PERKIN 2

Isolation and spectroscopic characterisation of $C_{60}F_{17}CF_2CF_3$ and isomers of $C_{60}F_{17}CF_3$; insertion of :CF_2 into fluorofullerene C–F bonds

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The perfluoroalkylfluoro[60]fullerenes $C_{60}F_{17}CF_2CF_3$ (C_s) and three isomers of $C_{60}F_{17}CF_3$ [C_s (major, 65%), enantiomeric C_1 pair (minor, 35%)] have been separated by HPLC from the many products obtained by fluorination of [60]fullerene by K_2PtF_6 at *ca.* 465 °C. They have been characterised by ^{19}F NMR spectroscopy, and for the trifluoromethyl compound, by single crystal X-ray structure determination. The trifluoromethyl compound shows either *extremely weak* or *no* resonances for the CF_3 group in the ^{19}F NMR spectrum, which led to an earlier misidentification of the major isomer in this compound as a CF_2 derivative. Isolation of these compounds indicates that trifluoromethyl compounds are formed under these conditions by insertion of :CF_2 groups (from fragmentation of other fluorinated fullerene cages) into C–F bonds.

Introduction

Hydrogenation of fullerenes results in formation of methylene species from cage fragmentation, which add to other intact hydrogenated cages. This gives rise for example to the formation of species of 780 amu[1] [believed to be $C_{60}H_{18}(CH_2)_3$, rather than $C_{60}H_{60}$]. Fragmentation giving difluoromethylene species likewise accompanies fluorination[2] (which like hydrogenation, is a radical addition process). The formation of methanofullerenes (in which a methylene group is added across a fullerene 'double' bond) is well established,[3] hence the analogous addition of difluoromethylene could be expected. Strong circumstantial evidence that difluoromethanofullerenes exist is obtained during mass spectrometry of $C_{60}(CF_3H)_n$ derivatives, which eliminate HF (20 amu) when the CF_3 and H addends are adjacent.[4]

Recently, from the fluorination of [60]fullerene by K_2PtF_6, we isolated by HPLC a fraction of 1112 amu from amongst the numerous fluorofullerene products.[5] This is consistent with either $C_{60}F_{18}CF_2$ or $C_{60}F_{17}CF_3$. Analysis by both 1 D and 2 D ^{19}F NMR spectroscopy showed the following features:

1. The fraction consisted of a mixture of C_s (major) and C_1 (minor) components, in a 65:35 ratio.
2. Both components were based on the $C_{60}F_{18}$ motif.
3. There were *no resonances for the CF_3 group in the ^{19}F NMR spectrum*, indicating that the major component could not be $C_{60}F_{17}CF_3$, leaving $C_{60}F_{18}CF_2$ as the only feasible alternative. Moreover, addition of the CF_2 group across a double bond would give a three-membered ring (literature values are −143.2, −142.7 and −143.2 for CF_2 in such rings),[6] a peak at −143 ppm in the spectrum being attributed to this group.

We have now isolated a further quantity of this material, obtained further 1 D and 2 D ^{19}F NMR spectra as well as a single crystal X-ray structure and find, despite the NMR evidence, that it consists of three isomers of $C_{60}F_{17}CF_3$ *viz.* a major C_s isomer and a minor enantiomeric pair of C_1 isomers. We have isolated also a species of 1162 amu which in principle could be either $C_{60}F_{17}CF_2CF_3$ or $C_{60}F_{18}(CF_2)_2$, but is unambiguously shown to be the former. We now describe the full characterisation of all of these components, propose a mechanism by which they are formed and draw attention to the major problem that arises in the ^{19}F NMR analysis of CF_3-containing fullerenes.

Experimental

[60]Fullerene (*ca.* 300 mg) was fluorinated at *ca.* 0.1 bar/465 °C. A dry toluene solution of the crude fluorofullerene mixture was carefully filtered and purified by HPLC, (10 mm × 250 mm Cosmosil Buckyprep column) with toluene elution at a flow rate of 4.7 ml min^{-1} (≡1 ml min^{-1} for a 4.6 mm diameter column). This gave recovered [60]fullerene (*ca.* 75 mg), $C_{60}F_{18}$[7] (*ca.* 200 mg) together with 20 other components in 2–10 mg yields.

