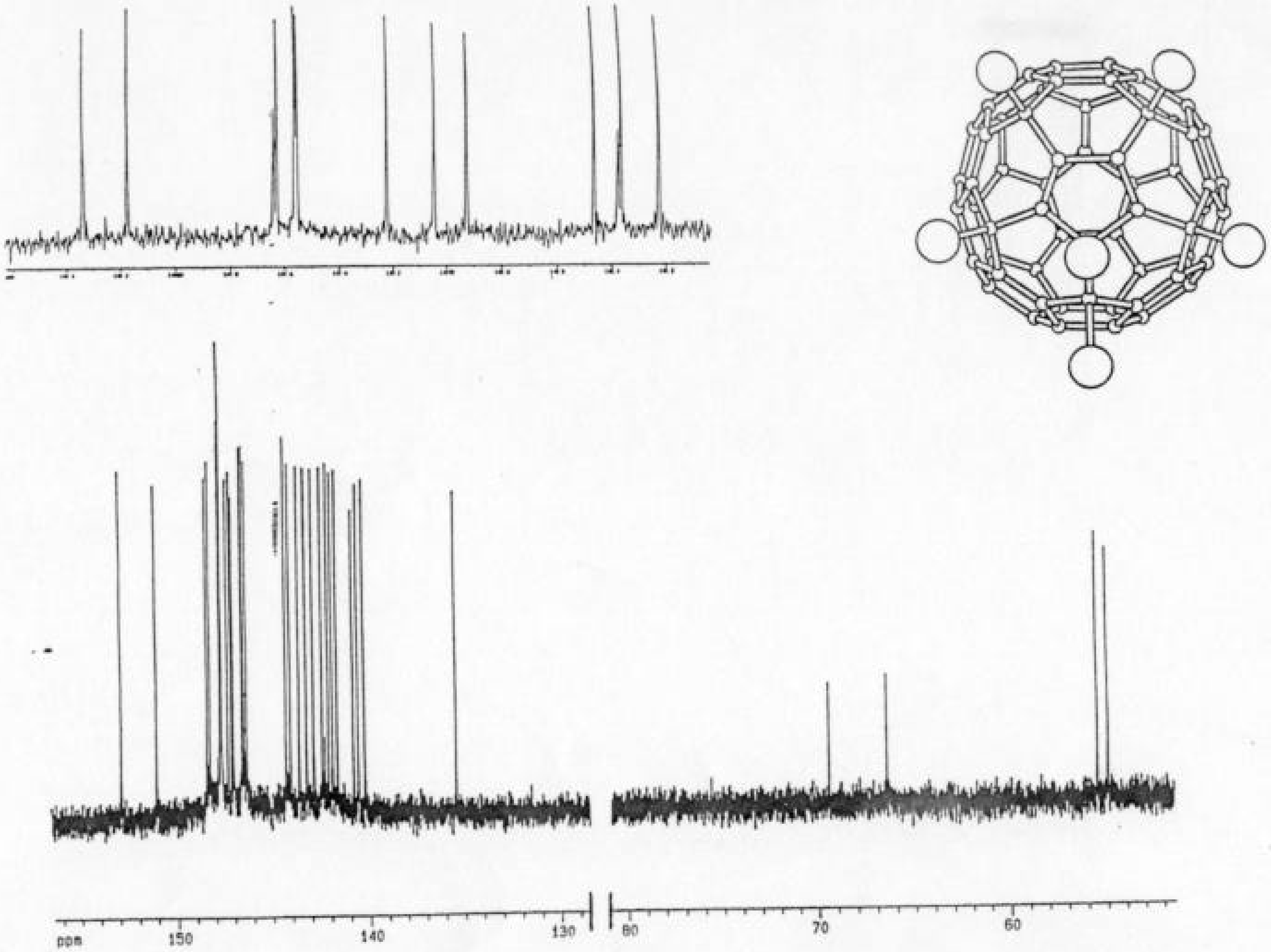
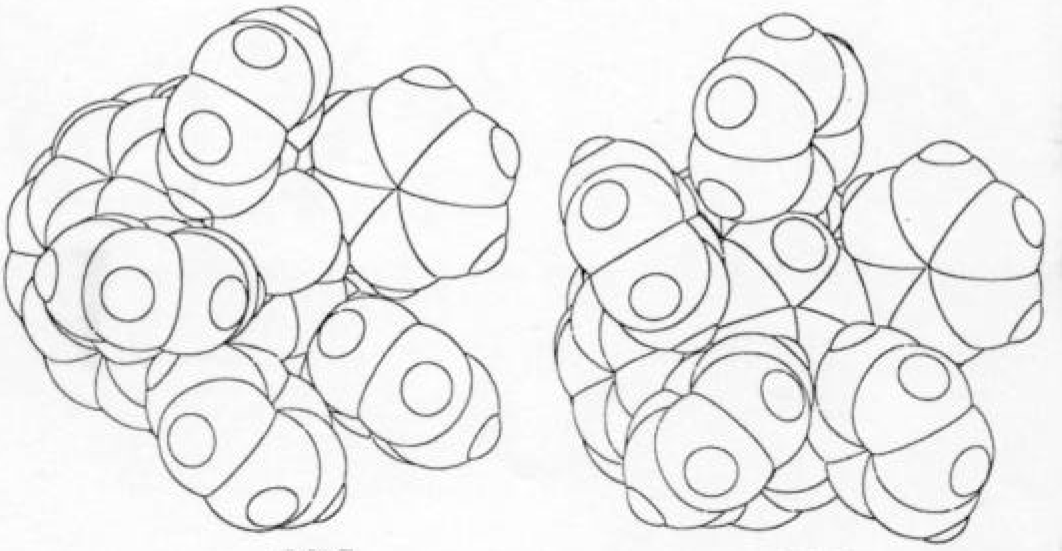


