C₆₀F₁₈, a Flattened Fullerene: Alias a Hexa-Substituted Benzene**

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The aromaticity of fullerenes[1] is restricted by the increase in (bond-shortening) strain within the pentagonal rings that arises from the degree of double-bond character they must acquire following electron delocalization.[2] Nevertheless, some degree of delocalization in the carbon cage exists, as shown by the sequential pattern of polyadditions to fullerenes. Addition to one 6−6 "double" bond localizes the electrons in the remaining double bonds of the same hexagon and causes them to undergo preferential addition,[3] as exemplified by the products of hydrogenation,[4] and fluorination.[5]

The strain caused by the presence of a delocalized double bond within a pentagon is diminished when any of the remaining three carbon atoms in the pentagon changes its hybridization from sp^2 to sp^3; this change facilitates delocalization in the adjacent hexagons. This principle was invoked when the tetrahedral (T) molecular structure for $C_{60}H_{36}$ was suggested[6] and accounts for the octahedral addition patterns to [60]fullerene,[7] for example, in the formation of $[C_{60}\{Pt(PEt_3)_2\}_6]$.[8] In each case more-delocalized benzenoid rings are created. A novel D_3 addition pattern resulting from the addition of tetramethylazomethine ylide to [60]fullerene was observed recently by Rubin and co-workers and is likewise a consequence of the creation of a combination of benzenoid and naphthalenoid rings.[9]

Relatively few single-crystal X-ray structures have been determined for fullerenes, and only three are known for halogenofullerenes, namely, $C_{60}Br_{24}$,[10] $C_{60}Br_8$, and $C_{60}Br_6$.[11] Two X-ray structures have provided evidence for the addition-driven delocalization of electrons described above. The lengths of the 6−6 and 6−5 bonds are 1.39 and 1.42 Å, respectively, in the eight semi-benzenoid rings of $C_{66}(COOEt)_{12}$, produced by the octahedral addition of six

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diethyl malonyl moieties to [60]fullerene. Similar values have been obtained for a related tethered hexakis adduct.[12] The alternation is thus less than in [60]fullerene itself (about 1.40 and 1.45 Å).[13]

A few fully characterized fluorofullerenes have been produced, for example, $C_{60}F_{48}$,[14] $C_{60}F_{36}$ (both T and C_3 isomers),[15] and C_{3v}-$C_{60}F_{18}$.[16] The high stability of the latter three derivatives is attributed to the presence of four-, three-, and one π-delocalized benzenoid rings, respectively. We now report the first single-crystal X-ray structure of a fluorinated fullerene, $C_{60}F_{18}$ (as a toluene solvate), which reveals that one half of the [60]fullerene cage is flattened (Figure 1). The
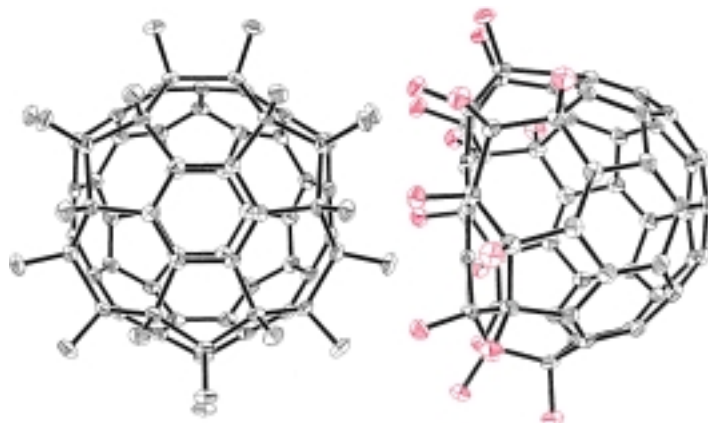

Figure 1. Two projections of $C_{60}F_{18}$ (ORTEP).

hexagonal face at the center of the fluorinated crown has equal bond lengths, which shows it is fully aromatic. It is the first truly benzenoid ring identified on a fullerene surface. The unique geometry of the molecule makes it also a hexa-substituted benzene (specifically here a "pseudocyclophane" with a nondistorted fullerene hemisphere opposite to the arene ring).