Mass spectra (EI 70 eV)

The species eluting at 30 and 28 min gave parent ions of 1112 and 1162 amu (Fig. 1), respectively; the spectrum for the 1112 amu species was identical to that given previously.[1] Fig. 1 ($C_{60}F_{17}C_2F_5$) solves an ongoing problem associated with fluorofullerene mass spectra, namely the frequent appearance of fragmentation ions at 790 and 860 amu, which could arise from $C_{60}F_2O_2$ or $C_{60}CF_3H$, and $C_{60}(F_2O_2)_2$ or $C_{60}(CF_3H)_2$, respectively. Whilst the oxides are rather improbable (given the parent compounds), the hydrogenated species often fail to show the expected M − 1 mass peak.

These peaks are observed in the present case also, but the main fragmentation ion at 840 amu (which is not due to [70]fullerene because of the M + 1 isotope peak intensity and HPLC retention time) clearly arises from $C_{60}C_2F_5H$, there being no mass-equivalent oxide. This fragment is notable in being able to undergo 1,2-elimination of HF (unlike $C_{60}CF_3H$), to give a peak of 820 amu (see Fig. 1).

^{19}F NMR spectra

The peak data are given in Table 1 and the 1 D spectrum for the 1112 species is shown in Fig. 2. This is identical in the cage-F region to that obtained previously,[1] as is the 2 D spectrum (not shown).

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Table 1 Chemical shifts (ppm) and integrated intensities (*n*)[a] for the cage-F fluorines in $C_{60}F_{18}$, $C_{60}F_{17}C_2F_5$ and the major/minor isomers of $C_{60}F_{17}CF_3$

$C_{60}F_{18}$			$C_{60}F_{17}C_2F_5$			$C_{60}F_{17}CF_3$ (major)			$C_{60}F_{17}CF_3$ (minor)		
Shift	*n*	Posn.	Shift	*n*	Posn.	Shift	*n*	Posn.	Shift	*n*	Posn.[b]
−131.6	3	A	−130.97	2	A	−130.99	2	A	−131.45	1	a^2
									−131.62	1	a^1
									−131.82	1	a
									−133.62	1	c^4
									−135.48	1	c^1/c^2
−136.0	6	C	−136.32	2	C	−136.28	2	C	−135.94	2[c]	c/c^5, c^3
			−136.45	2	C′	−136.42	2	C′	−136.42	2[c]	c/c^5, c^1/c^2
			−137.47	2	C″	−138.0	2	C″			
									−139.40	1	d^4
									−142.32	1	d^3
			−142.84	2	D′	−143.26	2	D′			
−143.4	6	D	−143.35	2	D	−143.29	2	D	−143.50	2[c]	$d/d^1/d^2$
									−143.62	1	$d/d^1/d^2$
			−146.01	2	D″	−145.18	2	D″			
			−153.05	1	B′	−156.93	1	B′	−157.08	1	b^2
−158.1	3	B	−157.85	2	B	−157.75	2	B	−157.79	1	b^1
									−157.94	1	b

[a] Intensities for the minor isomer of $C_{60}F_{17}CF_3$ are 54% of that for the major isomer. [b] Where alternatives are shown, no distinction can be made from the 2 D data. [c] Coincident peaks.

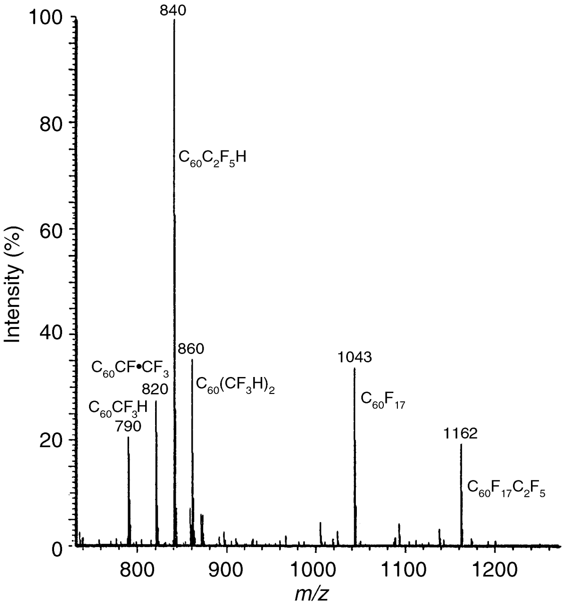

Fig. 1 EI mass spectrum (70 eV) for $C_{60}F_{17}CF_2CF_3$ (1162 amu).

