

# Correlation between Observed Crystalline Self-Assembly of Fluorocarbon and Hydrocarbon Amphiphiles at the Air-Water Interface and Calculated Lattice Energy. Determination of Electrostatic Properties of the CF<sub>2</sub> Group from a Low-Temperature X-ray Diffraction Study of Perfluoroglutaramide

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**Abstract:** Recently, grazing-incidence X-ray diffraction studies of insoluble amphiphilic molecules have shown that molecules possessing fluorocarbon chains crystallize more efficiently on the surface of water than those possessing hydrocarbon chains. Here, we perform lattice energy calculations involving atomic electrostatic and van der Waals parameters on model two-dimensional crystals of hydrocarbon chains and fluorocarbon chains which possess crystalline arrangements similar to those of the corresponding amphiphilic films on water. The electrostatic parameters of CF<sub>2</sub> groups were determined from an X-ray study of the deformation electron density of perfluoroglutaramide, using single-crystal low-temperature (~100 K) X-ray diffraction data. The net charge on the fluorine atoms  $q = -0.14 e$  is almost twice that on hydrogen atoms  $q = +0.06 e$ , suggesting that intramolecular repulsion between fluorines will limit the possibility for conformational disorder in fluorocarbon chains. The calculated lattice energy of the model 2-D crystalline films of vertical fluorocarbon chains containing 20 carbons is lower by about 3.0 kcal per CF<sub>2</sub> group than the lattice energy of the model 2-D crystalline films of vertical hydrocarbon chains with the same number of carbons. We conclude that the crystallization behavior of amphiphilic molecules with fluorocarbon chains is determined by a higher backbone stiffness and higher interchain attractive van der Waals forces than for molecules with hydrocarbon chains. In addition, we show that it is possible to simply correlate the calculated lattice energies and the observed crystalline self-assembly at the air-water interface in various amphiphilic systems, in particular the homologous series of carboxylic acid molecules C<sub>n</sub>H<sub>2n+1</sub>CO<sub>2</sub>H ( $n = 13, 19, 20, 21, 29$ ): for more attractive lattice energies, the extent of crystalline order is larger.

## Introduction

Despite the considerable amount of observations on aggregation phenomena of amphiphilic molecules in solution, it is still a challenge to understand the molecular interactions which govern the molecular assembling.<sup>1,2</sup> This is due in a large part to the fact that the degree of crystalline order in lipid membranes in solution is low, and consequently very little information about the aggregate structure on the molecular level is to date attainable.

Nevertheless, insoluble amphiphilic molecules, which are potential models for biological membranes, were shown to form spontaneously large two-dimensional (2-D) crystalline clusters at the air-water interface,<sup>3-5</sup> presumably because of the constraints imposed: a "flat" interface and solvent in contact only from the hydrophilic side. The crystalline structure of such clusters may be determined on the molecular level by direct methods of investigation, the most successful one being grazing-incidence X-ray diffraction.<sup>6,7</sup> As a consequence, accurate models on the atomic level of the 2-D crystalline clusters can now be proposed on the basis of the X-ray data refinement. Such a refinement can be complemented by empirical lattice energy calculations,<sup>8</sup> which involve computation of the intermolecular van der Waals and electrostatic interactions.

Recently, a striking difference in crystallization at room temperature was observed by grazing-incidence X-ray diffraction between insoluble amphiphilic molecules possessing hydrocarbon chains and those possessing fluorocarbon chains. Indeed, the crystalline order in uncompressed films of the hydrocarbon  $\alpha$ -amino acid PL (palmitoyllysine, C<sub>15</sub>H<sub>31</sub>CONHC<sub>4</sub>H<sub>8</sub>CHNH<sub>3</sub><sup>+</sup>CO<sub>2</sub><sup>-</sup>) was insufficient to yield any diffraction signal. In contrast, self-assembled crystalline domains 1500 Å in diameter were detected in uncompressed films of the perfluorinated  $\alpha$ -amino acid

PFA ((perfluorodecyl)ethyl aspartate, C<sub>10</sub>F<sub>21</sub>C<sub>2</sub>H<sub>4</sub>OCOCH<sub>2</sub>-CHNH<sub>3</sub><sup>+</sup>CO<sub>2</sub><sup>-</sup>).<sup>3,4</sup> Diffraction data for fluorinated monolayers of C<sub>10</sub>F<sub>21</sub>CH<sub>2</sub>CO<sub>2</sub>H suggested the spontaneous crystalline aggregation of most of the molecules, even for very low surface concentrations.<sup>9</sup> This result may be compared with those obtained for arachidic acid monolayers (C<sub>19</sub>H<sub>39</sub>CO<sub>2</sub>H) at low surface pressure where the solid phase coexists with a fluid phase.<sup>10,11</sup> Diffraction data on the homologous series of carboxylic acid amphiphiles C<sub>n</sub>H<sub>2n+1</sub>CO<sub>2</sub>H also showed a difference in self-assembly at low temperature depending on the chain length: the longer the chain, the larger the extent of crystalline order. Here, we investigate these differences in self-assembly of amphiphiles by empirical lattice energy calculations.

A reliable comparison of lattice energies requires atomic van der Waals and electrostatic parameters of sufficient accuracy. Electrostatic parameters for the CH<sub>2</sub> groups, as derived from

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**Table I.** Symmetry Restrictions for Atomic Deformations in Perfluoroglutaramide<sup>a</sup>

atom	<i>L</i>	<i>M</i>	<i>N</i>
N1		<i>m</i>	<i>m</i>
O2			<i>m</i>
C2			<i>m</i>
C3, C4		<i>m</i>	<i>m</i>
F			<i>m</i>
H	<i>c</i>		

<sup>a</sup>Mirror symmetry normal to an axis is designated by *m*. Cylindrical symmetry along an axis is designated by *c*. *L*, *M*, and *N* are the local atomic axes, centered on the atoms (cf. Figure 1).

deformation electron density distribution,<sup>12</sup> were readily available.<sup>13</sup> The electrostatic parameters for the CF<sub>2</sub> groups are determined here from an X-ray study of the deformation electron density of perfluoroglutaramide (NH<sub>2</sub>CO(CF<sub>2</sub>)<sub>3</sub>CONH<sub>2</sub>), using single-crystal low-temperature (~100 K) X-ray diffraction data. This molecule was chosen because it was expected that the hydrogen bonding at the amide groups would render the packing rigid and so reduce atomic thermal motion. Also, the parameters of the amide group had already been determined for several crystal structures<sup>14,15</sup> and would therefore serve as markers for evaluating the correctness of the parameters of the CF<sub>2</sub> groups.