Fig. 3. The ^{13}C NMR spectrum of $C_{60}Cl_6$.



$C_{60}Ph_5Cl$

$C_{60}Ph_5H$

Fig. 4. Space-filling representations of the molecular structures of $C_{60}Ph_5Cl$ and $C_{60}Ph_5H$.

$C_{60} \cdot I_2 \cdot C_6H_5CH_3$ [25]. This compound crystallises in an orthorhombic space group, but 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 1.43(3) Å and the average radius of the C_{60} molecules 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 center-to-centre distances of 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 $C_{60}(I_2)_2$ [24]. The second iodine atom of the I_2 molecule also has a short $C(C_6H_5CH_3)$–$I(I_2)$ 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.

3. (2 + 4) Cycloadducts of fullerenes

3.1. $C_{60}C_5H_6$, $C_{60}C_5H_8$ and $C_{60}C_5H_6Br_2$

C_{60} reacts with one equivalent of cyclopentadiene to yield $C_{60}C_5H_6$ [26–29] (Fig. 6). The pendant bicyclopentene (C_5H_6) spans one of the interpentagonal (6:6) bonds with the C_{60} cage remaining closed. $C_{60}C_5H_6$ is stabilised with respect to the retro Diels–Alder reaction by the reduction of the double bond in the C_5H_6 moiety using Adam's catalyst which gives $C_{60}C_5H_8$ or by reaction with Br_2 which results in the formation of $C_{60}C_5H_6Br_2$ [26]. ^1H and ^{13}C NMR spectra, recorded for each of the derivatives, were in full accord with the proposed structures. The

