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STRUCTURES OF POLYFLUOROAROMATIC COMPOUNDS.

PART IX [1]. CRYSTAL STRUCTURE OF DECAFLUOROFLUORANTHENE

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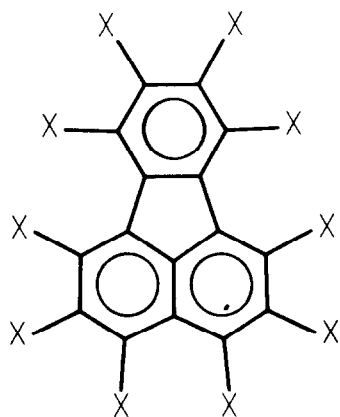
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SUMMARY

Crystals of decafluorofluoranthene, $C_{16}F_{10}$, are monoclinic, space group $C2/c$ with unit cell dimensions $a = 18.92(1)$, $b = 4.84(1)$, $c = 29.01(2)$ Å, $\beta = 105.34(5)^\circ$. The structure was refined to a conventional discrepancy factor R of 4.7% and weighted discrepancy factor R_w of 4.9% for 1841 observed counter amplitudes. Estimated standard deviations average 0.004 Å for bond lengths and 0.3° for bond angles. The molecule is essentially planar. Detailed comparison with the parent hydrocarbon indicates that substitution of fluorine for hydrogen has brought about only quite small changes in molecular geometry.

INTRODUCTION

Fluoranthene(I), a non-alternant aromatic hydrocarbon, has been extensively studied by a variety of techniques, including X-ray and neutron diffraction in the solid state [2,3], ^{13}C [4] and proton [5] NMR spectroscopy in solution, photoelectron spectroscopy in the gas phase [6], and by theoretical calculations [7-11]. The recent synthesis [12] of decafluorofluoranthene(II) gave us the opportunity to determine the crystal structure of this compound to assess the effect of fluorine substitution on bonding and conformation.



(I) X = H

(II) X = F

EXPERIMENTAL

X-Ray measurements

Crystals in the form of yellow plates were obtained by recrystallization from tetrachloromethane. The crystal used in the analysis had dimensions 1.0 x 0.4 x 0.15 mm. It was sealed inside a Pantak capillary tube and aligned about the direction of elongation which coincided with the crystallographic y axis. Cell dimensions and intensity data were measured on a Stoe computer-controlled two-circle diffractometer, operating in the ω scan mode, with graphite-monochromated Mo-K α radiation. The scan speed was 0.6° min⁻¹ and 30 s background counts were taken at each end of the scan. The intensities of four zero-layer reflections, which were remeasured after each layer of data collection, showed no significant variation over the period of the measurements. Of 3188 unique reflections scanned in the range $0.1 < \sin\theta/\lambda < 0.74 \text{ \AA}^{-1}$, 1841 with $I > 2.5\sigma(I)$ were used in the final analysis.

Crystal data

C₁₆F₁₀. Monoclinic, $a = 18.92(1)$, $b = 4.84(1)$, $c = 29.01(2) \text{ \AA}$, $\beta = 105.34(5)^\circ$, $U = 2562 \text{ \AA}^3$, $Z = 8$, $D_c = 1.98 \text{ g cm}^{-3}$. Systematic absences: hkl when $h + k$ is odd, $h0l$ when l is odd. Space group Cc or C2/c. C2/c established as a result of the analysis. Absorption coefficient for Mo-K α radiation ($\lambda = 0.71069 \text{ \AA}$) = 1.58 cm⁻¹.

Structure determination

The structure was solved by direct methods with the SHELX system of programs [13]. The E map calculated from the most probable phase set showed the positions of all the atoms. The initial value of the discrepancy factor R was 38% and this fell to 18% after three cycles of least-squares refinement varying isotropic temperature factors and atomic coordinates. The atoms were then allowed to vibrate anisotropically and the refinement process continued until all calculated shifts were $< 0.01\sigma$ and R was 4.7% (R_w 4.9%) for the 1841 observed structure amplitudes.[†] The weighting scheme used was $w = 1/\sigma^2(F)$ where $\sigma(F)$ is the estimated standard deviation in the observed amplitudes based on counting statistics. Final atomic positional parameters are given in Table 1.