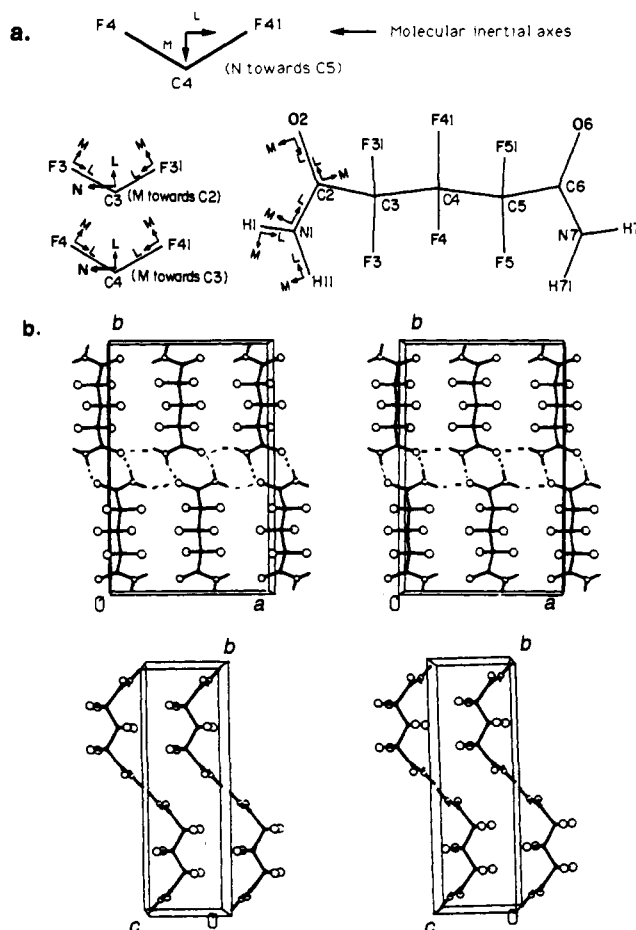
### Experimental Section

**1. Preparation of Perfluoroglutaramide Crystals and X-ray Measurements.** Perfluoroglutaramide was obtained from the PCR Co., Gainesville, FL, and was not further purified. Crystals were grown from a 1:1 ethyl acetate/ethanol solution by slow evaporation. A crystal of dimensions 0.2 × 0.3 × 0.15 mm<sup>3</sup> was removed from the mother liquor and mounted on a Rigaku AFC-5R four-circle diffractometer. The crystal was shock-cooled to a temperature of about 100 K. The diffraction measurements were made using a rotating molybdenum-anode source and a graphite monochromator (λ = 0.71 Å). The reflections were measured to a Bragg angle of 55° using ω-2θ scans. The scan widths were Δω = (A + B tan θ)°, with A = 2° and B = 0.3°.

**2. Structure Refinement.** Perfluoroglutaramide crystallizes in the space group *Pnma*, giving an orthorhombic cell with the dimensions *a* = 10.049 (2) Å, *b* = 15.576 (2) Å, and *c* = 5.014 (1) Å. There are four molecules per unit cell. A total of 7346 reflections were collected from two symmetry-related quartets; 3819 symmetry-averaged unique reflections were used in the crystal structure refinement. The crystal structure was determined by direct methods using the SHELX-76 program.<sup>16</sup>

The structure was further refined with the program LSEXP,<sup>17</sup> where the electron density is described as a sum of spherical atom distributions plus atomic deformations. The latter are expanded in atom-centered spherical-harmonic-like functions, whose coefficients are refined together with the positional and thermal parameters.<sup>17</sup> Symmetry restrictions were applied to the deformations of individual atoms in order to reduce the number of refined parameters. These restrictions are listed in Table I. In addition, the deformation parameters of all the fluorine atoms were made identical, as were the deformations of the hydrogen atoms. Also, the deformations of the hydrogens were limited by not including quartic terms. This is necessary in view of the difficulty in determining hydrogen positions and thermal parameters from X-ray data. The theoretical cusp constraint was imposed on the spherical terms.<sup>14</sup>

The thermal motion of the hydrogen atoms was estimated as the sum of rigid-body motion amplitudes of the C, N, O, and F atoms plus bond-stretching and angle-bending amplitudes taken from vibration spectra.<sup>18</sup> The rigid-body parameters were obtained from a refinement in which atoms N1, C2, O2, C3, F3, and F31 (the atom-numbering scheme is shown in Figure 1a) were constrained to move as a rigid body. These parameters were used only for describing hydrogen vibrations. The N-H bond lengths were kept fixed at 1.02 Å.



**Figure 1.** Packing arrangement of crystalline perfluoroglutaramide. (a) Atom-numbering scheme showing the local atomic axes centered on each atom. The *L* axis of atoms C3 and C4 points along the F-C-F angle bisector. The local axes are shown for only half of the molecule. The other half is related by a mirror plane in which lie the atoms C4, F4, and F41. The molecular inertial axes system is also shown. (b) Stereoscopic views of the packing arrangement in the crystal: (top) along the *c* axis; (bottom) along the *a* axis.

As the refinement proceeded, a systematic error in the strong reflections became apparent. Thus, an isotropic extinction correction was introduced:  $F(\text{obs})_{\text{cor}} = F(\text{obs}) / (1 - c^2 F(\text{obs})^2)$ , where  $c = 0.00015$ . All reflections were weighted by  $w = 1 / \text{SD}^2(F^2)$ , where  $\text{SD}^2(F^2) = 4F^6 K^6 + 4F^2 \sigma^2(F)$  and  $K = 0.002$ . The number of refined parameters, including deformations, was 213. The final agreement factors were  $R(F) = 0.0430$  and  $R_w(F^2) = 0.0306$ .

### Structure and Deformation Density of Perfluoroglutaramide

Atomic coordinates, anisotropic thermal parameters, bond lengths, and angles are given in Table II. The calculated root-mean-square deviations of the vibration amplitudes of bonded atoms along the bonds for all non-hydrogen atoms (rigid-bond test) are small enough to be expected from bond stretching.<sup>19</sup>

The perfluoroglutaramide molecules form cyclic hydrogen bonds across centers of inversion (Figure 1b), yielding hydrogen-bonded chains running parallel to the *b* axis. These chains are stacked by translation along the *c* axis to form (100) layers. These layers are interlinked by hydrogen bonds via glide symmetry along the *a* axis to complete the crystal structure.

Perfluorinated segments are expected to have a helical conformation.<sup>20-23</sup> In the crystal of perfluoroglutaramide, however,

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(23) The crystal structure of CF<sub>3</sub>(CF<sub>2</sub>)<sub>7</sub>C<sub>7</sub>H<sub>9</sub>I was solved in this laboratory. The perfluorinated chain adopts a helical conformation.