The single-crystal X-ray crystallographic study confirms the conclusions reached previously from the ¹⁹F NMR spectrum,[16] namely, that all the fluorine atoms are bound to one hemisphere of the [60]fullerene cage. The "upper" six-membered ring of sp^2 carbon atoms is isolated from the residual molecular π system by a "belt" of sp^3-hybridized carbon atoms. The Schlegel diagram (Figure 2) shows the positions of the fluorine atoms, together with the notation for the symmetry-independent C−F and C−C bonds and the conformations of the nonplanar polygons. A similar addition pattern was earlier predicted for $C_{60}H_{18}$ by semiempirical AM1 quantum chemistry calculations,[17] and confirmed by ¹H NMR spectroscopy.[18] Although such calculations (and indeed simple molecular models) indicate substantial cage flattening, the X-ray data (Figure 1) now reveal the actual extent to which this occurs.

The distances (Δ_i) of the C atoms from the center of the carbon cage,[19] and the spherical excesses (φ_i) of the "surface" environments of the carbon atoms were used, respectively, to characterize the radial atomic displacements and surface puckering in $C_{60}F_{18}$. The latter φ_i parameter was defined as 360° minus the sum of three C-C-C bond angles at the ith
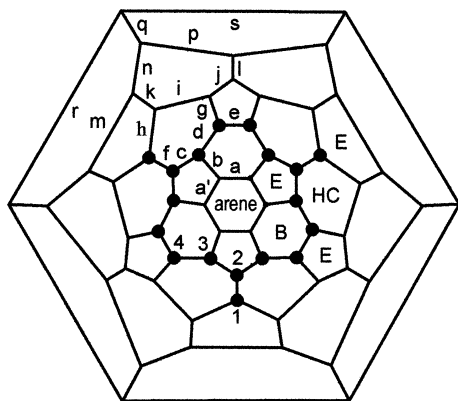
Figure 2. Schlegel diagram for $C_{60}F_{18}$ showing the symmetry-independent fluorine atoms (1–4), C—C bonds (a–s) and ring conformations (see text) within the idealized C_{3v} symmetry.

carbon atom. Standard values in [60]fullerene itself are $\Delta = 3.57$ Å and $\varphi = 12°$ for all atoms. Using these parameters four regions on the surface of the distorted cage may be distinguished in $C_{60}F_{18}$: 1) a planar six-membered "upper" cycle with $\Delta = 2.97$ Å and $\varphi < 0.1°$; 2) a puckered fluorinated belt of eighteen C(sp³) atoms ($3.8 < \Delta < 4.0$ Å; $26.4 < \varphi < 29.9°$); 3) a flattened equatorial belt of twelve C(sp²) atoms bonded directly to C(sp³) atoms ($3.5 < \varphi < 5.2°$); 4) a residual bottom hemisphere made up of 24 C(sp²) atoms which is close to the normal fullerene geometry ($7.8 < \varphi < 13.3°$). The Δ_i parameter, which is strongly dependent on the choice of the molecule center, is not informative in the last two regions because of the small radial distortions (2–3 pm).[19]

Table 1 shows the bond lengths in $C_{60}F_{18}$ averaged within the ideal C_{3v} symmetry (the lengths of symmetry-related bonds mostly agree within a few pm). The "upper" hexagonal ring, planar within 0.003 Å, shows no alternation in the 6–5

Table 1. Bond lengths [Å] in $C_{60}F_{18}$ (for notations, see Figure 2).

	C—C				C—F
a,a′	1.372	j	1.428	1	1.396
b	1.476	k	1.435	2	1.361
c	1.623	l	1.386	3	1.385
d	1.557	m	1.437	4	1.377
e	1.672	n	1.387		
f	1.558	p	1.436		
g	1.500	q	1.453		
h	1.524	r	1.387		
i	1.363	s	1.447		

and 6–6 carbon–carbon bond lengths and is thus fully aromatic. Neighboring C(sp³) atoms deviate from the mean plane of this ring towards the rest of the molecule by 0.055–0.075 Å. The average C—C bond lengths in the arene ring (1.372 Å) and those attached to it (1.476 Å) are noticeably shorter than in either the related fluorocarbon species, perfluorinated indacene $C_{15}F_{18}$ (1.389 and 1.499 Å),[20] or hexa(trifluoromethyl)benzene (1.405 and 1.541 Å).[21] The bond lengths of the ring are essentially the same as the average CSD value in hexafluorobenzene (1.368 Å), which is indicative of the strong electron-withdrawing effect of the eighteen fluorine atoms in the "upper" hemisphere.

