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Packing conflicts in the Z' = 5 structure of $CF_3(CF_2)_3(CH_2)_{10}COOH$

Hans-Joachim Lehmler,[a] Sean Parkin[b] and Carolyn Pratt Brock[b]*

[a]Department of Occupational and Environmental Health,100 Oakdale Campus, 124 IREH, The University of Iowa, Iowa City, IA 52242-5000, USA, and [b]Department of Chemistry, University of Kentucky, Lexington, KY 40506-0055, USA

Correspondence e-mail: cpbrock@uky.edu

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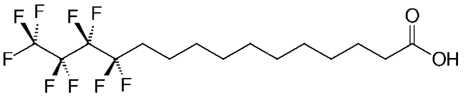
Dimers of the partially fluorinated amphiphile 1-(perfluorobutyl)undecanoic acid, $CF_3(CF_2)_3(CH_2)_{10}COOH$, crystallize in the same basic packing arrangement found for many *n*-alkyl carboxylic acids. The unit cell of the fluorinated compound, however, contains five independent molecules rather than the one found for most *n*-alkyl carboxylic acids including $CH_3(CH_2)_{13}COOH$. The structures of the two C_{15} acids are compared. The structural modulations that lead to the large value of Z' can be understood as resulting from the conflict between the necessity of filling space densely and uniformly and the tendency of unlike groups to be segregated spatially. The few other known structures of compounds with both $(CF_2)_n$ and $(CH_2)_m$ regions show evidence of the same conflict.

1. Introduction

Only a very few structures of molecules containing both $(CF_2)_n$ and $(CH_2)_m$ regions, n and $m \geq 3$, are known, even though there has been considerable interest in such compounds (Arora *et al.*, 2003; Lehmler *et al.*, 2000; Lehmler *et al.*, 2001; Lehmler & Bummer, 2002*a*,*b*; Krafft, 2001). We were able to obtain crystals of the partially fluorinated amphiphile 1-(perfluorobutyl)undecanoic acid, $CF_3(CF_2)_3(CH_2)_{10}COOH$ (hereafter, 4-10COOH). One of the extremely thin crystals, when cooled to 90.0(2) K, gave a diffraction pattern that allowed the structure to be determined. The number of independent molecules in the asymmetric unit (Z' = 5) was found to be exceptionally large (see Steed, 2003).



(I)

The structure of the closely related compound $CH_3(CH_2)_{13}COOH$ (0-14COOH hereafter) has been published very recently (Bond, 2004) as part of a systematic study of the structures of the even and odd *n*-alkylcarboxylic acids. The packing in 4-10COOH is closely related to that in 0-14COOH; the F atoms in the former perturb, but do not really change, the basic structure of the latter, which is typical of other odd (and even) *n*-alkylcarboxylic acids. Comparisons of the 4-10COOH and 0-14COOH structures make clear the conflict in 4-10COOH between:

(i) the tendency for groups that are similar electronically to be segregated spatially, and

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Table 1
Crystal data.

Crystal data	
Chemical formula	$C_{15}H_{21}F_9O_2$
M_r	404.32
Cell setting, space group	Triclinic, $P\bar{1}$
a, b, c (Å)	11.253 (2), 13.750 (2), 29.289 (6)
α, β, γ (°)	78.01 (2), 89.72 (2), 81.16 (2)
V (Å^3)	4378.7 (14)
Z	10
D_x (Mg m^{-3})	1.533
Radiation type	Mo $K\alpha$
No. of reflections for cell parameters	15 988
θ range (°)	1.0–25.4
μ (mm^{-1})	0.16
Temperature (K)	90.0 (2)
Crystal form, color	Thin flakes, colorless
Crystal size (mm)	0.45 × 0.20 × 0.03
Data collection	
Diffractometer	Nonius KappaCCD diffractometer
Data collection method	1.0° ω scans at fixed χ = 55°
Absorption correction	Multi-scan (based on symmetry-related measurements)
$T_{\min}$	0.93
$T_{\max}$	1.00
No. of measured, independent and observed reflections	30 811, 15 437, 8076
Criterion for observed reflections	$I > 2\sigma(I)$
$R_{\rm int}$	0.067
$\theta_{\max}$ (°)	25.0
Range of h, k, l	$-13 \Rightarrow h \Rightarrow 13$ $-16 \Rightarrow k \Rightarrow 16$ $-34 \Rightarrow l \Rightarrow 34$
Refinement	
Refinement on	F^2
$R[F^2 > 2\sigma(F^2)]$, $wR(F^2)$, S	0.050, 0.107, 0.97
No. of reflections	15 437
No. of parameters	1565
H-atom treatment	Mixed
Weighting scheme	$w = 1/[\sigma^2(F_o^2) + (0.0425P)^2]$, where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{\max}$	0.002
$\Delta\rho_{\max}$, $\Delta\rho_{\min}$ (e Å^{-3})	0.33, −0.28

Computer programs used: *COLLECT* (Nonius, 1999), *SCALEPACK* (Otwinowski & Minor, 1997), *DENZO-SMN* (Otwinowski & Minor, 1997), *SHELXS*97 (Sheldrick, 1997*a*), *SHELXL*97 (Sheldrick, 1997*b*), *XP* in Siemens *SHELXTL* (Sheldrick, 1994), *Mercury* (Bruno *et al.*, 2002), *SHELXTL-PC* (Sheldrick, 1994) and local procedures.