Results and discussion

$C_{60}F_{18}$

Fig. 3a shows the Schlegel diagram for C_{3v} $C_{60}F_{18}$, characterised previously.[7] There are four distinct fluorines and these are labelled A–D as in ref. 5. Features of this molecule, used in identifying the fluorines in the $C_{60}F_{17}C_2F_5$ and $C_{60}F_{17}CF_3$ derivatives are:

(i) Fluorines B, which have three sp^3 neighbours, are the most upfield.

(ii) Fluorines A, which have one sp^3 and two sp^2 neighbours, are the most downfield.

(iii) Fluorines C and D each have two sp^3 and one sp^2 neighbours, but C nearest to the central aromatic[8] ring are more downfield.

$C_{60}F_{17}C_2F_5$ and the major isomer of $C_{60}F_{17}CF_3$

The peaks for these compounds, labelled in Fig. 3b, are identified as follows:

(i) Peaks A–D are the most remote from the perturbing perfluoroalkyl groups and can be expected to have virtually the same chemical shifts as in $C_{60}F_{18}$. Four such peaks are found (Table 1), moreover peaks A and B are unique (the latter is of 2 F intensity, whereas B′ is of 1 F intensity).

(ii) Peak B′ is downfield compared to B and the corresponding position in $C_{60}F_{18}$ due to the stronger electron-withdrawing effect of CF_3 (and of C_2F_5) compared to F.[9]

(iii) There are differences in shift magnitudes between the CF_3 and C_2F_5 compounds, which can be attributed to a through-space effect that is possible in the latter. Thus the resonances for fluorines B′, C″, and D′ are more downfield in the C_2F_5 compounds by 3.88, 0.53 and 0.42 ppm, respectively; by contrast fluorine D″ is more upfield (by 0.83 ppm) due probably to induced polarisation arising from the neighbouring C″ and D′ fluorines. All other resonances are essentially identical in both compounds.

The minor isomer of $C_{60}F_{17}CF_3$

The peaks for these compounds, labelled in Fig. 4, are identified as follows:

(i) The lack of a symmetry plane results in three non-equivalent ‘a’ and ‘b’ fluorines. Fluorine b^2 is in the vicinity of the CF_3 group and the resonance is therefore shifted downfield relative to those for b and b^1; the latter is nearer to the CF_3 group and so its resonance is assumed to be the more downfield of the pair.

(ii) Fluorines a and a^1 are assigned by coupling to b and b^1 respectively. Fluorine a^2 shows no coupling in the 2 D spectrum but is both the most downfield, and broadened due to interaction with the nearby CF_3 group.

(iii) The resonance for fluorine c^4 is significantly more downfield than the other ‘c’ fluorines due to the adjacent CF_3 group; it is also strongly coupled to fluorine b^2. Fluorine c^3 is identified by coupling to fluorine b^2. One of fluorines c^1 and c^2 (which cannot be distinguished) is coupled to fluorine b. Likewise one of fluorines c or c^5 is coupled to b^1.

(iv) The ‘d’ fluorines do not show any coupling. However, the very downfield peak at −139.4 ppm can be assigned to d^4, the shift arising from the adjacent CF_3 group; this adjacency also causes substantial broadening of the peak. The peak at −142.32 ppm can probably be assigned to d^3 as it is the next nearest to the CF_3 group; the other ‘d’ fluorines cannot be distinguished.