**Table II.** Structural Data for Perfluoroglutaramide: Atom Fractional Coordinates, Anisotropic Thermal Parameters, and Bond Lengths and Angles, with Standard Deviations (SD) in Parentheses<sup>a</sup>

Fractional Coordinates ( $\times 10^5$ )							
	x	y	z		x	y	z
N1	35 466 (7)	94 286 (3)	16 290 (11)	C4	45 368 (5)	75 000 (0)	32 132 (17)
O2	57 495 (5)	93 900 (3)	26 238 (12)	F4	36 406 (5)	75 000 (0)	12 105 (10)
C2	46 029 (8)	91 270 (4)	28 765 (12)	F41	57 655 (5)	75 000 (0)	21 587 (10)
C3	43 553 (3)	83 552 (3)	47 593 (12)	H1	36 592	98 980	2 288
F3	31 104 (4)	83 828 (2)	57 691 (9)	H11	25 945	92 144	18 625
F31	52 266 (4)	83 859 (2)	67 485 (8)				

Anisotropic Thermal Parameters ( $\times 10^5$ ; Average SD = 0.00015)						
	U(1,1)	U(2,2)	U(3,3)	U(1,2)	U(2,3)	U(1,3)
N1	834	1534	1819	4	276	-79
O2	848	1640	2110	-178	353	-72
C2	808	1199	1413	-60	42	12
C3	1013	1277	1082	-28	-55	60
F3	1276	1622	1687	44	-23	584
F31	1820	1739	1284	-159	-69	-474
C4	977	1195	1054	0	0	71
F4	1734	1484	1200	0	0	-420
F41	1211	1619	1896	0	0	658
H1	2880	2413	2979	29	778	-34
H11	1450	3218	3950	-307	257	8

Bond Lengths ( $\text{\AA}$ )							
N1-H1	1.020 (fixed)	C2-O2	1.229 (1)	C3-F3	1.350 (1)	C4-F4	1.349 (1)
N1-H11	1.020	C2-C3	1.549 (1)	C3-F31	1.342 (1)	C4-F41	1.343 (1)
N1-C2	1.319 (1)	C3-C4	1.552 (2)				

Bond Angles (deg)							
N1-C2-O2	125.94 (7)	H1-N1-H11 <sup>a</sup>	114.70	C2-C3-C4	110.05 (7)	C3-C4-F4	107.07 (15)
N1-C2-C3	115.87 (6)	O2-C2-C3	118.17 (6)	F3-C3-F31	108.64 (6)	C3-C4-F41	107.74 (14)
C2-N1-H1 <sup>a</sup>	119.48	C2-C3-F3	110.65 (4)	F3-C3-C4	108.88 (4)	F4-C4-F41	108.70 (9)
C2-N1-H11 <sup>a</sup>	125.72	C2-C3-F31	109.20 (4)	F31-C3-C4	109.39 (5)		

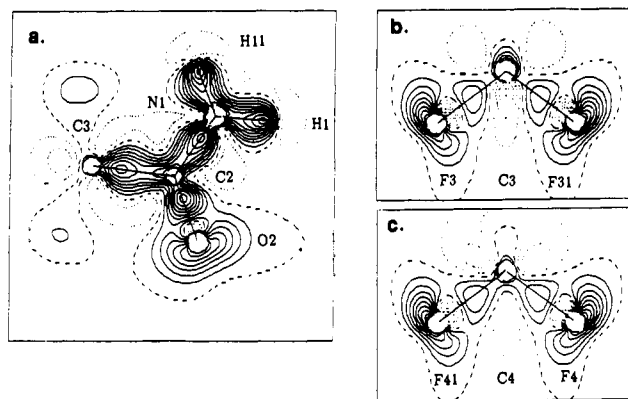
Torsion Angles (deg)			
N1-C2-C3-C4	90.93	C2-C3-C4-C5	179.98
		O2-C2-C3-C4	-87.41

<sup>a</sup> Hydrogen atom positions and thermal parameters were partially restrained and so are not given SD values.

the central  $\text{CF}_2$  group of each molecule lies on a mirror plane (Figure 1) and the dihedral angles, listed in Table II, show that the fluorinated segment has a trans conformation. We may speculate that the fluorinated section is too short to impose helicity.<sup>24</sup> In addition, the presence of the amide groups in the molecule might override the forces which usually induce a twist in perfluorinated chains.<sup>25</sup>

Slices of the static deformation density of molecular fragments are shown in Figure 2, with contours every  $0.1 \text{ e } \text{\AA}^{-3}$ . The deformation density was partitioned into atomic fragments by the stockholder method<sup>12,26</sup> and the fragments were integrated on a  $0.1\text{-\AA}$  rectangular grid to produce the atomic multipole moments listed in Table III.

The deformation density in the amide group plane is shown in Figure 2a. It resembles closely the corresponding portion in diformohydrazide.<sup>14</sup> The charge found for the oxygen atom ( $q = -0.26 \text{ e}$ ) is more similar to the charge found for the oxygen atom in carboxylic acids both by calculation<sup>13</sup> ( $q = -0.33 \text{ e}$ ) and by experiment<sup>13,28</sup> ( $q = -0.22 \text{ e}$ ), than the charge found for the oxygen atom in amides by calculation<sup>14</sup> ( $q = -0.38 \text{ e}$ ) or by experiment<sup>14,15</sup> ( $q = -0.38 \text{ e}$  in diformohydrazide and  $q = -0.39 \text{ e}$  in acetamide). Also, there is almost no dipole component on the oxygen atom in the direction of the  $\text{O}=\text{C}$  bond as found in carboxylic acids,<sup>13,27</sup> whereas in acetamide<sup>15</sup> and in diformohydrazide<sup>14</sup> the nonbonding



**Figure 2.** Deformation density maps with contour lines every  $0.1 \text{ e } \text{\AA}^{-3}$ . Whiteness around atom centers are where the error in the maps is above  $0.2 \text{ e } \text{\AA}^{-3}$ : (a) in the N1, O2, C2, C3 plane; (b) in the C3, F3, F31 plane; (c) in the C4, F4, F41 plane.

density of the oxygen outweighs the bonding density, producing a dipole moment in the  $\text{O}=\text{C}$  direction. Thus, the charge distribution around the oxygen atom in perfluoroglutaramide is closer to that of an acid than to that of an amide.<sup>28</sup> This is in accordance with the  $\text{C}=\text{O}$  bond length of  $1.23 \text{ \AA}$ , which is shorter than in formamide and closer to that of a carboxylic acid, reflecting more double-bond character.<sup>28</sup> This behavior can be attributed to the electronegative character of the neighboring  $\text{CF}_2$  groups, which bear a small residual charge of  $-0.05 \text{ e}$ .

A remarkable feature of the deformation density maps is the low-density peak of the C-F bond (Figure 2b,c). This was also observed in tetrafluoroterephthalonitrile<sup>29</sup> (TFT) and in the ab-

(24) Force field calculations show that there is no evidence for twisting about the C-C bond in perfluoropropane,  $\text{CF}_3\text{CF}_2\text{CF}_3$ , and that it has a staggered structure.<sup>22</sup>

(25) Calculation of the intramolecular electrostatic energy of interaction between a  $\text{CF}_2$  group and the attached fluorocarbon chain  $-(\text{CF}_2)_n-\text{CF}_3$  ( $n \geq 3$ ) showed that, when the chain adopts a helical conformation ( $12^\circ$  twist per  $\text{CF}_2-\text{CF}_2$  bond), the intramolecular electrostatic energy is lowered by approximately 1 kcal/mol.