(ii) the drive for dense and uniform filling of space.

This conflict has been invoked previously to explain the behavior of monolayers formed by similar compounds at the air–water interface (see the references in the previous paragraph).[1]

2. Experimental

2.1. Crystals and data collection

The compounds $CF_3(CF_2)_nC(CH_2)_{10}COOH$, n = 3, 5 and 7 (4-10COOH, 6-10COOH and 8-10COOH), were synthesized by the method referenced in Lehmler *et al.* (2001). When recrystallized from *n*-hexane the three acids gave colorless leaflets too thin and small for a diffraction study. Slow evaporation of ethanol solutions also gave very thin flakes, but some of the crystals of the n = 4 compound seemed worth a closer look. A number of crystals were examined on the diffractometer at 90.0 (2) K before one was found that gave a diffraction pattern that could be measured and indexed satisfactorily. The thickness of that slightly bent crystal was *ca* 0.03 mm.

Since the **c** axis is long (see Table 1), data were collected with the CCD detector set 60.0 mm away from the crystal. As the average intensity was low, 10 different scans (1234 frames total; 1° rotation in ω with 50 s exposure for each) were made; the number of measured reflections was 4.8 times larger than

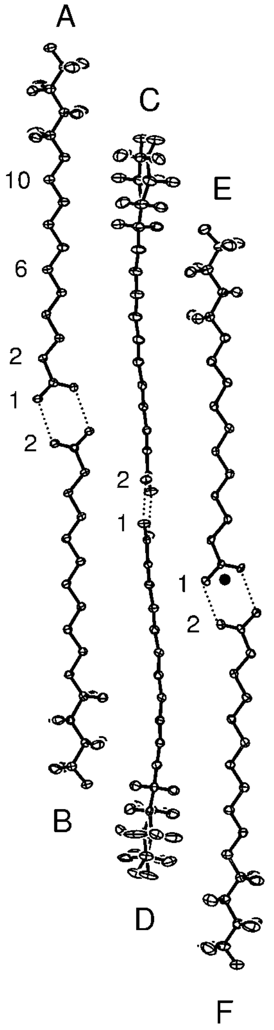

Figure 1
A perspective drawing of the asymmetric unit of 4-10COOH at 90 K, which is viewed perpendicular to the least-squares plane of the non-H atoms. Ellipsoids are drawn at the 50% level and H atoms have been omitted in this and all subsequent drawings. The disorder of molecules E and F across the inversion center (filled circle) is not shown. The atom-numbering scheme is the same for all molecules. The numbers for one O atom in each molecule and several C atoms in molecule *A* are shown. Atoms O1 and O2 are connected to C1 and the C and F atoms are numbered sequentially. Atoms F1 and F2 are connected to C12 and atoms F7–F9 are connected to C15.

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[1] Supplementary data for this paper are available from the IUCr electronic archives (Reference: DE5003). Services for accessing these data are described at the back of the journal.

the number of unique reflections. Additional details of the data collection are given in Table 1. After the orientation matrices had been determined, the information in the frames was transformed using the routine PRECESSION in *COLLECT* (Nonius, 1999) to give undistorted views of thin slices centered on the layers $nk\ell$, $hn\ell$ and hkn, n = 0–3, of the reciprocal lattice. These slices show that some regions of the diffraction pattern are relatively weak; only 52% of reflections to $\sin\theta/\lambda$ = 0.60 Å^{-1} had $I > 2\sigma(I)$, even though data were collected at 90 K. There are, however, no simple patterns in the indices of the weak reflections and there is no obvious non-Bragg (*e.g.* diffuse) scattering.

2.2. Structure solution

The structure was solved without much difficulty using the program *SHELXS* (Sheldrick, 1997*a*). There are three carboxylic acid dimers in the asymmetric unit (see Fig. 1). The dimer composed of molecules *A* and *B* appears to be completely ordered. Molecules *C* and *D* both show disorder in their $CF_3(CF_2)_3$ regions (see below). The dimer composed of molecules *E* and *F*, on the other hand, is completely disordered around an inversion center. As the center of this disordered dimer is offset from the inversion center (see Fig. 1), the two halves of the dimer are clearly different.

Since Z = 10 the structure can be thought of as containing five independent molecules, but it is perhaps better to write Z' = 4 + 2($\frac{1}{2}$) and to think of the structure as containing three independent dimers formed from six independent molecules. Large Z' values are often associated with pseudosymmetry, but we find no strong non-crystallographic relationships between the coordinates of the independent molecules. There is no correlation coefficient in the final refinement cycles larger than 0.50 for parameters in two different molecules other than in molecules *E* and *F*, which occupy nearly the same site.