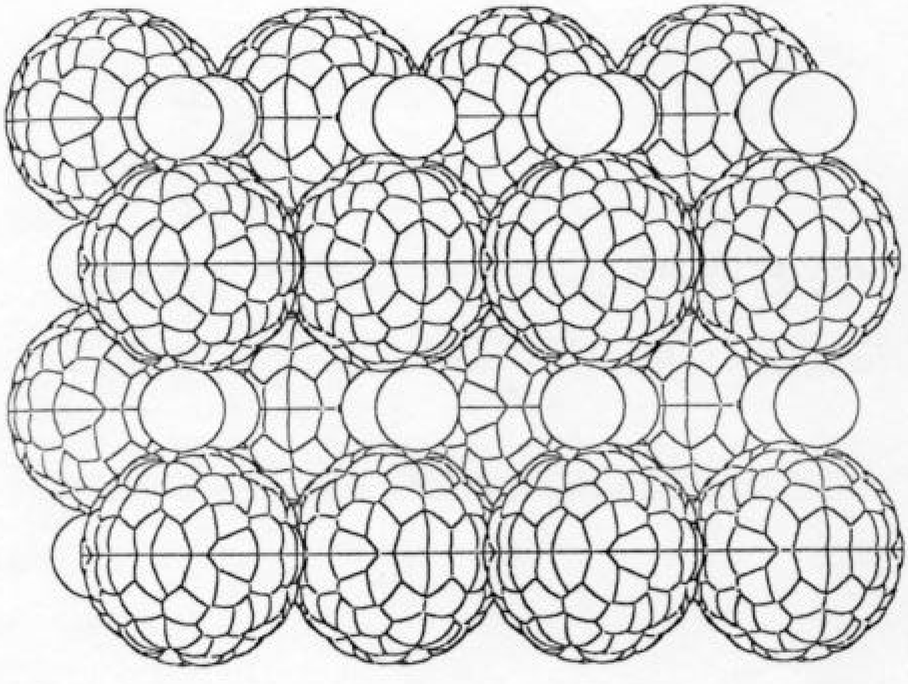


Fig. 5. Space-filling representation of the packing of the C_{60} and I_2 molecules in $C_{60} \cdot I_2 \cdot C_6H_5CH_3$; view perpendicular to the *ac* plane (both orientations of the disordered C_{60} molecules are included and the $C_6H_5CH_3$ molecules are omitted for clarity).

new compounds, $C_{60}C_5H_8$ and $C_{60}C_5H_6Br_2$, were sufficiently stable to allow their molecular ions to be observed using EI mass spectrometry, thus assisting in the identification of the less stable cycloadduct, $C_{60}C_5H_6$.