Computations were carried out on the Birmingham University ICL 1906A computer and on the CDC 7600 at the University of Manchester Regional Computer Centre.

RESULTS AND DISCUSSION

Bond lengths and angles calculated from the atomic coordinates of Table 1 are listed in Table 2. The atomic numbering scheme and the labelling of the bonds are shown in Figure 1. Bond lengths corrected for the effect of rigid-body thermal libration [14] are listed beside the uncorrected values. The molecule is essentially planar (Table 3). The parent hydrocarbon, although also nearly planar, exhibits somewhat greater deviations from planarity [3]. The r.m.s. deviation of carbon atoms from the mean plane is 0.024 Å, averaged over the two independent molecules of the hydrocarbon (I) in the unit cell, compared with 0.010 Å for the fluorocarbon (II).

Carbon-carbon aromatic bonds range from 1.365 to 1.439 Å, corrected for thermal libration. The four shortest bonds are C(1)-C(16), C(6)-C(13), C(2)-C(3) and C(4)-C(5) of the naphthalene moiety, with a mean length of 1.373 Å. The lengths of the other naphthalene bonds average 1.421 Å, and those of the phenyl moiety average 1.398 Å. These values are in agreement with simple theoretical considerations based on superposition of valence bond structures as described by Pauling [15], according to which these three classes of bonds have, respectively, 2/3,

[†]Lists of observed and calculated structure factors and anisotropic thermal parameters have been deposited (N. Goodhand, Thesis, University of Birmingham, 1979).

TABLE 1

Fractional atomic coordinates ($\times 10^4$)

	x	y	z
C(1)	3551(2)	-1756(6)	2010(1)
C(2)	2999(2)	-3568(6)	2072(1)
C(3)	2321(2)	-3632(6)	1761(1)
C(4)	1481(2)	-1678(7)	988(1)
C(5)	1401(2)	171(7)	618(1)
C(6)	1981(2)	1945(6)	582(1)
C(7)	3600(2)	5318(6)	762(1)
C(8)	4316(2)	6285(6)	932(1)
C(9)	4775(2)	5202(7)	1346(1)
C(10)	4532(1)	3127(6)	1595(1)
C(11)	2142(1)	-1865(6)	1357(1)
C(12)	2702(1)	-82(5)	1307(1)
C(13)	2636(1)	1840(5)	921(1)
C(14)	3352(1)	3247(5)	1009(1)
C(15)	3825(1)	2132(5)	1435(1)
C(16)	3412(1)	19(5)	1626(1)
F(1)	4205(1)	-1914(4)	2333(1)
F(2)	3162(1)	-5301(4)	2453(1)
F(3)	1823(1)	-5423(4)	1847(1)
F(4)	913(1)	-3363(4)	993(1)
F(5)	767(1)	326(5)	274(1)
F(6)	1846(1)	3693(4)	209(1)
F(7)	3168(1)	6459(4)	361(1)
F(8)	4554(1)	8319(4)	689(1)
F(9)	5455(1)	6217(5)	1503(1)
F(10)	5001(1)	2139(4)	1990(1)

TABLE 2

Molecular dimensions

(a) Bond lengths (\AA) with estimated standard deviations in parentheses.

Values in the second column are corrected for thermal libration.

C(1)-C(16)	1.375(4)	1.380	C(6)-C(13)	1.365(4)	1.370
C(1)-C(2)	1.412(4)	1.416	C(5)-C(6)	1.417(4)	1.421
C(2)-C(3)	1.360(4)	1.365	C(4)-C(5)	1.373(5)	1.378
C(3)-C(11)	1.417(4)	1.422	C(4)-C(11)	1.418(4)	1.424
C(11)-C(12)	1.403(4)	1.407			
C(12)-C(16)	1.416(4)	1.421	C(12)-C(13)	1.434(4)	1.439
C(15)-C(16)	1.481(4)	1.485	C(13)-C(14)	1.476(4)	1.481
C(14)-C(15)	1.426(3)	1.432			
C(10)-C(15)	1.382(4)	1.387	C(7)-C(14)	1.384(4)	1.388
C(9)-C(10)	1.384(4)	1.388	C(7)-C(8)	1.394(4)	1.399
C(8)-C(9)	1.386(4)	1.392			
C(1)-F(1)	1.343(3)	1.348	C(6)-F(6)	1.345(3)	1.350
C(2)-F(2)	1.356(3)	1.361	C(5)-F(5)	1.345(3)	1.350

(continued on facing page)

TABLE 2 (cont.)