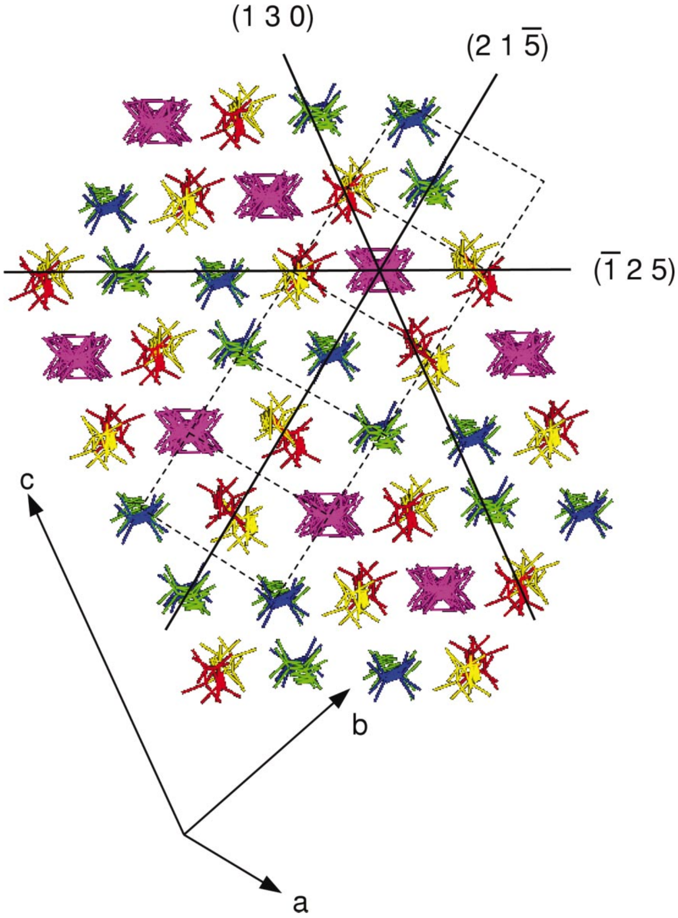

Figure 2
A projection of the 4-10COOH structure as viewed along [3$\overline{1}$1] drawn using the program *Mercury* (Bruno *et al.*, 2002). The colors of molecules *A*–*D* are green, blue, red and yellow. The color of disordered molecules *E* and *F* is magenta. The asymmetric unit is composed of three dimers in a horizontal line with the *E*/*F* dimer on the left. Projections of the densely packed planes (130), (21$\overline{5}$) and ($\overline{1}$25), which intersect in the line [3$\overline{1}$1], are shown. The dotted lines show the pseudocells typical of *n*-alkyl carboxylic acids (Bond, 2004).

2.3. Structure refinement

The extensive disorder meant that restraints were required for successful refinement, which was performed using the program *SHELXL*97 (Sheldrick, 1997*b*). Corresponding 1–2 and 1–3 distances in the six independent molecules were restrained to be similar by the use of five SAME instructions; each of the molecules *B*–*F* was restrained to have similar distances as molecule *A*. Rigid-bond restraints (Rosenfield *et al.*, 1978) were applied to the atomic displacment parameters (hereafter, ADPs) of all atoms using the instruction DELU 0.004. The instruction ISOR (tolerance 0.016) applied

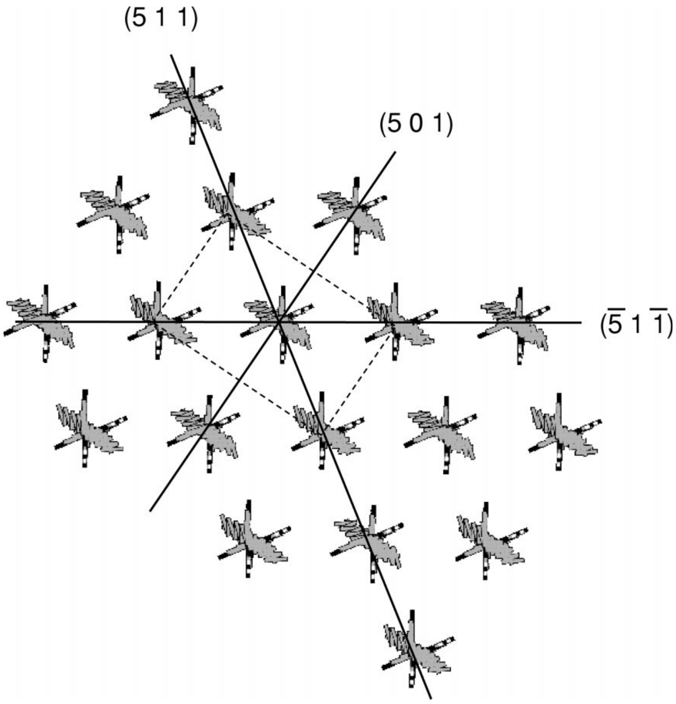

Figure 3
A projection of the structure of *n*-pentadecanoic acid (0-14COOH) as viewed along [10$\overline{5}$] . Traces of the planes (511), (501) and ($\overline{5}1\overline{1}$), all of which are perpendicular to the line [10$\overline{5}$], are shown. The dotted lines show the **b** axis, which is parallel to (501) and thus lies in the plane of the drawing, and the projection of the **c** axis (Bond, 2004).

Table 2
Comparison of angles and spacings for the crystal packing of 4-10COOH and 0-14COOH.

Uncertainties in the least significant digit are less than 1.