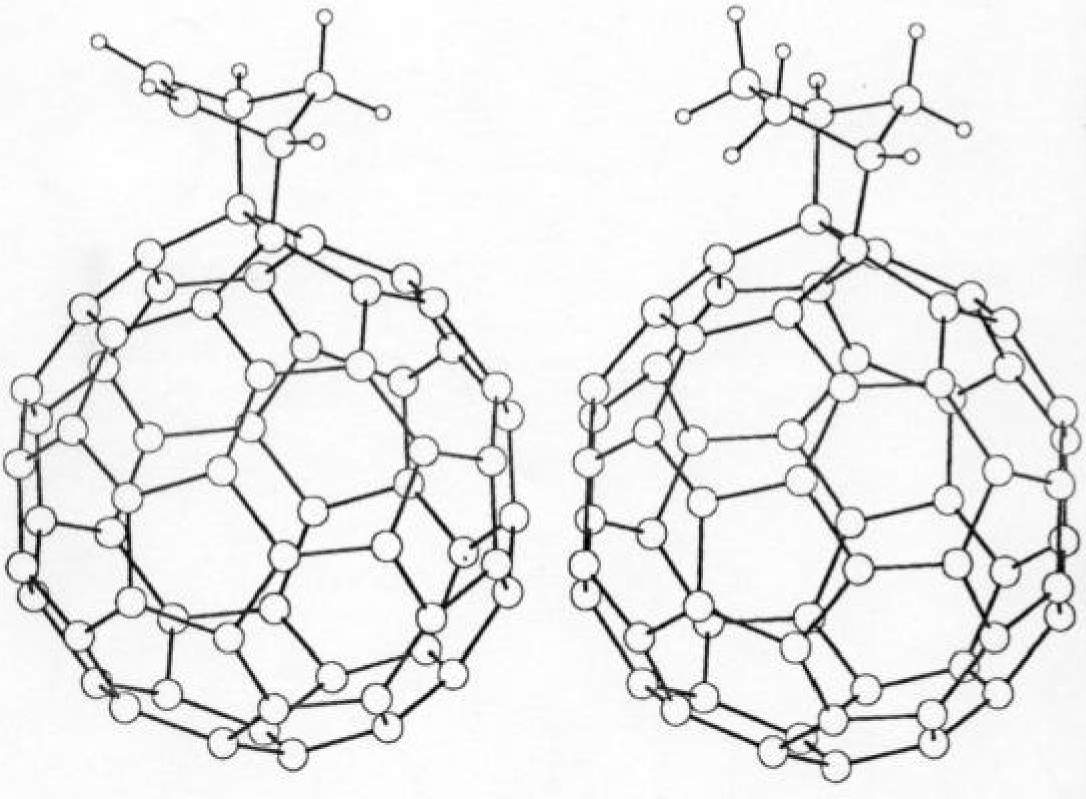
4. Fullerene-based molecular materials

4.1. $C_{60} \cdot 4C_6H_6$

Slow evaporation of a C_6H_6 solution of C_{60} gives black crystals of the solvate $C_{60} \cdot 4C_6H_6$ [30]. At 173 K the C_{60} molecule shows no significant distortions from sphericity, with an average radius of 3.50(3) Å. 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.

4.2. $C_{60} \cdot 2(Cp_2Fe)$

Mixing saturated C_6H_6 solutions of C_{60} and Cp_2Fe ($Cp = \eta^5$-C_5H_5) in the volume ratio 2 : 1 gives a deep red solution from which black plates of $C_{60} \cdot 2(Cp_2Fe)$ 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. 7); 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



$C_{60}C_5H_6$ $C_{60}C_5H_8$

Fig. 6. Ball and stick representations of the molecular structures of $C_{60}C_5H_6$ and $C_{60}C_5H_8$.

below 260 K it is only completely frozen out at about 90 K [31]. This indicates that in $C_{60} \cdot 2(Cp_2Fe)$ 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 radius 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 the ring 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.

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

Crystallisation of C_{60} from a saturated C_6H_6 solution of $Cp_4Fe_4(CO)_4$ yields black

