



# Article Short Fluoroalkanes Suppress a Thermally-Induced Phase Transition in a Layered Organic Crystal

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**Abstract:** Ensuring a consistent crystal structure over a wide temperature range can be desirable behaviour in organic devices. This study investigates a layered crystal system formed by hydrogenbonded chloro-*s*-triazine rings functionalised with alkyl or fluoroalkyl chains between the layers. When substituted with *N*-propyl groups (**C3**), the crystal undergoes a thermally-induced phase transition where the chains are ordered and bent below 170 K and disordered and extended above 175 K. Replacement with fluorinated *N*-propyl chains (**C3-F**) produces the same layered crystal but successfully suppresses the phase transition. The hydrocarbon and fluorocarbon analogues were found to be incompatible and unable to form co-crystals from solution or with mechanical mixing. Both effects were ascribed to more attractive C-F. . .F-C and C-H. . .F-C interactions in the fluorinated analogue. Long perfluoroalkanes are well known for controlling assembly in the solid state, but this study suggests that short-chain fluoroalkanes can exert strong control over the assembly and stability of an organic crystal.

Keywords: crystal engineering; fluoroalkane; hydrogen-bonding; phase transition

## 1. Introduction

Early work by Hoffman correlated thermally-induced phase transitions in molecular solids to changes to dielectric transitions in long-chain organic solids [1]. Thermally-induced phase transitions continue to be an important area in the study of functional molecular materials and pharmaceuticals [2]. Recent functional material applications include thermal control devices [3], semiconductors [4], novel memory systems [5], and energy storage materials [6]. The thermal behaviour of a crystallographic system adopted by a generic molecule can depend upon subtle changes in functional groups. An example is the fluorination of alkyl chains, where the fluorine atoms replacing hydrogen have increased volume requirements due to their larger van der Waals radii and the potential for new types of intermolecular interactions.

We have previously reported that the *s*-triazine heterocycle functionalised with one chlorine atom and two alkylamino groups reliably self-assembles using hydrogen bonds into tapes with the tape morphology controlled by the size or length of the alkyl chain [7]. An example is the *N*-propyl derivative **C3** (Figure 1a), which forms one-dimensional hydrogen-bonded tapes that interact via their propyl chains (Figure 1b). The tapes stack parallel to the crystallographic *ab*-plane to produce two-dimensional sheets analogous to lipid bilayers. The bilayer has an outer hydrophobic surface of alkyl chains that is a persistent feature in this class of molecule. Separation between the bilayers in the crystal is



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**Copyright:** © 2023 by the authors. Licensee MDPI, Basel, Switzerland. This article is an open access article distributed under the terms and conditions of the Creative Commons Attribution (CC BY) license (https:// creativecommons.org/licenses/by/ 4.0/). proportional to the length of the alkyl chain [8]. These layered systems are more than just conceptualised visualisations of their single crystals. They have been shown to adopt highly ordered, ultrathin bilayer films with controlled thickness on mica and silicon substrates [9].



**Figure 1.** (a) Compounds used in this study C3, a bis-N-propyltriazine, and C3-F, a bis-N-fluoropropyl analogue; (b) Stacked hydrogen-bonded tapes formed by C3 at 150 K showing separation of tapes by loosely-packed propyl chains with unit cell axis shown (H = white, C = grey, N = blue, Cl = green, dotted lines indicate hydrogen bonds).

As with lipid bilayers found at interfaces and in biological systems, the alkyl chains in these systems are ordered at low temperatures but show a structural transition on warming as the alkyl chains become disordered. This process can be measured and quantified using a combination of Raman spectroscopy and powder X-ray diffraction [10]. Such thermally-induced phase transitions may be undesirable in molecularly ordered thin films prepared via solution processing for thin-film organic semiconductors [11] and organic light-emitting diodes [12], so we are interested in crystal engineering approaches that suppress this behaviour. The phase change behaviour of C3 arises from the mobility of the propyl side chain, so these are a natural target for modification of the molecular structure and, by extension, the crystal structure. Modification of the side chains is also attractive as there should be relatively little effect on the photoactive behaviour of the aromatic core that might provide the functional aspect of the molecule. For example, OLEDs may have a photoactive aromatic core with side chains to permit solubility for spin-coating a functional layer on a substrate [12]. In this model study using C3, our intention was to (1) eliminate the thermally-induced phase transition over a wide temperature range whilst (2) ensuring the molecular assembly remains the same.