	4-10COOH	0-14COOH
Space group; *Z*′	$P\bar{1}$; 5	*C*2/*c*; 1
Column axis	$[3\bar{1}1]$	$[10\bar{5}]$ (or possibly $[1\bar{1}\bar{4}]$)
Repeat distance along column axis (Å)	43.43	89.99 = 2(44.99) {84.17 = 2(42.08) for $[1\bar{1}\bar{4}]$}
Closest-packed planes	(130); $(\bar{1}25)$	(511); $(\bar{5}1\bar{1})$
Angle between those planes (°)	68.9	67.6
Translation vectors in closest-packed planes (see Figs. 4 and 5)	$[3\bar{1}0]$; [210]	$[01\bar{1}]$; $[0\bar{1}\bar{1}]$
Angles of those translation vectors with column axis (°)	42.2; 56.1	54.8; 54.8
Components of those translation vectors normal to the column axis (Å)	4.63 = (23.15)/5 4.67 = (23.34)/5	8.91 = 2(4.46)
Other important plane including column axis	$(21\bar{5})$	(501)
Angles of this plane with closest-packed planes (°)	55.9; 124.8	56.2; 123.8
Translation vector in other important planes (see Figs. 4 and 5)	$[1\bar{2}0]$	[010]
Angle of this translation vector with column axis, °	69.6	90
Component of this translation vector normal to the column axis (Å)	5.26 Å = (26.30)/5	4.96
Molecular volume (*V*/*Z*; Å^3)	438	413

restraints to limit the eccentricity of the displacement ellipsoids of all atoms until the refinement had conveed, but the ISOR restraint was then removed. No other constraint or restraint was applied except for the requirement that the occupancy factors for the two parts of the CF_2 region of molecule *D* (see below) sum to unity. Convergence was not a problem. The elongation of some of the F-atom ellipsoids in the disordered molecules suggests the disorder model is only an approximation.

The positions of the H atoms of the COOH groups could be inferred from the molecular geometries; these H atoms were included in the least-squares cycles at idealized positions with the instruction AFIX 87. The methylene H atoms were placed in idealized positions and allowed to ride on the attached C atom (AFIX 23).

The results of the refinement (see Table 1) are surprisingly good considering the observation-to-parameter ratio (5.2:1) for reflections having $I > 2\sigma(I)$. The inclusion of *ca* 1350 restraints (as counted by *SHELXL*97) was undoubtedly key. The final peaks in the difference-Fourier map suggest unresolved disorder in the CF_3 group of molecule *F*.

Variation of an extinction parameter led to a negative and thus physically unreasonable value; the final cycles included no such correction. One low θ reflection (002) was omittted from the refinement because the agreement was poor and the backgrounds suspect.

3. Results

3.1. Overview of the packing

The packing in 4-10COOH is typical of *n*-alkyl carboxylic acids (see Bond, 2004, and references therein). Individual carboxylic acid molecules form hydrogen-bonded dimers (see Fig. 1) that have the standard $R_2^2(8)$ pattern (Bernstein *et al.*, 1995) of O—H···O bonds. Hydrogen-bonded dimers related by the translation $[3\bar{1}1]$ form columns. The columns then form an array that can be described as approximately hexagonal or as approximately rectangular (see Fig. 2). The *n*-carboxylic acid structures are usually described in terms of a centered array that is approximately orthorhombic (Bond, 2004; see dotted lines in Figs. 2 and Fig. 3).

3.2. Comparison with structure of *n*-pentadecanoic acid

The overall features of the 0-14COOH structure are the same as for most known structures of both even and odd *n*-alkylcarboxylic acids; the 4-10COOH structure can be considered to be a member of this general structure type. The important difference between the structures of 4-10COOH and the corresponding *n*-alkylcarboxylic acid 0-14COOH (space group *C*2/*c*; *Z*′ = 1) is a modulation that involves shifts of the 4-10COOH molecules in the direction of their long axes. Since a large shift takes place after every five molecules (or, after every five dimers) the value of *Z*′ in 4-10COOH is 5 rather than 1.

Comparisons show that the arrangements of the molecules in the densely packed planes of 4-10COOH (Figs. 2 and 4) and 0-14COOH (Figs. 3 and 5) are remarkably similar. The identification of the 'column axis' in 0-14COOH, however, is less straightforward than in 4-10COOH; in *n*-pentadecanoic acid that axis could be either $[1\bar{1}\bar{4}]$ or $[10\bar{5}]$. The latter has been chosen because it is common to the planes (511) and $(\bar{5}1\bar{1})$, which are the two most obvious close-packed planes. Detailed comparisons for the 4-10COOH and 0-14COOH structures of the angles between close-packed planes and of the repeat distances perpendicular to the column axis within those planes are given in Table 2.

The lefthand drawing of Fig. 5 (0-14COOH) can be superimposed almost exactly on the lefthand drawing [the (130) plane] of Fig. 4 (4-10COOH) and quite well on the righthand drawing [the $(\bar{1}25)$ plane]. These superpositions show that the packing in the 4-10COOH subunit composed of dimer columns *A*/*B*, *C*/*D*, *E*/*F*, *D*′/*C*′ and *B*′/*A*′ (where the prime indicates that the molecules have been taken through an inversion center) is very similar to the packing in the 0-14COOH structure. The important difference between the

4-10COOH and 0-14COOH structures is the shift along the column axis that occurs in the 4-10COOH structure after every fifth column.