C(3)-F(3)	1.351(3)	1.354	C(4)-F(4)	1.352(3)	1.356
C(10)-F(10)	1.337(3)	1.342	C(7)-F(7)	1.350(3)	1.356
C(9)-F(9)	1.339(3)	1.343	C(8)-F(8)	1.354(3)	1.358
(b) Selected non-bonded distances (Å)					
F(1)...F(2)	2.66		F(5)...F(6)	2.66	
F(2)...F(3)	2.68		F(4)...F(5)	2.70	
F(3)...F(4)	2.80				
F(1)...F(10)	2.81		F(6)...F(7)	2.77	
F(8)...F(9)	2.72				
F(9)...F(10)	2.70		F(7)...F(8)	2.70	
(c) Bond angles (deg.) with estimated standard deviations in parentheses.					
C(16) - C(1) - C(2)	120.1(3)		C(13) - C(6) - C(5)	119.9(3)	
C(16) - C(1) - F(1)	123.1(3)		C(13) - C(6) - F(6)	123.1(3)	
C(2) - C(1) - F(1)	116.8(3)		C(5) - C(6) - F(6)	117.0(3)	
C(1) - C(2) - C(3)	122.0(3)		C(6) - C(5) - C(4)	121.6(3)	
C(1) - C(2) - F(2)	118.2(3)		C(6) - C(5) - F(5)	117.9(3)	
C(3) - C(2) - F(2)	119.9(3)		C(4) - C(5) - F(5)	120.5(3)	
C(2) - C(3) - C(11)	120.8(3)		C(5) - C(4) - C(11)	121.6(3)	
C(2) - C(3) - F(3)	118.3(3)		C(5) - C(4) - F(4)	118.6(3)	
C(11) - C(3) - F(3)	120.9(3)		C(11) - C(4) - F(4)	119.8(3)	
C(3) - C(11) - C(12)	115.8(3)		C(4) - C(11) - C(12)	114.9(3)	
C(3) - C(11) - C(4)	129.2(3)				
C(11) - C(12) - C(16)	124.4(3)		C(11) - C(12) - C(13)	124.6(3)	
C(13) - C(12) - C(16)	111.0(2)				
C(12) - C(16) - C(1)	117.0(2)		C(12) - C(13) - C(6)	117.4(2)	
C(12) - C(16) - C(15)	106.4(2)		C(12) - C(13) - C(14)	106.2(2)	
C(15) - C(16) - C(1)	136.6(2)		C(14) - C(13) - C(6)	136.4(3)	
C(10) - C(15) - C(16)	132.4(2)		C(7) - C(14) - C(13)	131.8(2)	
C(14) - C(15) - C(16)	108.2(2)		C(15) - C(14) - C(13)	108.2(2)	
C(10) - C(15) - C(14)	119.4(2)		C(7) - C(14) - C(15)	120.0(2)	
C(9) - C(10) - C(15)	120.1(3)		C(8) - C(7) - C(14)	119.4(3)	
C(15) - C(10) - F(10)	121.9(3)		C(14) - C(7) - F(7)	122.0(3)	
C(9) - C(10) - F(10)	118.0(2)		C(8) - C(7) - F(7)	118.6(3)	
C(8) - C(9) - C(10)	120.6(3)		C(9) - C(8) - C(7)	120.5(3)	
C(10) - C(9) - F(9)	120.7(3)		C(7) - C(8) - F(8)	119.0(3)	
C(8) - C(9) - F(9)	118.7(3)		C(9) - C(8) - F(8)	120.5(3)	