The pentagons and hexagons adjacent to the planar face have envelope and boat conformations, respectively. Their neighboring pentagons and hexagons are flattened envelopes and half-chairs, respectively (Figure 2). Single C(sp³)—C(sp³) bonds in the fluorinated belt are elongated to 1.623 Å (bonds c) and 1.672 Å (bonds e). Such elongation is typical for fluoro-substituted hydrocarbons and polycyclic fluorocarbons.[22]

The lengths of four symmetrically independent C—F bonds (1–4) differ slightly, but significantly (1.361–1.396 Å, Table 1). The averaged C-C-F bond angles have normal tetrahedral values of 106.9–111.3° with a slight asymmetry relative to the C_{60} framework; this observation reflects the stronger asymmetry of their opposite C-C-C angles in the puckered five-membered (100.4–109.9°) and six-membered rings (108.3–122.6°), composed of sp² and sp³ carbon atoms.

The alterations in the cage C—C bonds in $C_{60}F_{18}$ relative to those in C_{60} (mapped[23] in Figure 3) are: a) a small shortening in the aromatic ring from the standard value of 1.399 in arenes;[24] b) a strong elongation of the C(sp³)—C(sp³) bonds in the fluorinated belt; c) a smaller but significant (0.01–0.03 Å) shortening of the C(sp²)—C(sp³) bonds in the adjacent "flattened" belt; and d) no significant bond redistribution in the "lower" hemisphere. The distribution of the charge mostly in the vicinity of the fluorinated belt agrees with the generally observed poor relay of electronic effects through the [60]fullerene framework, which is necessitated by the need to avoid the energetically unfavorable reduction in bond lengths in the pentagons.[25] Thus, for example, the unpaired electrons resulting from radical additions are highly localized,[26] and electron addition produces only minor changes in the Raman spectrum since the general cage structure is retained.[27]

The $C_{60}F_{18}$ molecules are linked by inversion centers in antiparallel zigzag chains along the [101] direction of the crystal lattice (Figure 4). The planar "upper" arene face of each molecule in these chains has normal van der Waals contacts with the "lower" fullerene hemisphere of the neighboring chain, with the shortest center-to-center distance in the chain being 9.4 Å. The shortest intermolecular CF···C(cage) contacts between neighboring chains are 2.75 and 2.92 Å (from the type 4 C—F bond to the i-type C(sp²)—C(sp²) bond). From the observation of a lack of elongation of these bonds and the slightly lower spherical excess φ_i values of the surrounding C(sp²) (3.5 and 4.4°) and C(sp³) (26.4°) atoms we suggest that these shortened F···C contacts are forced and therefore
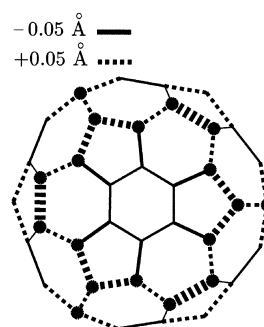
-0.05 Å ▬▬
$+0.05$ Å ▪▪▪▪▪

Figure 3. Shortening (filled lines) and elongation (dotted lines) of the C—C bonds in $C_{60}F_{18}$, averaged within a C_{3v} symmetry, from their standard lengths of 1.397 (sp²–sp²), 1.507 (sp²–sp³), and 1.530 Å (sp³–sp³; see ref. [24]). The thickness of the bonds is proportional to the extent of their shortening/elongation; fluorinated sp³ carbon atoms are marked by black circles. Bond lengths in the opposite hemisphere (not shown) coincide within 0.02 Å with those in C_{60}.
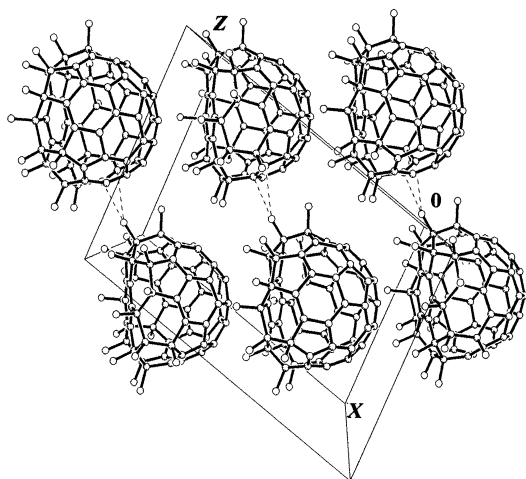
Figure 4. Molecules of $C_{60}F_{18}$ in the crystal lattice.