In the *n*-alkylcarboxylic acids the $-C(=O)OH$ dimers that are adjacent in the close-packed planes are oriented edge-to-face (see the left drawing of Fig. 5). This arrangement is thought to be structure determining (Bond, 2004). In 4-10COOH the edge-to-face orientation of the carboxylic acid groups is preserved within the five-column subunit (see Fig. 4), but not between subunits.

3.3. Disorder

In the densely packed planes (130) and ($\bar{1}25$), each completely disordered *E*/*F* pair is surrounded by partially disordered *C*/*D* pairs, which are adjacent to completely ordered *A*/*B* pairs (see Fig. 2). The disordered pairs are located in the center of the five-column subunit; the columns at the edge of that unit are completely ordered.

Even though the dimer composed of molecules *E* and *F* appears to be completely disordered across apparent inversion centers (see Fig. 1), there must be local order within the columns. Imperfect alternation within a column of molecules *E* and *F* would generate either impossible intermolecular contacts or significant empty space because there is an offset along the alkyl chain of *ca* 2 Å between molecules E^i and *F* [(i) $-x, 1-y, 1-z$]. Perfect *E*/*F* alternation within the columns, however, does not mean there is any communication between *E*/*F* columns, which are separated by *A*/*B* columns that seem to be completely ordered. Correlation of all the *E*/*F* columns would be required if the space group were to be lowered from $P\bar{1}$ to $P1$.

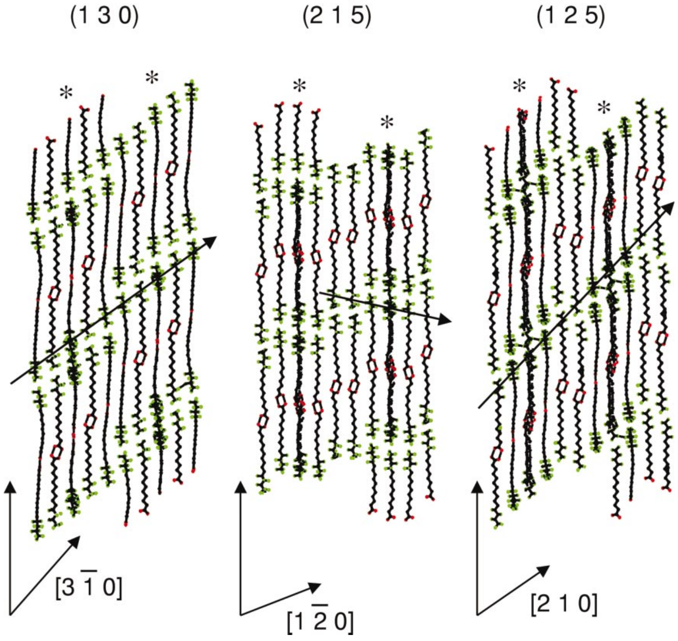

Figure 4
Drawings of the 4-10COOH packing in the planes (130), ($21\bar{5}$) and ($\bar{1}25$). The F atoms are shown in green and the O atoms in red. The [$3\bar{1}1$] vector points vertically upwards in each case; the vectors corresponding to translations within dimer layers are shown and identified below the drawings. The columns containing molecules *E* and *F* are marked with asterisks; the disorder is more obvious in ($21\bar{5}$) and ($\bar{1}25$) than in (310). Arrows indicate the alternating rows of regions with and without F atoms. If the drawing of the (130) plane were extended to the left or right the arrow shown would pass through ten CH_2 groups before passing through another CF_2 group. The pictures were drawn with the program *SHELXTL-PC* (Sheldrick, 1994).

The two CF_2 regions of the *C*/*D* dimer are disordered to different extents. During the initial refinement the occupancy factors for the major components of molecules *C* (disorder at C14 and C15) and *D* (disorder at C13, C14 and C15) refined to values of 0.502 (10) and 0.765 (5). All short contacts were then investigated using the program *Mercury* (Bruno *et al.*, 2002). The distance of 2.23 Å between F6*C* and F7F^i [(i) $-3-x, 2-y, -z$] in the plane ($\bar{1}25$) (see Fig. 4) would be impossible, so whenever molecule *C* is next to molecule *F* it must be that the *C*′ site is occupied. Since the conformation of molecule *C* depends on whether it is adjacent to a molecule *E* or *F*, the two occupancy factors are not independent. In the final refinement cycles the occupancy factor for *C* was set at 0.5. Molecule *D*, however is different; we find no really unfavorable contact involving its disordered F atoms. The occupancy factor for the major site of this molecule was refined freely to a value of 0.770 (5).

3.4. Modulations

The drawings of the close-packed planes (see Fig. 4) show the complex modulations associated with the large *Z*′ value. The most obvious modulation (see above) involves the position of the dimer along the [$3\bar{1}1$] direction, but the bending of the molecules is also affected. The modulations in the planes (130), ($\bar{1}25$) and ($21\bar{5}$) are all different.