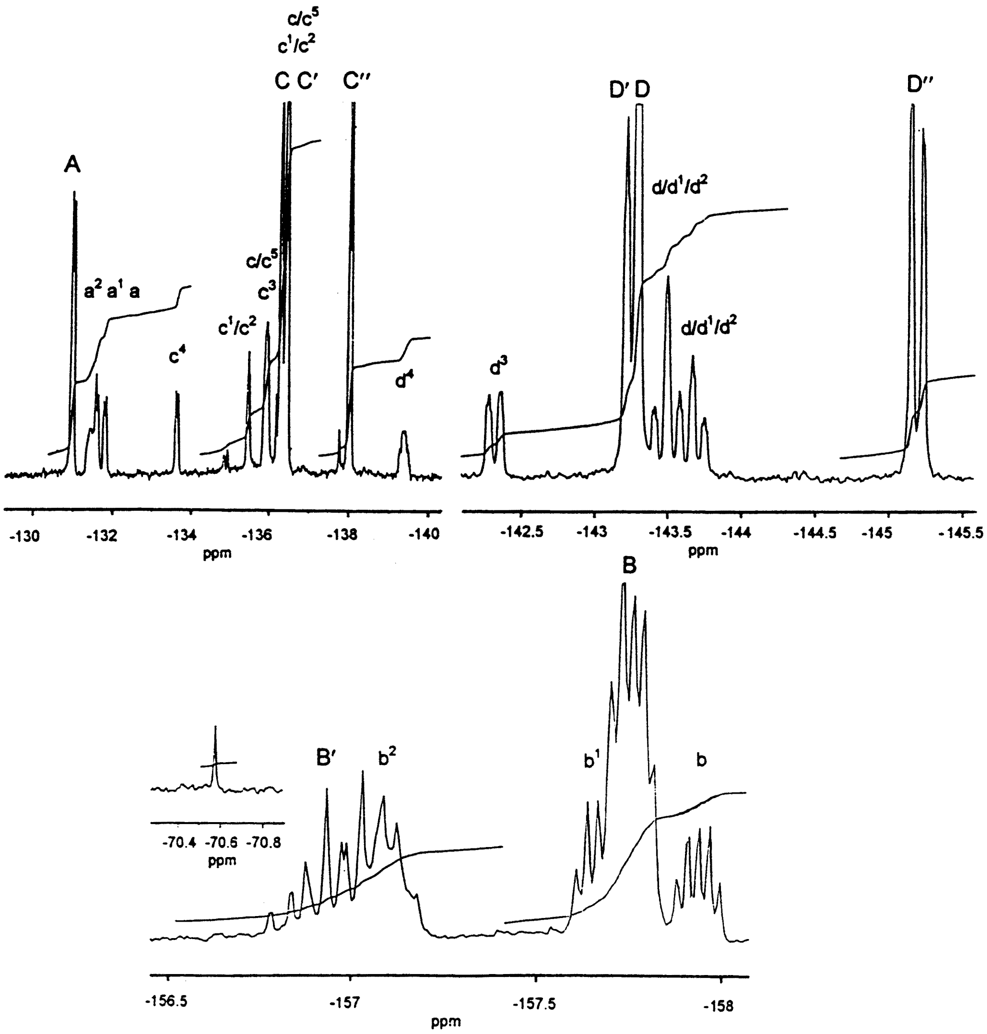

Fig. 2 ^{19}F NMR spectrum (338.9 MHz) for the mixture of $C_{60}F_{17}CF_3$ isomers.

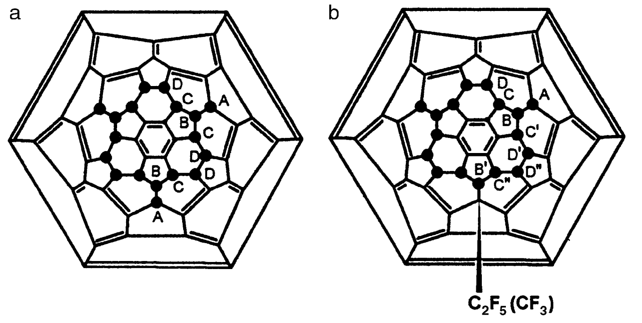

Fig. 3 Schlegel diagrams for (a) $C_{60}F_{18}$ and (b) $C_{60}F_{17}C_2F_5$/$C_{60}F_{17}CF_3$; ^{19}F NMR chemical shifts for the labelled fluorines are given in Table 1.