repulsive ones. Attractive electrostatic interactions between the strongly polarized $C_{60}F_{18}$ molecules probably account for the closeness of the molecules and the unusually high degree of molecular ordering in $C_{60}F_{18} \cdot C_6H_5CH_3$. Such electrostatic forces, expressed in multipole interactions, are believed to be a reason for a weak specific bonding to donors in molecular complexes of hexafluorobenzene.[28]

The distorted geometry of the $C_{60}F_{18}$ molecule is quantitatively reproduced by quantum chemistry calculations, even on a semiempirical PM-3 level. Ab initio HF calculations (GAUSSIAN-94, 3-21G* and 6-31G basis sets, geometry optimized) convergently predict a substantial polarization of the C–F bonds with charges of -0.34 to -0.39 on the fluorine atoms and charges of $+0.25$ to $+0.40$ on the sp³ carbon atoms. The calculated charges are mainly located in the "fluorinated" belt of the C_{60} moiety, which is in agreement with the experimental redistribution of the C–C bond lengths (Figure 3). The unique arene ring carries a small positive charge per carbon atom ($+0.04$ in 3-21G* and $+0.03$ in 6-31G). Both HF approximations used ascribe a large dipole moment to the molecule (12.4 D in 3-21G* and 15.7 D in 6-31G); however, smaller values of 6–7 D have been predicted independently.[29] DFT calculations (B3LYP/6-31G) give similar values to those obtained by HF, but with the C–F bond distance overestimated by 0.04 Å, a slightly more uniform charge distribution, and a predicted dipole moment of 13.3 D.

The very strongly electron-deficient planar region suggests that this molecule may find important applications in intramolecular electron-transfer complexes, whilst η^6 coordination with transition metal atoms may also be possible. These aspects are to be investigated.

Experimental Section

$C_{60}F_{18}$ was prepared and purified as described previously.[16] Light-yellow diamond-shaped plates of $C_{60}F_{18} \cdot C_6H_5Me$ with a good X-ray quality were grown from toluene. The structure was determined by X-ray diffraction.[30] Errors (esd) for the C–F and C–C bond lengths were 0.002–0.003 and 0.003–0.004 Å, respectively.

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[30] Crystal data for $C_{60}F_{18} \cdot (C_7H_8)$, $M_r = 1154$, monoclinic, space group $P2_1/n$, $a = 11.532(2)$, $b = 21.501(3)$, $c = 16.261(2)$ Å, $\beta = 101.798(5)°$, $V = 3947$ Å^3, $Z = 4$, $\mu(Mo_{K\alpha}) = 0.17$ mm^{-1}, $T = 100$ K. 49263 Reflections measured (Siemens SMART diffractometer, $2\theta max = 60°$) 11565 unique, refined on F^2 using SHELXTL, $R1 = 0.049$ (for 6426 reflections with $I > 2\sigma > (I)$, $wR2 = 0.118$ (for all reflections). Crystallographic data (excluding structure factors) for the structure reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication no. CCDC-142291. Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB21EZ, UK (fax: (+44)1223-336-033; e-mail: deposit@ccdc.cam.ac.uk).

The First Microporous Framework Cerium Silicate[**]

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Recently, much research has been carried out aimed at preparing inorganic microporous zeotype solids composed of interconnected octahedral- and tetrahedral-oxide polyhedra. One such family of materials of considerable interest embraces microporous titanosilicates and their derivatives which contain Ti[IV] usually in octahedral coordination.[1, 2] As part of a systematic search for novel microporous framework inorganic materials we have prepared (among others) AV-1, a synthetic analogue of the rare sodium yttrium silicate mineral montregianite ($Na_4K_2Y_2Si_{16}O_{38} \cdot 10H_2O$).[3, 4] In nature, montregianite usually occurs with framework substitution of some yttrium by cerium and this raised the possibility of obtaining a purely cereous form of AV-1. Here we report the synthesis and characterization of AV-5, a microporous framework sodium cerium silicate with the structure of montregianite.