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**Table III.** Atomic Multipole Moments for Perfluoroglutaramide: Net Charges  $q$  ( $e \times 10^3$ ), Dipole Moments  $d$  ( $e \text{ \AA} \times 10^3$ ), and Second Moments  $\mu$  ( $e \text{ \AA}^2 \times 10^3$ )<sup>a</sup>

a. Multipoles Referred to the Molecular Inertial Axes $L$ , $M$ , and $N$ <sup>b,c</sup>										
	$q$	$d_L$	$d_M$	$d_N$	$\mu_{LL}$	$\mu_{MM}$	$\mu_{NN}$	$\mu_{LM}$	$\mu_{LN}$	$\mu_{MN}$
N1	-179 (20)	-16 (13)	-20 (10)	-14 (12)	116 (15)	102 (19)	103 (18)	-4 (5)	2 (7)	4 (9)
O2	-264 (74)	54 (61)	-29 (24)	27 (42)	143 (82)	120 (55)	74 (68)	0 (19)	-22 (24)	-21 (19)
C2	224 (16)	18 (15)	-12 (13)	22 (16)	142 (28)	292 (31)	221 (29)	2 (7)	0 (11)	-81 (11)
C3	225 (10)	10 (6)	59 (8)	-10 (5)	224 (21)	219 (22)	198 (16)	-4 (3)	-5 (4)	-4 (3)
F3	-147 (9)	-4 (13)	-2 (13)	7 (3)	96 (16)	51 (17)	78 (15)	7 (5)	-4 (2)	-1 (1)
F31	-130 (11)	15 (14)	-9 (12)	-5 (4)	113 (20)	58 (19)	92 (18)	-12 (7)	-2 (3)	2 (2)
C4	223 (12)	11 (4)	-44 (9)	0 (0)	228 (21)	217 (21)	173 (12)	-1 (2)	0 (0)	0 (0)
F4	-152 (11)	-11 (12)	12 (12)	0 (0)	93 (16)	48 (17)	69 (12)	-6 (6)	0 (0)	0 (0)
F41	-129 (12)	23 (15)	14 (12)	0 (0)	112 (21)	57 (19)	92 (19)	6 (6)	0 (0)	0 (0)
H1	151 (36)	-10 (10)	-47 (23)	-47 (25)	92 (15)	62 (26)	60 (25)	-7 (4)	-2 (5)	-15 (16)
H11	152 (36)	-71 (28)	13 (10)	16 (11)	52 (32)	79 (17)	82 (18)	6 (7)	6 (8)	4 (3)

b. Multipoles Referred to the Local Orthogonal Axes on Each Atom $L$ , $M$ , and $N$ <sup>b</sup>										
	$q$	$d_L$	$d_M$	$d_N$	$\mu_{LL}$	$\mu_{MM}$	$\mu_{NN}$	$\mu_{LM}$	$\mu_{LN}$	$\mu_{MN}$
N1	-179	-25	14	5	113	110	98	5	3	1
O2	-264	-49	-26	-38	142	74	122	18	-4	-24
C2	224	12	17	-21	147	165	342	-11	-13	16
C3	225	59	7	10	219	198	223	3	-3	8
F3	-147	-2	-4	7	75	73	78	23	1	3
F31	-130	-7	-16	-19	83	89	93	30	3	2
C4	223	44	0	10	217	174	228	0	0	0
F4	-152	-2	-16	0	72	68	69	23	0	0
F41	-129	-11	-24	0	88	81	92	28	0	0
H1	151	-67	7	-1	46	93	76	5	1	4
H11	152	-72	14	1	52	84	76	8	0	-1

<sup>a</sup>The net charge for atom  $i$  is  $q_i = -\int \delta\rho_i(r) dv$ ; the negative sign obeys the convention that electrons are negatively charged. The atomic dipole moment  $d_{i,L} = -\int x\delta\rho_i(r) dv$ , where  $x$  is the first component of the vector  $r$  in the  $L$  direction. Similar expressions apply to  $d_{i,M}$  and  $d_{i,N}$ . The second moment tensor of  $\delta\rho_i(r)$  has six independent components:  $\mu_{i,LL}$ ,  $\mu_{i,MM}$ ,  $\mu_{i,NN}$ ,  $\mu_{i,LM}$ , etc.;  $\mu_{i,LM} = -\int xy\delta\rho_i(r) dv$ . <sup>b</sup>Cf. Figure 1. <sup>c</sup>The standard deviations are given in parentheses.

initio deformation density map of HCOF.<sup>30</sup> This feature was discussed in depth for TFT.<sup>29</sup> The four independent fluorines in perfluoroglutaramide are of the same deformation type and the small differences in their multipoles arise from the partitioning scheme. The average charge for the fluorine is  $-0.14 e$ , close to the value obtained experimentally for TFT and theoretically for HCOF ( $-0.13 e$ ). This charge is substantially greater than that found for aliphatic  $\text{CH}_2$  hydrogens ( $q = 0.06 e$ ), and one would expect electrostatic repulsion between neighboring fluorine atoms.

The lone-pair density of the fluorine is asymmetric (Figure 2b,c), showing the effect of the F-F repulsion between the 1- and 3-neighbors. This charge polarization is not reflected in the atomic dipoles on the fluorine atoms, which point away from the neighboring fluorine. Apparently the dipoles are dominated by the more distant portions of the F-fragment electron density, which are oppositely polarized, as can be judged from the shape of the zero contour (Figure 2b,c).

### Calculations of the Lattice Energies of Model Two-Dimensional Crystals of Amphiphilic Molecules with Hydrocarbon and Fluorocarbon Chains

**1. Method of Calculation.** The intermolecular potential energy for a pair of atoms  $i$  and  $j$  separated by a distance  $r_{ij}$  can be represented in the form

$$V(r) = -Ar_{ij}^{-6} + Br_{ij}^{-9} + \int \frac{\rho_i(r)\rho_j(r)dv_i dv_j}{r_{ij}}$$

The first two terms are van der Waals interactions, the third term is the Coulomb energy, where  $\rho_i(r)$  and  $\rho_j(r)$  are the atomic charge distributions, and  $r$  is measured from the nucleus. One can replace  $\rho_i(r)$  by  $\delta\rho_i(r)$  in the preceding equation, where  $\delta\rho_i(r)$  is the electron density of the bonded atom minus that of the free atom,<sup>12,26</sup> since the Coulomb energy is invariant to this substitution for nonoverlapping atoms. The Coulomb energy can be approximated by a multipole moment expansion of  $\rho(r)$ . It is sufficient to employ only the first three moments, namely, the atomic net charge, the atomic dipole moment, and the quadrupole moment.<sup>12,26</sup>

The lattice energy of a 2-D crystal, given by  $V/2$  is obtained by summing  $V$  over all atoms  $i$  of a molecule  $A$  and all atoms  $j$  of surrounding molecules  $B$ . For neutral molecules, it is sufficient to consider in the summation all molecules  $B$  at a cutoff distance of about  $25 \text{ \AA}$  from molecule  $A$ . Typically, the energy of interaction between two molecules separated by such a distance is as low as  $5 \times 10^{-3}$  kcal/mol. Thus, the contribution to the lattice energy from all the molecules at a distance of  $25 \text{ \AA}$  from molecule  $A$  is approximately  $0.1$  kcal/mol, compared with lattice energies that are of the order of tens of kilocalories per mole.