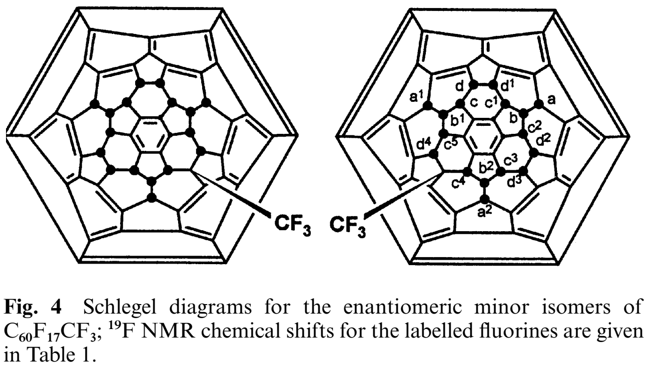

Fig. 4 Schlegel diagrams for the enantiomeric minor isomers of $C_{60}F_{17}CF_3$; ^{19}F NMR chemical shifts for the labelled fluorines are given in Table 1.

The problem of the CF_3 signal

As noted in the Introduction, the spectrum that we obtained previously for the 1112 amu component showed no resonance for the CF_3 group, which led us to believe that this compound was $C_{60}F_{18}CF_2$. (This spectrum was duplicated on two separate instruments, and run by extremely experienced operators.) The present spectrum is identical in every respect to that previous one except that a very small peak can be seen for a CF_3 group at −70.58 ppm. However, assuming that this is due to the major isomer, the intensity is just 3% of that required; if it is due to the minor isomer it is 5% of that required. We have no explanation for this deficiency, but note that signals for this group are absent in the ^{19}F NMR spectra of a number of other compounds, clearly indicated by the mass spectra to contain the CF_3 group, which we have isolated. In other cases, peaks are seen in the −(63–70) ppm region.

The single crystal X-ray structure†

Crystals of $C_{60}F_{17}CF_3$ were grown from toluene. The molecular structure (Fig. 5) is disordered and shows the CF_3 group to occupy an ‘a’ position (C10) to the extent of 68% and two enantiomeric ‘d’ positions (C2 and C37) to the extent of 16% each. This 68:32 ratio is in excellent agreement with that (65:35) deduced from the NMR spectrum. Fig. 6 shows a side view of the main isomer.

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† CCDC reference number 188/274. See http://www.rsc.org/suppdata/p2/b0/b006890j/ for crystallographic files in .cif format.

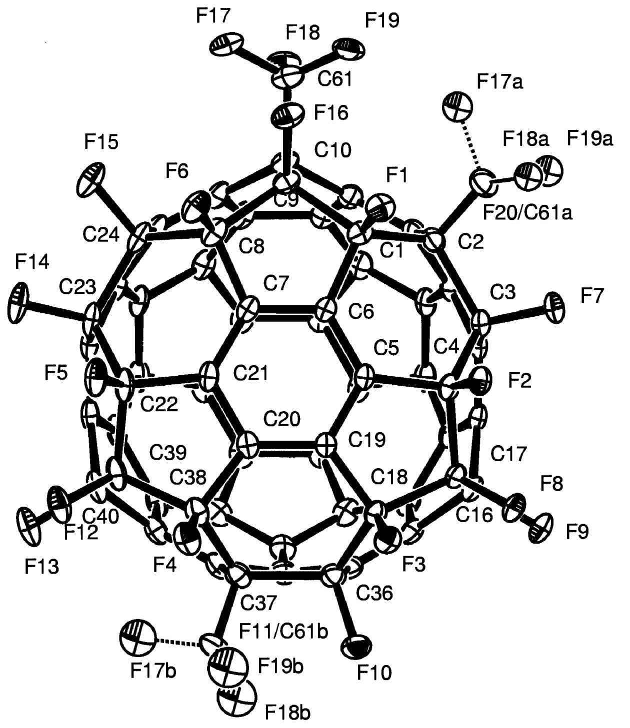

Fig. 5 Single crystal X-ray structure (disordered) for $C_{60}F_{17}CF_3$ showing occupancy at C10 (major C_s isomer) and C2/C37 (minor enantiomeric C_1 isomers).

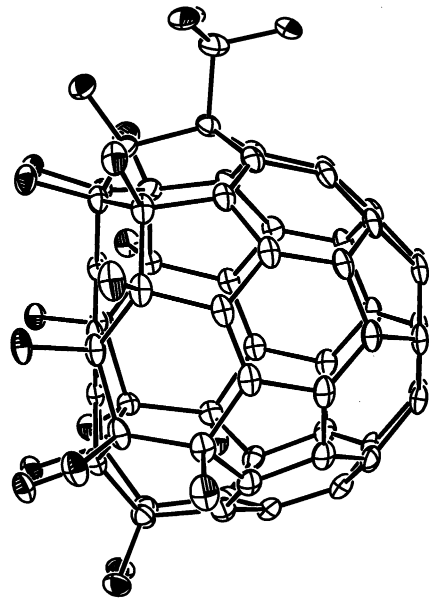

Fig. 6 Side view of the major isomer structure.