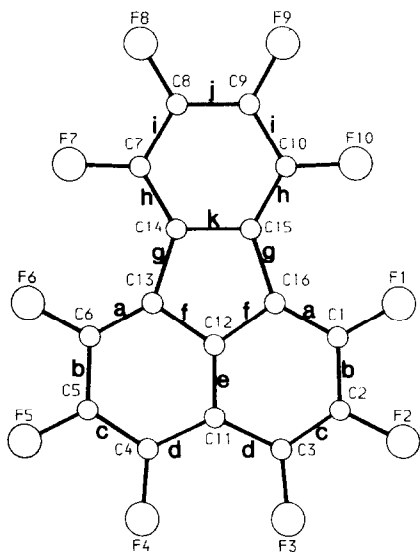


Fig. 1. Decafluorofluoranthene. Labelling of atoms and bonds

1/3 and 1/2 double bond character. Phenyl bond C(14)-C(15) at 1.432 Å is, however, longer than might be expected, possibly due to steric strain introduced by the fusion of the five-membered ring to the naphthalene moiety. The lengths of the two non-aromatic bonds C(15)-C(16), 1.485 Å, and C(13)-C(14), 1.481 Å, fall within the expected [15,16] range for a pure single bond between trigonally hybridized carbon atoms. The carbon-fluorine bond lengths are 1.342 - 1.361, mean 1.352 Å, in good agreement with previous results [17].

The fluoranthene (I) and decafluorofluoranthene (II) molecules have symmetry $\overline{mm}2$ (C_{2v}). The lengths of chemically equivalent bonds agree quite closely, as do corresponding bond angles, and carbon-carbon lengths averaged over equivalent bonds are listed in Table 4, together with the results of theoretical calculations [7-9]. The bonds are labelled by letters a - k as shown in Figure 1. In column (7) are bond lengths calculated from bond orders based on simple Pauling superposition of Kekulé structures, as described above, by the bond length-bond order relationship of Cruickshank [16]. Hazell and co-workers [3] concluded that their X-ray analysis [column (1)] has yielded more reliable results than the neutron analysis [column (2)] and we therefore use exclusively the X-ray results for comparison purposes.

TABLE 3

Mean plane calculation

Deviation of atoms (\AA) from the mean plane of the carbon atoms					
C(1)	-0.004	C(2)	-0.001	C(3)	0.009
C(4)	-0.016	C(5)	-0.010	C(6)	-0.001
C(7)	0.010	C(8)	0.007	C(9)	0.001
C(10)	-0.015	C(11)	0.013	C(12)	0.016
C(13)	0.004	C(14)	-0.004	C(15)	-0.012
C(16)	0.004				
F(1)	-0.045	F(2)	-0.021	F(3)	0.014
F(4)	-0.062	F(5)	-0.027	F(6)	0.013
F(7)	0.037	F(8)	0.027	F(9)	0.022
F(10)	-0.035				

The overall mean bond lengths are 1.410 \AA in the fluorocarbon and 1.402 \AA in the hydrocarbon. This is contrary to the results of previous comparisons of bond lengths in aromatic and fluoroaromatic compounds [17], which have generally shown a slight shortening of C-C bonds in the fluorinated compounds. Theoretical considerations [18] lead to a similar conclusion. Overall, however, the agreement between the bond lengths in fluoranthene and decafluorofluoranthene is close. Agreement between bond angles is also good, so that the substitution of fluorine for hydrogen has only a marginal effect on the geometry of the fluoranthene molecule. This is consistent with the strong similarity of the u.v./visible spectra of the two compounds noted previously [12].

The comparison of bond lengths with theoretically calculated values is noteworthy for the success of the simple Pauling superposition treatment, according to which the fluoranthene molecule consists of a naphthalene residue and a benzene residue linked by single bonds. Only the values of Dewar and Trinajstić [8] [column (4)] of the more sophisticated treatments are slightly closer to the experimental bond lengths. All the theoretical treatments [columns (3)-(6)], except the Pauling superposition [column (7)], seriously underestimate the length of the formal single bond, *g.* The experimental values [columns (1), (2), (8)], mean 1.486(6) \AA , correspond to the length of a pure single

TABLE 4

Bond lengths in fluoranthene and decafluorofluoranthene (Å)

Column headings (1)-(8) refer to: (1) fluoranthene, X-ray diffraction, (2) fluoranthene, neutron diffraction, (3)-(6) fluoranthene, theoretical calculations, (7) Pauling superposition (see text), (8) decafluorofluoranthene, X-ray diffraction.