**2. Electrostatic and van der Waals Parameters (Table IV).** Atomic moments (charge, dipoles, and quadrupoles) can be derived from X-ray diffraction data measured at low temperature. As was demonstrated earlier,<sup>12,31</sup> electrostatic properties of molecular fragments are very similar in any molecule containing this fragment; in other words, the atomic moments are transferable from one molecule to another of similar character. We made use of this transferability property to derive multipole moments of long hydrocarbon and fluorocarbon molecules because no low-temperature X-ray diffraction studies of such molecules are to date available. The electrostatic parameters for the hydrocarbon chains are an average of those obtained for the ethyl groups of the 1,3-diethylbicyclobutane-*exo,exo*-2,4-dicarboxylic acid molecule (Table IVa).<sup>13</sup> The parameters for the fluorocarbon chains are an average of those obtained here for perfluoroglutaramide (Table IVa). In addition, the parameters were slightly modified so that each  $\text{CH}_2$  and each  $\text{CF}_2$  group as well as the  $\text{CH}_3$  and  $\text{CF}_3$  groups are neutral.

The van der Waals parameters for each pair of atoms excluding fluorine atoms are those of Lifson, Hagler, and Dauber<sup>32</sup> (Table IVb). The van der Waals parameters for fluorine atoms were derived from parameters used in force field calculations.<sup>33</sup>

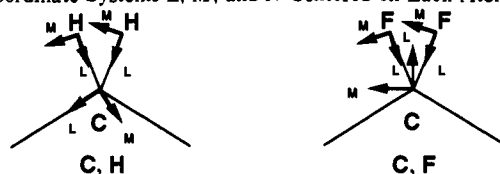
**3. Model 2-D Crystals of Hydrocarbon and Fluorocarbon Chains.** The model hydrocarbon chain contains 20 carbons and

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Table IV. Electrostatic Properties and van der Waals Parameters for Energy Calculations

a. Net Atomic Charges ( $\times 10^4$ ) and Dipole and Quadrupole Moments ( $\times 10^4$ ) of Hydrocarbon and Fluorocarbon Chains in Local Cartesian Coordinate Systems  $L$ ,  $M$ , and  $N$  Centered on Each Atom



atom	atom charge $q$ , e	dipole moment, e Å			second moment, e Å <sup>2</sup>					
		$d_L$	$d_M$	$d_N$	$\mu_{LL}$	$\mu_{MM}$	$\mu_{NN}$	$\mu_{LM}$	$\mu_{MN}$	$\mu_{LN}$
Hydrocarbon Chain (CH <sub>2</sub> ) <sub>n</sub> CH <sub>3</sub>										
C(CH <sub>2</sub> )	-1140	200	0	0	790	970	1400	0	0	0
C(CH <sub>3</sub> )	-1740	0	0	0	1170	1170	1170	0	0	0
H(H <sub>2</sub> C)	570	-830	0	0	600	560	790	0	0	0
H(H <sub>3</sub> C)	580	-860	0	0	620	670	730	0	0	0
Fluorocarbon Chain (CF <sub>2</sub> ) <sub>n</sub> CF <sub>3</sub>										
C(CF <sub>2</sub> )	2800	440	0	100	2170	1740	2280	0	0	0
C(CF <sub>3</sub> )	4200	0	0	0	2060	2060	2060	0	0	0
F(F <sub>2</sub> C)	-1400	-70	-200	0	800	750	810	260	0	0
F(F <sub>3</sub> C)	-1400	-70	-200	0	800	750	810	260	0	0

b. Atom-Atom van der Waals Potential Parameters  $A$  and  $B$

atom pair	$A$ , kcal/mol	$B$ , kcal/mol	atom pair	$A$ , kcal/mol	$B$ , kcal/mol	atom pair	$A$ , kcal/mol	$B$ , kcal/mol
Hydrocarbon Chain								
C(CH)-C(CH)	1230.0	38 900.0	C(CH)-H(HC)	135.8	4 160.6	H(HC)-H(HC)	15.0	445.0
Fluorocarbon Chain								
C(CF)-C(CF)	1230.0	38 900.0	C(CF)-F(FC)	1166.9	32 223.0	F(FC)-F(FC)	1082.5	25 934.7

possesses an all-trans conformation. The model two-dimensional crystal structure is characterized by a chain packing in plane group  $pg$  with the chain standing vertically in a primitive rectangular cell ( $a = 4.98$  Å,  $b = 7.42$  Å) (Figure 3a). Such a 2-D layer structure describes the most commonly observed packing in 3-D crystal structures of molecules possessing long hydrocarbon chains.<sup>34,35</sup> Monolayers of compressed amphiphilic carboxylic acids (C<sub>n</sub>H<sub>2n+1</sub>COOH) and alcohols (C<sub>n</sub>H<sub>2n+1</sub>OH) organize in such 2-D crystals on the water surface at low temperature.<sup>7,11,36</sup>

The model fluorocarbon chain contains 20 carbons and was geometrically built to match the molecular structure of the room-temperature phase of poly(tetrafluoroethylene) (PTFE, phase IV), which means that the fluorocarbon chain is helical with a 12° twist per CF<sub>2</sub>-CF<sub>2</sub> bond (the chain twists by about 180° every 15 CF<sub>2</sub> groups).<sup>20-22</sup> The model 2-D crystal structure is characterized by a chain packing in a hexagonal cell with the chains standing vertically (Figure 3b), as in the 3-D crystal structure of PTFE (phase IV),<sup>20,21</sup> the 2-D crystal structure of compressed PFA,<sup>3,4,37</sup> and the C<sub>10</sub>F<sub>21</sub>CH<sub>2</sub>CO<sub>2</sub>H<sup>9</sup> monolayers over

water. We note that the unit cell axes differ for the above mentioned crystals:  $a = 5.66$  Å in phase IV of PTFE,  $a = 5.74$  Å for PFA, and  $a = 5.82$  Å for C<sub>10</sub>F<sub>21</sub>CH<sub>2</sub>CO<sub>2</sub>H.

A chain of 20 carbons is sufficiently long to eliminate end effects in the lattice energy calculation.