It is well known that Ce[III]-containing materials present potential for applications in optoelectronics. For example, Ce[III] in a $LiYF_6$ matrix has been shown to lase.[5] This system may find important applications since Ce[III] lasers emit in the high-energy region of the spectrum (blue or UV) and they exhibit tunability due to the inherently broad emission lines. Glass-supported cerium is used in Faraday rotators, which protect lasers from back-reflected light.[6] As for other lanthanides, cerium has been used in transducers designed to detect or modify IR, UV, X-ray, and gamma radiation.[6] The luminescence of Ce[III]/silica systems prepared by sol – gel methods has also been studied.[7] Our main aim with this work

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was to explore the possibility of preparing porous cerium silicates with potential for use in optoelectronics.

The crystal structure of montregianite (and AV-5) consists of two different types of layers alternating along the [010] direction (Figure 1): a) a double silicate sheet, in which the
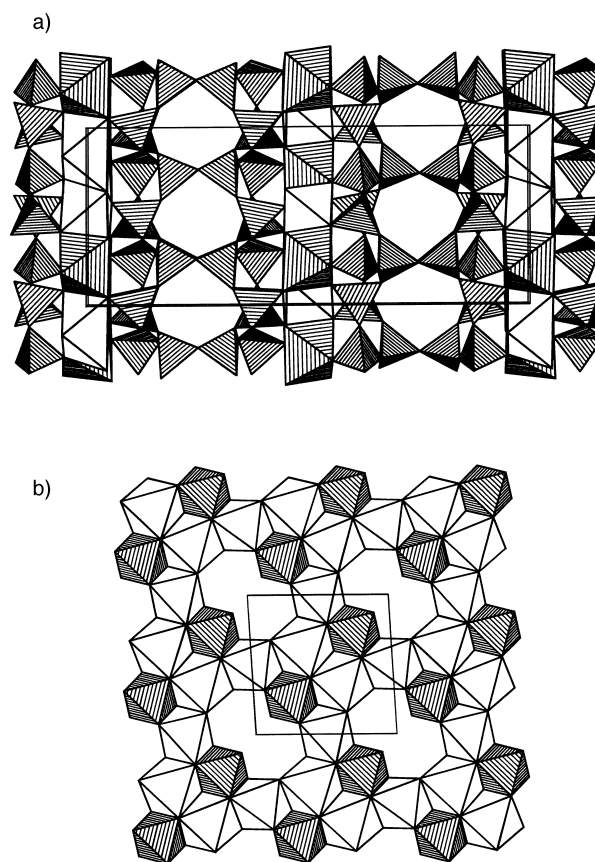

Figure 1. Polyhedral representation of the montregianite structure: a) viewed along [100] showing the alternating octahedral sheet and double silicate sheet along [010]; b) open octahedral sheet, viewed along [010], consisting of Y and three different Na^+ octahedra (unfilled octahedra).

single silicate sheet is of the apophyllite type with four- and eight-membered rings, and b) an open octahedral sheet composed of $[YO_6]$ (or $[CeO_6]$ in AV-5) and three distinct $[NaO_4(H_2O)_2]$ octahedra.[8] The layers are parallel to the (010) plane. The potassium ions are ten-coordinate and the six water molecules (not shown) are located within large channels formed by the planar eight-membered silicate rings.

Figure 2 shows the experimental and simulated powder X-ray diffraction (XRD) patterns of AV-5. The differences observed are due to the presence of a small amount of an, as-yet, unknown impurity. The unit cell parameters have been refined by assuming a monoclinic unit cell, space group $P2_1/n$, and cell dimensions $a = 9.6906(9)$, $b = 24.055(2)$, $c = 9.5759(8)$ Å, and $\beta = 93.683(7)°$ and are similar to those reported for montregianite, dimensions $a = 9.512$, $b = 23.956$, $c = 9.617$ Å, and $\beta = 93.85°$).[9]

Presumably owing to the presence of paramagnetic Ce[III] centers we were unable to record a ^{29}Si magic-angle spinning (MAS) NMR spectrum of AV-5. It is, however, possible to oxidize Ce[III] to Ce[IV] by calcining AV-5 in air at 300°C for 3 h.