Experimental values have been corrected for thermal libration effects and have been averaged over chemically equivalent bonds.

	(1)[3]	(2)[3]	(3)[7]	(4)[8]	(5)[9]	(6)[9]	(7)	(8)*
a	1.367(2)	1.361(3)	1.389	1.380	1.390	1.393	1.375	1.375(5)
b	1.411(1)	1.433(8)	1.412	1.420	1.416	1.408	1.421	1.419(3)
c	1.368(3)	1.383(10)	1.383	1.375	1.384	1.386	1.375	1.372(7)
d	1.422(1)	1.415(8)	1.423	1.427	1.425	1.421	1.421	1.423(1)
e	1.400(3)	1.413(1)	1.413	1.404	1.415	1.417	1.421	1.407(4)
f	1.411(1)	1.415(6)	1.428	1.429	1.428	1.425	1.421	1.430(9)
g	1.476(1)	1.498(4)	1.456	1.466	1.464	1.456	1.477	1.483(2)
h	1.384(3)	1.390(4)	1.400	1.401	1.404	1.405	1.397	1.388(1)
i	1.386(5)	1.413(4)	1.399	1.394	1.398	1.395	1.397	1.394(6)
j	1.379(3)	1.375(10)	1.397	1.399	1.402	1.401	1.397	1.392(4)
k	1.417(2)	1.408(3)	1.415	1.403	1.410	1.410	1.397	1.432(3)

Root mean square deviations between sets of bond lengths

(1)	(2)	(3)	(4)	(5)	(6)	(7)
(8) 0.010	0.014	0.012	0.011	0.012	0.015	0.012
(1)	0.015	0.015	0.012	0.015	0.016	0.013

*Present work

bond between sp^2 -hybridized carbon atoms. Angular distortions are noticeable in the naphthalene portion of the molecule. For example, angle dd is 129.2° (128.3° in the hydrocarbon) whereas ff is 111.0° (111.1° in the hydrocarbon). In naphthalene itself these angles are identical and close to 120° .

The packing arrangement in the crystal is illustrated in Figure 2. All intermolecular distances are greater than the sum of the van der Waals radii [15] of the atoms concerned.

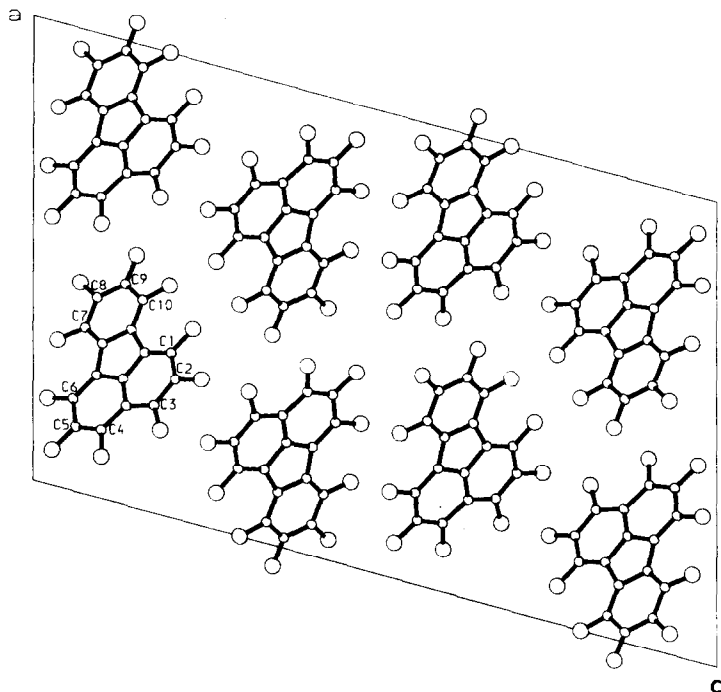


Fig. 2. Projection of the contents of one unit cell along the crystallographic y axis.

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