**4. Validity of the Parameters.** The set of electrostatic and van der Waals parameters given in Table IV can be readily tested by evaluating the lattice energy of the observed 2-D crystals and checking that this energy is not far from the energy minimum. The results in Figure 4 show that the energy minima for the model crystals correspond to cell dimensions close to the experimental values. The energy minimum for the model crystal of the fluorocarbon chains yields a hexagonal unit cell where  $a = b = 5.30$  Å (compared with  $a = b = 5.66$  Å for 3-D crystals of PTFE, phase IV<sup>20,21</sup>); the energy minimum for the model crystal of the hydrocarbon chains yields a primitive rectangular unit cell where  $a = 4.70$  and  $b = 7.00$  Å (compared with  $a = 4.98$  Å and  $b = 7.42$  Å for 3-D crystals of long-hydrocarbon-chain molecules.<sup>34,35</sup>). Thus, we find using our parameters that the energy minima correspond to 2-D crystals of fluorocarbon and hydrocarbon chains that are about 6% more dense than the observed ones. As shall be seen, the major contribution to the lattice energy arises from van der Waals interactions, and one may speculate that this discrepancy in crystal density probably arises from imperfect van der Waals parameters. In terms of lattice energies, the calculated energy per CH<sub>2</sub> of the hydrocarbon chain in its 2-D crystal is 2.1 kcal/mol for the observed structure and 2.3 kcal/mol at the energy minimum. These numbers compare well with the heat of sublimation data for organic crystals, which indicate that normal paraffins C<sub>n</sub>H<sub>2n+2</sub> possess a heat of sublimation of 2 kcal/mol per CH<sub>2</sub> group.<sup>34b</sup> The calculated energies per CF<sub>2</sub> of the fluorocarbon chain in the 2-D crystal is 6.3 kcal/mol for the observed structure (in the hexagonal cell  $a = b = 5.66$  Å) and 7.2 kcal/mol at the energy minimum. Surely, the large lattice energy difference between hydrocarbon and fluorocarbon chains, discussed further in the next section, cannot arise simply from uncertainties in the parameters.<sup>33</sup>

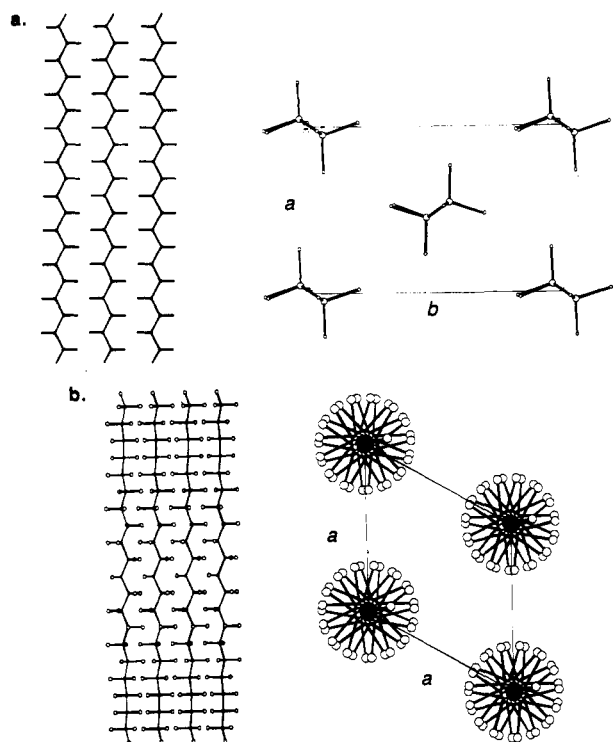
(33) (a) The van der Waals parameters for fluorine  $r^*_F$  and  $\epsilon_F$  (where  $r^*$  is the interatomic distance at the minimum of the potential and  $\epsilon$  is the potential minimum) were not available for the 6-9 potential formalism which we used in this study. Thus, we extracted these parameters from a different force field<sup>33c</sup> and matched them to the 6-9 potential formalism. This was done by rescaling the potential depth  $\epsilon_F$  so that the relative potential energy depths for F-F, C-C, and H-H interactions are preserved. (b) Other sources for van der Waals parameters for fluorine were also considered.<sup>33d,e</sup> Using van der Waals parameters from the studies of Spackman et al.<sup>33d</sup> gave less attractive energies for fluorocarbon chains, nevertheless by amounts that would not change the overall conclusions derived in this paper. The van der Waals parameters which were used in the studies of Allinger et al.<sup>33e</sup> and Meyer et al.<sup>33f</sup> gave more attractive energies for fluorocarbon chains and so are completely in agreement with the thread of this paper. The parameters which we used lie between those two sets of parameters, allowing for a qualitative comparison between the calculated lattice energies for fluorocarbon and hydrocarbon crystals. (c) Steliou, K. Model Program. Montreal University. (d) Spackman, M. A. *J. Chem. Phys.* **1986**, *85*, 6579. (e) Allinger, N. L.; Hirsch, J. A.; Miller, M. A.; Tyminski, I. *J. Am. Chem. Soc.* **1969**, *91*, 337. (f) Meyer, A. Y. *J. Mol. Struct.* **1978**, *49*, 383.

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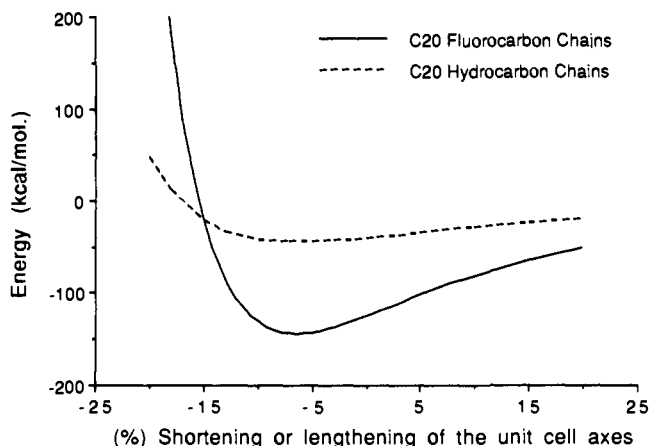
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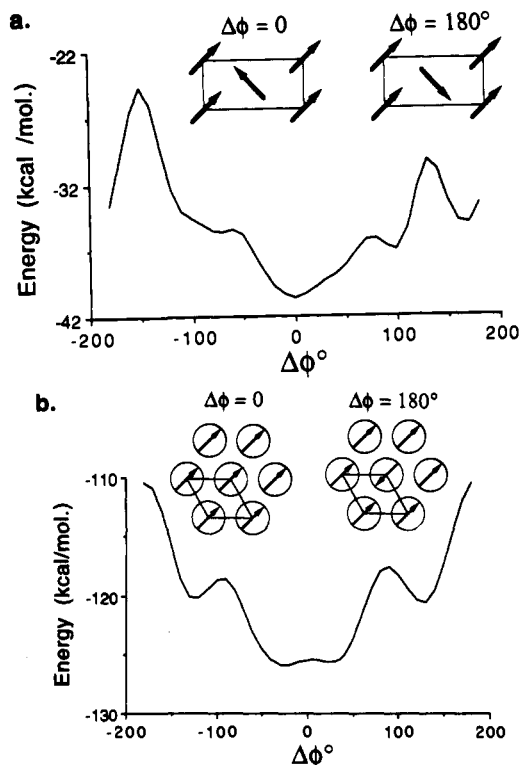
**Figure 3.** Model of 2-D crystals of vertical chains  $CX_3(CX_2)_{18}CX_3$  ( $X = H, F$ ) viewed (left) perpendicular to the molecular axis and (right) along the molecular axis: (a) hydrocarbon chains ( $X = H$ ) in a primitive rectangular cell ( $a = 4.98 \text{ \AA}$ ,  $b = 7.42 \text{ \AA}$ ); (b) fluorocarbon chains ( $X = F$ ) in a hexagonal unit cell ( $a = b = 5.66 \text{ \AA}$ ).