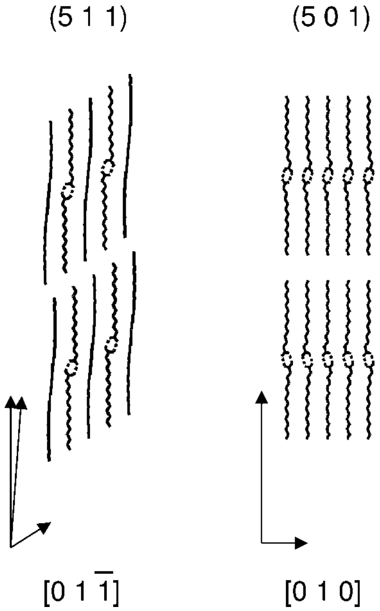

Figure 5
Drawing of the packing in the (511) [as well as ($\bar{5}1\bar{1}$)] and (501) planes of 0-14COOH (Bond, 2004). The vertical direction in the lefthand drawing is [$1\bar{1}\bar{4}$]; the [$10\bar{5}$] direction also lies within the plane but is rotated clockwise from [$1\bar{1}\bar{4}$] by 6.1°. The vertical direction in the righthand drawing is [$10\bar{5}$].

In the three closest-packed planes of 4-10COOH the molecules are arranged so that the CF_2, CH_2 and COOH parts of the molecule are segregated into different regions of space. The segregation of the $CF_3(CH_2)_3$ parts in the (130) plane is easiest to spot; in that plane the basic pattern runs along $[3\bar{1}0]$ for five dimer columns between discontinuities. The sixth column is shifted along $[3\bar{1}1]$ so that the 'top' $CF_3(CF_2)_3$ group of one molecule in the molecular bilayer is aligned with the 'bottom' $CF_3(CF_2)_3$ group of the next (see the lefthand drawing in Fig. 4). Just before, and immediately after, that vertical shift there is a pronounced bend in the CH_2 region of an adjacent molecule; that bend makes room for the larger CF_2 groups. Note that the vertical shift, or sheared interface, occurs between two columns of fully ordered *A*/*B* dimers.

There is a similar pattern of vertical shifts in the other close-packed plane (see the righthand drawing in Fig. 4), but in the $(\bar{1}25)$ plane the vertical shift is 'down' rather than 'up'. In these two planes vectors can be drawn that pass through alternating regions of ten fluorinated and then ten unfluorinated groups. In the $(21\bar{5})$ plane, which is not quite as close packed (see Table 2), the number of $CF_3(CF_2)_3$ groups aligned in a row is five rather than 10. The vertical shift again occurs between two columns of fully ordered *A*/*B* dimers.

3.5. Molecular geometry

No unusual bond length or angle was observed. Most of the torsion angles are within 8° of their expected values. The molecules are, however, significantly bent. The most noticeable bending (see Fig. 1) involves the direction in which the resistance is expected to be weakest; *i.e.* in the direction in which the molecules can curl like ribbons. There is also, however, some twisting around the long axes of the molecules in the regions containing atoms C11–C15. Almost all of the torsion angles that deviate by more than 8° from their expected values are in these regions. The average deviation is about 12° and the maximum, except for molecule *C*, is 17°. In molecule *C* deviations as large as 26° are found. No bending within the C-atom backbone of the type that would result in an alternate expansion and compression of C—C—C angles is observed.

The differences within molecules between the lengths of the C—OH (*i.e.* O1*n*) and C═O (*i.e.* O2*n*) bonds are 0.10–0.11 Å, so there is no question about the point of attachment of the acid H atoms. Furthermore, the average C2*n*—C1*n*—O2*n* (*i.e.* C—C═O) angle, 124.7 (2)°, is substantially larger than the average C2*n*—C1*n*—O1*n* (*i.e.* C—C—OH) angle, 112.0 (2)°. The carboxylic acid group (C1*n*, O1*n*, O2*n*) is nearly coplanar with the plane defined by C1*n*, C2*n* and C3*n*; the maximum twist is 8 (1)° (molecules *B* and *C*).

The average C—F distance decreases towards the end of the chain from 1.361 (2) Å at C12, through 1.342 (2) and 1.338 (3) Å at C13 and C14, to 1.312 (2) Å at C15. The effect of thermal motion on the apparent length of the bonds seems to be quite important, even though data were collected at 90.0 (2) K.

3.6. Related structures

A search of the November 2002 (5.24) release of the Cambridge Structural Database (Allen, 2002; hereafter the CSD), as well as of the updates through July of 2003, for organic molecules having both $(CF_2)_n$ and $(CH_2)_m$ groups, n and $m > 3$, yielded only one hit, $F_3C(CF_2)_5(CH_2)_{10}CH_2OH$ (TULQOG; Lapasset *et al.*, 1996). A similar search for organic molecules having both $(CF_2)_n$ and $(CH_2)_m$ groups, n and $m > 2$, yielded two additional hits: $H_3C(CH_2)_{10}O;PhC({=}O)O\text{-}PhC({=}O)O(CF_2)_2CF_3$ (YUJGOZ; Kromm *et al.*, 1995; substituents *para* around the two phenyl rings) and $F_3C(CF_2)_3(CH_2)_3O(CH_2)C(CH_3)(CH_2OH)_2$ (XORMAS; Omotowa *et al.*, 2002).