The lattice packing (Fig. 7) shows that each fullerene cage is associated with two molecules of toluene.

Crystal data: $C_{61}F_{20}\cdot 2(C_7H_8)$, $M = 1296.88$. Monoclinic, $P2_1/c$ (no. 14), $a = 21.2325(6)$, $b = 12.0459(5)$, $c = 18.7578(8)$ Å, $\beta = 91.173(2)°$, $V = 4796.6(3)$ Å^3, $Z = 4$, μ(Mo-Kα) $= 0.16$ mm^{-1}, $T = 173$ K. 21663 reflections measured on an Enraf-Nonius KCCD diffractometer, 8373 unique ($R_{\text{int}} = 0.065$), refinement on all F^2, $R^1 = 0.066$ [for 5709 reflections with $I > 2\sigma(I)$], $wR^2 = 0.159$ (for all reflections).

Mechanism of formation of perfluoroalkyl derivatives

Hitherto we considered that (trifluoromethyl)fullerenes were formed by addition of CF_3 groups (produced from fluorofullerene cage fragmentation) onto other fullerene cages. Circumstantial evidence for this included the observation of species of 69 amu (CF_3) in the EI mass spectra of fluorofullerenes; species of 50 amu (CF_2) were also seen.[10] However, the present results indicate a different mechanism for the following reasons:

(i) The compounds we have isolated and characterised are all based on the $C_{60}F_{18}$ motif, which imposes substantial mechanistic constraints. For example, formation of $C_{60}F_{17}CF_3$ by $^\bullet CF_3$ addition would require the $C_{60}F_{17}$ radical (for which there is no evidence of separate existence) as a precursor.

(ii) The much more probable alternative is that $C_{60}F_{17}CF_3$ arises from insertion of **:**CF_2 into a C–F bond of $C_{60}F_{18}$. Very strong evidence to support this notion is that the C_s isomer arises from insertion into the most accessible C–F bond, and the C_1 isomers from insertion into the next most accessible one.

(iii) This process can continue with insertion of a further **:**CF_2 group into a C–F bond of the previously formed $C_{60}F_{17}CF_3$ to give $C_{60}F_{17}CF_2CF_3$. Less of the latter should be obtained compared to $C_{60}F_{17}CF_3$, and this is found to be the case.

This process predicts that compounds $C_{60}F_{16}(CF_3)_2$ and $C_{60}F_{15}(CF_2)_3$ should also be isolable. The fact that we have not yet found them reflects the difficulty (and especially the time expenditure) of the HPLC separation of product mixtures containing a very large number of components. Our work in this area is continuing.

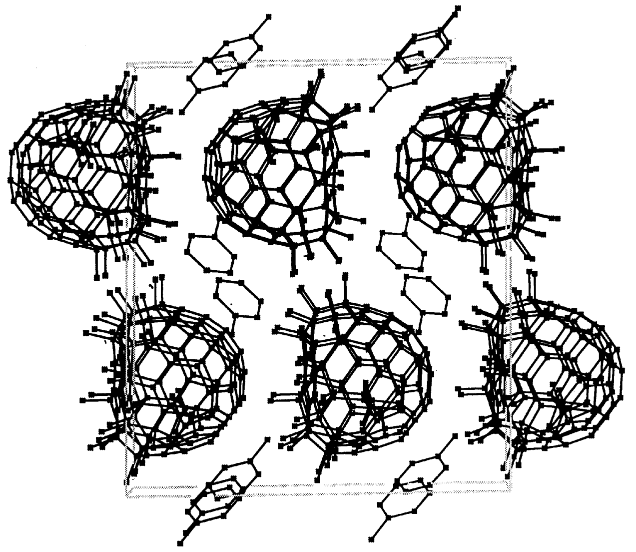

Fig. 7 Lattice packing for $C_{60}F_{17}CF_3\cdot 2(C_7H_8)$.

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