**Figure 4.** Calculated lattice energies as a function of the unit cell axes for the model 2-D crystals shown in Figure 3. The axes were shortened (negative percentage) or lengthened (positive percentage) relative to the axial lengths indicated in the caption of Figure 3. For the 2-D crystal of hydrocarbon chains, axes  $a$  and  $b$  are varied simultaneously such that the ratio  $a/b$  remains constant for the entire curve.

## Results and Discussion

**1. Lattice Energy Calculations.** The results of the calculations shown in Figure 4 reveal a dramatic difference in lattice energy between the model 2-D crystal composed of hydrocarbon chains and that composed of fluorocarbon chains. Indeed, the lattice energy of the model crystal of hydrocarbon chains in the rectangular unit cell where  $a = 4.98 \text{ \AA}$  and  $b = 7.42 \text{ \AA}$  is  $-41 \text{ kcal/mol}$  ( $2.1 \text{ kcal/mol}$  per  $CH_2$  group), whereas the lattice energy of the model crystal of fluorocarbon chains in a hexagonal unit cell ranges from  $-126 \text{ kcal/mol}$  ( $6.3 \text{ kcal/mol}$  per  $CF_2$  group) for  $a = 5.66 \text{ \AA}$  (unit cell of PTFE, phase IV) to  $-119 \text{ kcal/mol}$  ( $6.0 \text{ kcal/mol}$  per  $CF_2$  group) for  $a = 5.74 \text{ \AA}$  (unit cell of compressed PFA monolayers, and to  $-113 \text{ kcal/mol}$  ( $5.7 \text{ kcal/mol}$  per  $CF_2$  group) for  $a = 5.82 \text{ \AA}$  (unit cell of compressed  $C_{10}F_{21}CH_2CO_2H$  monolayers). This represents a gain in crystal stability of about  $3 \text{ kcal/mol}$  per carbon on going from hydrocarbon to fluorocarbon



**Figure 5.** Calculated lattice energies as a function of a chain rotation about its mean molecular axis (parameter  $\phi$ ), with the surrounding chains kept fixed within the model 2-D crystals shown in Figure 3: (a) rotation of a hydrocarbon chain; (b) rotation of a fluorocarbon chain. The chains contain 20 carbons. The schemes represent the packing arrangements corresponding to  $\Delta\phi = 0$  and  $180^\circ$ , as viewed down the chain axis. The arrows indicate a molecular polarity to highlight the difference between the two packing arrangements.

chains. Also, the gain in lattice energy upon bringing the chains closer in the crystal (i.e., upon reducing the unit cell axis lengths) is much higher for fluorocarbon chains. This is readily seen in Figure 4, where the curve corresponding to the fluorocarbon chains shows a marked potential well.

What kind of interactions account for these differences? The energy of interactions in the model 2-D crystal of fluorocarbon chains (hexagonal cell,  $a = 5.66 \text{ \AA}$ ) between a chain and one of its closest neighbors is on the average  $-19.1 \text{ kcal/mol}$ , where only  $-0.05 \text{ kcal/mol}$  arises from electrostatic interactions and the remaining  $-19.05 \text{ kcal/mol}$  is due to van der Waals interactions. In the model 2-D crystal of hydrocarbon chains (primitive rectangular cell where  $a = 4.98 \text{ \AA}$  and  $b = 7.42 \text{ \AA}$ ), the energy of interaction between two neighbors is on average  $-6.6 \text{ kcal/mol}$ , where  $-0.2 \text{ kcal/mol}$  is due to electrostatic interactions and  $-6.4 \text{ kcal/mol}$  to van der Waals interactions.

Thus, we can conclude that the crystallization of the fluorocarbon chains is strongly favored in comparison to the crystallization of hydrocarbon chains due to higher attractive interactions of the van der Waals type. We note that the larger charge on the fluorine atoms ( $q = -0.14 e$ ) than on the hydrogen atoms ( $q = +0.06 e$ ) yields a slightly less attractive electrostatic interaction between neighboring fluorocarbon chains, but this effect is completely overwhelmed by the attractive van der Waals forces. In fact, the larger charge on the fluorine atoms can also be regarded as a stabilizing factor in the crystals of fluorocarbon molecules. Indeed, intramolecular electrostatic repulsions between fluorines force the molecule into a helical conformation.<sup>25</sup> Thus, the possibility of conformational disorder that exists in hydrocarbon chains (gauche-trans isomerization, for instance) is greatly reduced for fluorocarbon chains. Thus inherent property of the fluorocarbon chain, which one can call "stiffness",<sup>38</sup> may be an additional factor for the higher crystallinity of fluorocarbon systems relative to hydrocarbon ones. This argument is further supported by recent molecular dynamics studies of the packing structures in monolayers of fluorinated amphiphiles.<sup>39</sup>

We also calculated the lattice energy of the model 2-D crystals as a function of the rotation of a chain containing 20 carbons around its mean axis, keeping all surrounding chains fixed in the 2-D crystal. The results of the calculation (Figure 5) show that a fluorocarbon chain can rotate much more easily around its axis in its 2-D crystal than a hydrocarbon chain. Indeed, a rotation of amplitude  $\Delta\phi = \pm 40^\circ$  of a fluorocarbon chain in its 2-D crystal does not induce any increase in the lattice energy whereas a rotation of similar amplitude for a hydrocarbon chain yields lattice energy increases of 2 kcal/mol for  $\Delta\phi = +40^\circ$  and 3.5 kcal/mol for  $\Delta\phi = -40^\circ$ . Thus, in the crystalline phase, libratory motion of the fluorocarbon chain causes less repulsion than that of a hydrocarbon chain. This might be an additional factor easing the crystallization process of the fluorocarbon chains.