Given the interest in partially fluorinated amphiphiles (see Arora *et al.*, 2003; Lehmler *et al.*, 2000, 2001; Lehmler & Bummer, 2002*a*,*b*; Krafft, 2001; Omotowa *et al.*, 2002), the very small number of their structures in the CSD is strong, if indirect, evidence of the difficulty in obtaining crystals of such compounds.

4. Discussion

Partially fluorinated hydrocarbons and, especially, partially fluorinated amphiphiles fail to crystallize readily or well because of the conflict between the tendency towards spatial segregation of different functional groups and the drive to fill space densely and uniformly. This conflict is clear in Fig. 4. The $(COOH)_2$ groups, and the hydrogenated and the fluorinated regions of the independent molecules each form layers so that the number of contacts between molecular regions that are similar electronically is large. This spatial segregation, however, leads to space-filling problems because the size of a CF_2 group is different from the size of a CH_2 group, and neither has the dimensions of a —C(═O)OH dimer.

4.1. Tendency to spatial segregation

The tendency of electronically different parts of molecules to segregate into one or two dimensions (chains or columns; layers) is well known to those who have looked at large numbers of packing diagrams. This behavior is almost certainly related to the observation that positive deviations from Raoult's Law are much more common than negative deviations, and that minimum-boiling azeotropes are therefore much more common than maximum-boiling azeotropes (see the *CRC Handbook of Chemistry and Physics*, 1995). Interactions $A\cdots B$ are usually less favorable than the mean of $A\cdots A$ and $B\cdots B$ interactions (unless the *A* and *B* molecules have complementary functional groups and are otherwise similar). This tendency to segregation almost certainly also accounts for the observation that separation by fractional crystallization is usually successful. Solid-state compounds (or co-crystals) are rare except in the case of strong attractive interactions between the different components or special host–guest interactions. A carboxylic acid group and a long hydrocarbon chain would be very unlikely to occur in the same crystal if they were not covalently bonded. If a covalent bond forces those unlike groups to crystallize together then the groups usually form separate layers.

While F atoms may be less likely to be segregated from H atoms than are Cl and Br atoms (Boese *et al.*, 2001; Thalladi *et al.*, 1999), $(CF_2)_n$ segments seem likely to be separated from $(CH_2)_m$ segments if *n* and *m* are 3 or more.

4.2. Different sizes of the molecular regions

If the hydrogenated and fluorinated regions of 4-10COOH are segregated spatially, then how can space be filled densely in both regions? The CF_2 region of the alkyl chain has a substantially larger cross section than does the CH_2 region.

Since all C—C—C—C torsion angles in the chain are near 180°, the molecular cross sections are approximately rectangular. If the average C—F distance is 1.36 Å, as it is at C12 in this structure, then the C—F distance is something like 0.3 Å longer than the average C—H distance measured by neutron diffraction. Pauling (1960) and Bondi (1964) agree that the van der Waals radius of an H atom should be 1.2 Å; Rowland & Taylor (1996) give the slightly smaller value of 1.1 Å. The van der Waals radius of F is given as 1.35 Å by Pauling (1960) and as 1.47 Å by Bondi (1964); Rowland & Taylor (1996) conclude that the radius should be 1.45 Å. The difference in van der Waals radii of H and F atoms is then probably closer to 0.3 Å than to 0.2 Å. Consideration of both the van der Waals radii and the bond lengths leads to the conclusion that a CF_2 chain extends in some directions at least 0.5 Å farther than does a CH_2 chain.

Measurements at the air–water interface (Lehmler *et al.*, 2001) of long-chain carboxylic acids show that three acids with hydrocarbon chains (C15, C17, C19) have a cross-sectional area of *ca* 20 (1) Å^2, while three acids with perfluorocarbon chains (C12, C13, C14) have an area of *ca* 30 (1) Å^2. Four partially fluorinated acids $CF_3(CF_2)_n(CH_2)_mCOOH$ (C10, C15, C17, C18) have cross-sectional areas that are larger than 35 Å^2.

The —C(=O)OH dimer regions are perhaps a little thinner, or at least more compressible, in the direction perpendicular to the $(COOH)_2$ plane than is the rest of the molecule. Within that plane, however, the O atoms protrude slightly from the van der Waals surface of the rest of the molecule. The 'jog' introduced by the $R_2^2(8)$ hydrogen-bonding pattern keeps the molecular dimers from being linear.

4.3. Packing in 4-10COOH

In the *n*-alkyl carboxylic acids the dimers adjacent along the short edge of the subcell (**b** in 0-14COOH) are related by translation, but are offset by 0.3 (in decanoic acid) to 0.2 Å (in pentadecanoic acid) in the direction of the chains (see Fig. 5; Bond, 2004). The independent molecules in 4-10COOH, however, are shifted by different and much larger amounts along the column axis (see the lefthand drawing of Fig. 4). The modulations may be understood as arising from the need to fill space densely.