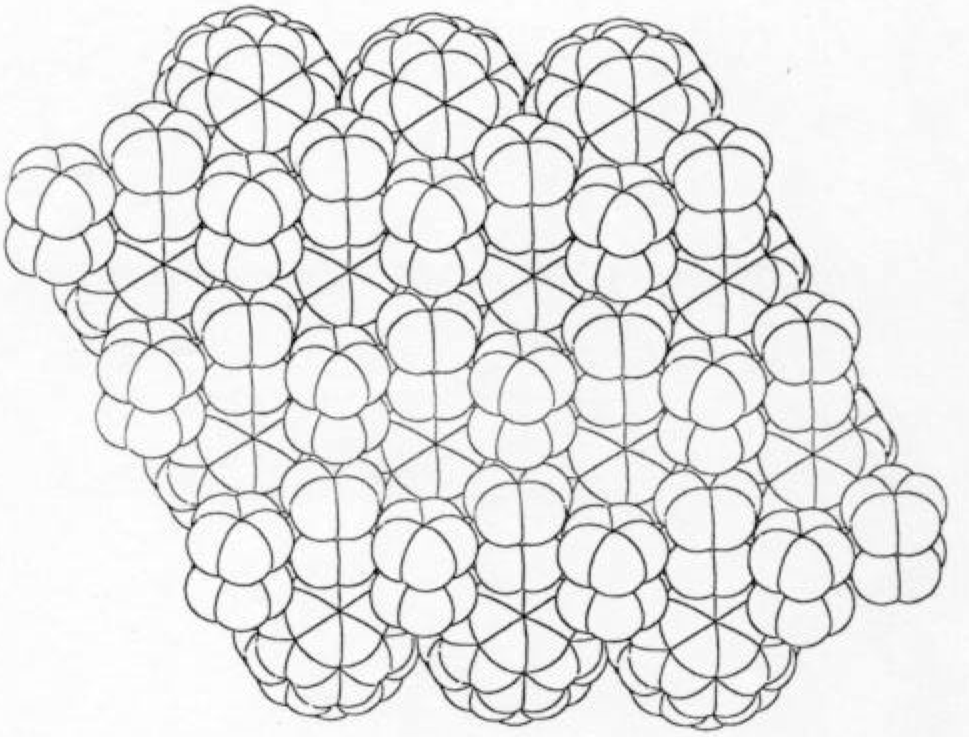


Fig. 7. Space-filling representation of the structure of $C_{60} \cdot 2(Cp_2Fe)$; view perpendicular to the *ab* plane showing how the Cp_2Fe molecules are arranged on the close-packed layer of C_{60} molecules.

needles of the lattice structure $C_{60} \cdot Cp_4Fe_4(CO)_4$ as the solvate $C_{60} \cdot Cp_4Fe_4(CO)_4 \cdot 3C_6H_6$ [32]. At the temperature of the crystal structure determination (173 K) all the molecules are ordered and possess no crystallographically imposed symmetry (Fig. 8). 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) Å and 1.46(5) Å respectively.

The structure can be described as a three dimensional $C_{60} \cdot Cp_4Fe_4(CO)_4$ 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 the *a* axis) and 9.91 Å, with the next nearest neighbour at 14.38 Å. The geometry of these contacts is similar to that found in the close-packed layers in $C_{60} \cdot 2(Cp_2Fe)$. 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.

5. Conclusion

We have successfully used single crystal X-ray diffraction, ^{13}C and ^{1}H NMR spectroscopies to determine the structures of a range of pure C_{60}-containing compounds. The characterisation of

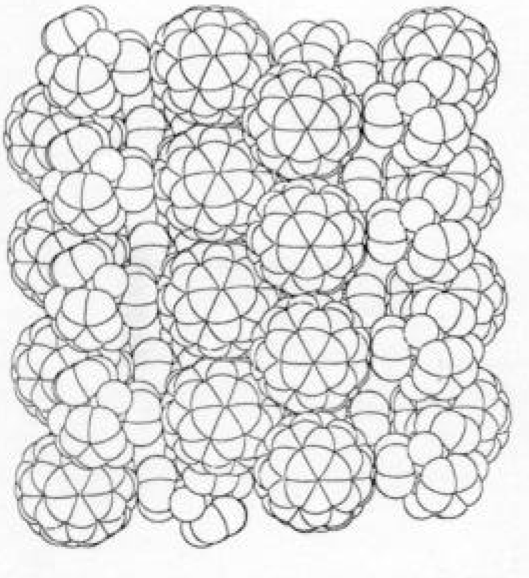


Fig. 8. Space-filling representation of the $C_{60}\cdot Cp_4Fe_4(CO)_4$ host lattice structure; view perpendicular to the *ac* plane (C_6H_6 molecules omitted for clarity).

the halogenated derivatives $C_{60}Br_6$, $C_{60}Br_8$, and $C_{60}Cl_6$ represents an important advance in fullerene chemistry. Each 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. Additionally, $C_{60}Cl_6$ has been shown to be an important synthon in fullerene synthesis, allowing the preparation of $C_{60}Ph_5Cl$ and $C_{60}Ph_5H$ in good yield. Reaction of thermally unstable derivatives such as $C_{60}C_5H_6$ yielding new more stable homologues, in this case $C_{60}C_5H_8$ and $C_{60}C_5H_6Br_2$, by selective reaction of pendant functionality is shown to be an important procedure to assist in the identification of new fullerene derivatives. Molecular materials containing discrete C_{60} molecules have also been prepared and characterised. In $C_{60}\cdot I_2\cdot C_6H_5CH_3$, $C_{60}\cdot 4C_6H_6$, $C_{60}\cdot 2(Cp_2Fe)$, and $C_{60}\cdot Cp_4Fe_4(CO)_4\cdot 3C_6H_6$ 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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