**2. A Correlation between Crystalline Self-Assembly of Uncompressed Langmuir Films of Amphiphilic Molecules at the Water Surface and Attractive van der Waals Energy.** At this point, we discuss in more detail some of the relevant experimental results that were obtained with uncompressed Langmuir monolayers on water by grazing-incidence X-ray diffraction. We focus on the uncompressed or "relaxed" monolayers because it is in this state that we may glean information as to the mechanisms and interactions governing their spontaneous crystallization at the water surface. To date, the only hydrocarbon and fluorocarbon amphiphilic derivatives that have been studied are carboxylic acids and  $\alpha$ -amino acids.

Films of fatty carboxylic acids  $C_nH_{2n+1}CO_2H$  tend to partially crystallize, in their relaxed state, in the crystalline phase labeled  $L_2$ . In this phase, the molecules are tilted by an angle of about  $30^\circ$  relative to the water surface normal and pack in a unit cell which, when projected onto the monolayer plane, has dimensions close to those of the orthorhombic unit cell ( $a = 4.98 \text{ \AA}$ ,  $b = 7.42 \text{ \AA}$ ).<sup>7,8,11,36</sup> This crystalline phase is generally in coexistence with a "liquid" disordered phase. The degree of crystallinity of these films depends largely on the hydrocarbon chain length and the temperature.<sup>40</sup> Also, the extent of perfect crystalline order is anisotropic, being shorter along the molecular tilt direction.<sup>8,11,36</sup> Uncompressed films of myristic acid ( $n = 13$ ) at  $5^\circ\text{C}$  did not yield any measurable crystallinity,<sup>41</sup> under similar conditions, uncompressed films of arachidic acid ( $n = 19$ ),<sup>42</sup> heneicosanoic<sup>43</sup> ( $n = 20$ ), and docosanoic acid<sup>11</sup> ( $n = 21$ ) spontaneously formed crystallites with coherence lengths of about 500  $\text{\AA}$ , in the direction corresponding to the maximal extent of crystalline order. Finally, uncompressed films of triacontanoic acid<sup>8</sup> ( $n = 29$ ) spontaneously formed crystallites with coherence lengths larger than or equal to 1000  $\text{\AA}$ , in the direction corresponding to the maximal extent of crystalline order. This trend can be easily understood by the fact that the calculated lattice energy of longer chain acids is more attractive (by approximately 2 kcal/mol per additional  $CH_2$  group) due to improved van der Waals contacts. We stress that these improved van der Waals contacts seem to overrule the possibility of conformational defects (gauche-trans defects) in compounds with longer hydrocarbon chains.

Recently, a direct correlation was also established between the observed extent of crystallinity along a direction in the 2-D self-assembled crystal of amphiphiles and the energy of attachment of a molecule to a molecular row perpendicular to that direction.<sup>8</sup> Indeed, the aliphatic carboxylic acid<sup>8</sup>  $C_nH_{2n+1}CO_2H$  and ester-alcohol<sup>44</sup>  $C_nH_{2n+1}CO_2C_mH_{2m}OH$  monolayers in their uncompressed state were shown to exhibit crystalline positional coherence lengths which were much smaller along the molecular tilt direction. The attachment energy, calculated as the energy of interaction

between a single molecule and a molecular row in the crystal, was found to be decidedly less attractive for the molecular row corresponding to the smaller correlation length.

The results for aliphatic carboxylic acid amphiphiles have to be compared with those reported for uncompressed monolayers of  $C_{10}F_{21}CH_2CO_2H$  at room temperature over water.<sup>9</sup> As mentioned in the Introduction, it was deduced from the diffraction data that probably all the molecules crystallize in clusters with a hexagonal unit cell where  $a = 5.82 \text{ \AA}$ . It is remarkable that such a short-chain molecule (only 12 carbons) spontaneously yields a complete crystalline film on the water surface, whereas longer hydrocarbon chains, containing e.g. 20–22 carbons, exhibit lateral order to a much lesser extent. Evaluation of the lattice energies of these different systems shows that the lattice energy of the fluorinated acid  $C_{10}F_{21}CH_2CO_2H$  is approximately  $-57 \text{ kcal/mol}$  ( $10 \times 5.7 \text{ kcal/mol}$ , mainly attractive van der Waals interactions), which is equivalent to the lattice energy of an acid with a hydrocarbon chain containing about 28 carbons.<sup>45</sup>

There is one additional example of a comparative study between the amphiphilic  $\alpha$ -amino acids  $C_{15}H_{31}CONHC_4H_8CHNH_3^+CO_2^-$  (PL) and  $C_{10}F_{21}C_2H_4OCOCH_2CHNH_3^+CO_2^-$  (PFA) in their relaxed state at room temperature. The latter spontaneously formed large crystalline clusters whereas the former did not yield any diffraction signal.<sup>3,4</sup> Compressed PL monolayers form 2-D crystals stabilized by two hydrogen-bonding nets, one at the  $\alpha$ -amino acid head group ( $-CHNH_3^+CO_2^-$ ) and one at the amide group ( $-CONH$ ) in the hydrophobic chain.<sup>46</sup> These hydrogen-bonding moieties induce a molecular area as high as  $25.9 \text{ \AA}^2$ , leading to weak van der Waals contacts between the hydrocarbon chains of the molecule. The two hydrogen-bonding interactions do not seem sufficient to induce at room temperature a spontaneous formation of a highly crystalline material. In the 2-D crystal of PFA, the molecular area is  $28.5 \text{ \AA}^2$  and the crystal stability is mainly ensured by effective van der Waals interactions between the fluorinated segments of the molecule which contribute  $-60 \text{ kcal/mol}$  to the lattice energy.

## Conclusion

This study proves that by using empirical lattice energy calculations it is possible to shed light on molecular assembling processes in relaxed systems of insoluble amphiphilic molecules. The energy calculations indicate that a main driving force for crystallization in these systems is attractive van der Waals interactions. It follows that molecules containing fluorinated chains or very long hydrocarbon chains are desirable if one needs to create highly crystalline films. Thus, this study suggests the existing possibility of designing chemically amphiphilic systems with controllable assembling properties on the surface of water.

We also wish to emphasize that insoluble amphiphilic crystals can be useful models for studying crystallization processes in three dimensions. For example, the results of a recent comparative study of 3-D crystallization of polyethylene (PE) and poly(tetrafluoroethylene) (PTFE) by density functional methods<sup>47</sup> are in qualitative agreement with ours. Indeed, the higher melting point observed for PTFE polymers was accounted for in terms of a higher chain stiffness and probably a higher interchain connectivity compared to those in PE.

**Acknowledgment.** All our grazing-incidence diffraction measurements and the structural analysis of monolayer films were performed in collaboration with Drs. Jens Als-Nielsen and Kristian Kjaer of Risø National Laboratory, Roskilde, Denmark. We thank them as well as Dr. Ed Wasserman of Du Pont Experimental Station, Wilmington, DE, for fruitful discussions. We acknowledge financial support from the Petroleum Research Fund, administered by the American Chemical Society, the Fund for Basic Research of the Israel Academy of Sciences and Humanities, and the Minerva Foundation.

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