If 4-10COOH adopted the structure type known for the *n*-alkylcarboxylic acids then there would be too much space for the CH_2 regions of the molecules while the fluorinated regions would be too crowded. The shift along the molecular (or column) axis means that no vectors through the structure (see Fig. 4) pass through fluorinated groups only. The modulation thus guarantees that the filling of space is more uniform and more dense than it would be in a simpler structure. Why the translational shift occurs after every fifth molecule rather than after every third, fourth or sixth molecule is not understood; the length of the modulation must represent a compromise. If the need to fill space densely and uniformly were determining, then there would probably be a shift after every molecule. The longer modulation period indicates that the spatial segregation of groups that are electronically similar is important.

The complexity of the modulations raises the question of how the molecules manage to form an (mostly) ordered crystal. The number of crystals examined that failed to give satisfactory diffraction patterns suggests that not all 4-10COOH crystals are well ordered.

4.4. Melting-point comparisons

While the melting points (Lehmler *et al.*, 2001) for 4-10COOH and 0-14COOH are the same (321–322 K), the melting point for 6-10COOH (335 K) is 4 (1) K higher than for 0-16COOH and the melting point for 8-10COOH (359 K) is 21 (1) K higher than for 0-18COOH. As the lengths of the fluorinated and hydrogenated chains become more equal the difference in melting point between the hydrogenated and partially fluorinated compounds increases.

The displacement ellipsoids for 4-10COOH at 90 K are surprisingly large and therefore suggest a loosely packed crystal with a relatively low melting point.

4.5. Packing in other partially fluorinated amphiles

The structure of TULQOG (Lapasset *et al.*, 1996; 6-10CH_2OH in the style of abbreviation used for 4-10COOH) is particularly instructive. The OH groups form hydrogen-bonded chains; the three regions of the molecule are segregated spatially into layers that are perpendicular to **a** (see Fig. 6). The problem of matching the spacings of the hydrogenated

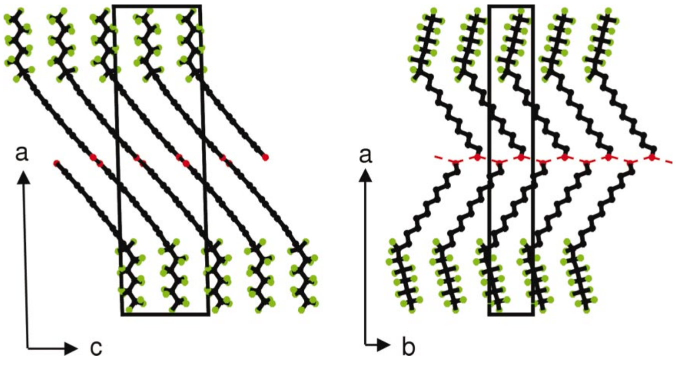

Figure 6
Projections showing the crystal packing in 6-10CH_2OH (Lapasset *et al.*, 1996). The drawing on the right shows only those molecules having centers of mass with $0 < z < 0.5$.

and fluorinated regions of the alkyl chain is solved by the introduction of a *gauche* interaction (torsion angle C11—C12—C13—C14 of 71°) around the bond between the first two fluorinated C atoms. This *gauche* interaction causes a kink in the alkyl chain, which is otherwise in an all-*trans* conformation. The angle of the alkyl chain with respect to **a** is larger in the hydrogenated region than in the fluorinated regions (see Fig. 6). The translation along **b** or **c** therefore corresponds to a shorter perpendicular distance between the hydrogenated chain segments than between the fluorinated segments. The problem of matching spacings is solved at the expense of the introduction of one somewhat unfavorable *gauche* interaction.

Why does 4-10COOH not solve its packing problem in a similar way? The differences between 4-10COOH and 6-10CH_2OH are the number of CF_2 units and the disposition of the hydrogen-bonding units (—COOH *versus* —OH). Perhaps it is the former that is the more important factor; there may not be enough CF_2 units in 4-10COOH to support the introduction of the *gauche* interaction.

In YUJGOZ (Kromm *et al.*, 1995) the molecules are bent and the molecular regions are segregated. Low-energy torsions within the molecules allow the degree of bend to be optimized. The presence of two independent molecules ($Z' = 2$) allows additional adjustments in the spacings.

The structure of XORMAS (Omotowa *et al.*, 2002) is interesting because packing diagrams show clearly that the CH_2 groups are not in contact. The spacings within the layers are determined by the hydrogen bonds formed by the terminal $C(Me)(CH_2OH)_2$ group as well as by the F···F contacts, but those spacings are larger than would be optimal for the CH_2 groups.

5. Summary

The tendency of groups that are similar electronically to form columns or layers in crystals, *i.e.* to be segregated spatially, is often at odds with the drive to fill space densely and uniformly. This conflict is particularly obvious in the structure of $CF_3(CF_2)_3(CH_2)_{10}COOH$, which is closely related to the structure of $CH_3(CH_2)_{13}COOH$, but which has $Z' = 5$ rather than 1. The modulation makes the distribution of CF_2 and CH_2 groups more uniform, while preserving much of their spatial separation. The same conflict in $F_3C(CF_2)_5(CH_2)_{10}CH_2OH$ is solved by the introduction of a kink into the chain rather than by a structural modulation. This conflict may explain the rarity of crystal structures of molecules containing both $(CF_2)_n$ and $(CH_2)_m$ regions.

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