Substitution of the propyl groups in C3 with pentafluoropropane groups gives C3-F (Figure 1a) an analogue that successfully adopted the same packing as the high-temperature structure of C3. The use of fluorinated side chains in C3-F also successfully suppressed conformational flipping of the propyl side chains through attractive C-F...F-C and C-H...F-C intermolecular interactions. Attempts to create a co-crystal using solution-based and mechanical mixing methods suggest that disruption of the fluorine-based interactions is not favoured. The use of short, fluorinated side chains for crystal engineering is not a well-studied crystal engineering approach but is highly successful here at retaining crystal packing while enforcing thermal stability in the crystal.

#### 2. Materials and Methods

## 2.1. Synthesis

Synthesis of compound **C3** has been described previously [8]. A slight modification was employed to obtain the fluoropropyl analogue, 6-chloro- $N^2$ , $N^4$ -bis(2,2,3,3,3-pentafluoropropyl)-1,3,5-triazine-2,4-diamine, **C3-F**. It was synthesised by reacting 2,2,3,3,3-pentafluoropropylamine (2.0 equiv.) with cyanuric chloride (1.0 equiv.) in the presence of

Na<sub>2</sub>CO<sub>3</sub> (2.4 equiv.) in a sealed tube at 60 °C overnight. The resulting mixture was purified according to the previously reported methods to provide **C3-F** in 22% yield. [8]. The resulting prisms (melting point 209.1 °C) were characterised using <sup>1</sup>H NMR, <sup>19</sup>F-decoupled <sup>1</sup>H NMR, and <sup>1</sup>H-decoupled <sup>19</sup>F NMR in which two signals were observed for the CH<sub>2</sub> and CF<sub>2</sub>, presumably due to conformational isomerism [13], X-ray crystallography and high-resolution mass spectrometry. <sup>1</sup>H NMR (300 MHz, Acetone *d*<sub>6</sub>)  $\delta$  7.57 (d, *J* = 33.4 Hz, 2H, *NH*), 4.34 (ddd, *J* = 22.7, 14.3, 7.7 Hz, 4H, *CH*<sub>2</sub>). <sup>19</sup>F-decoupled <sup>1</sup>H NMR (300 MHz, Acetone *d*<sub>6</sub>)  $\delta$  7.63 (bs, 1H), 4.40–4.33 (m, 2H, *CH*<sub>2</sub>), 4.33–4.23 (m, 2H, *CH*<sub>2</sub>). <sup>1</sup>H-decoupled <sup>19</sup>F NMR (283 MHz, Acetone *d*<sub>6</sub>)  $\delta$  -85.28, -122.20, -122.29. Mass spectrometry M+H ion [C<sub>9</sub>H<sub>7</sub>N<sub>5</sub>F<sub>10</sub><sup>35</sup>Cl]<sup>+</sup> ion at m/z 410.0221 (calculated 410.0230).

Preparation of a mixture of **C3:C3-F** was attempted by (a) crystallisation of an ethanol solution using equimolar quantities of **C3** and **C3-F** and (b) grinding of equimolar quantities of **C3** (14 mg) with **C3-F** (26 mg) in an agate mortar and pestle for 5 min. The efficiency of mixing in this **C3:C3-F** blend was confirmed with Raman mapping and ToF-SIMS mapping (see below).

## 2.2. Raman Spectroscopy

Raman spectra of C3 were obtained on an inVia Raman microscope (Renishaw, Wottonunder-Edge, UK) using a  $20 \times$  objective and an excitation wavelength of 532 nm, ca. 33 mW at the sample. The spectra were collected in static mode from 2350 to 3400  $\text{cm}^{-1}$  using 1 s exposure and 100 scans. Multiple regions were selected for measurement to avoid the possibility of laser damage to the sample. Data were processed using the WiRE software (Version 5.3, Renishaw, Wotton-under-Edge, UK). Variable temperature Raman measurements were performed between 170 K and room temperature using a THMS600 stage (Linkam, Redhill, UK) by collecting two sequential runs of cooling, then heating, of the sample. Raman mapping was performed by operating in Streamline mode using a 785 nm excitation source to suppress fluorescence, operating at ca. 165 mW at the sample. The Raman maps of the equimolar mixture of C3:C3-F on a stainless-steel slide were collected over  $300 \times 300$  micrometres using a  $50 \times$  objective with an *x*-axis step size of 1.3 micrometre. Spectra at each point were collected using a static scan centred at 1120 cm<sup>-1</sup> (515–1644 cm<sup>-1</sup>) using a 2 s exposure. Images were produced by identifying unique peaks from the Raman spectrum of each compound (Supplementary Materials Figure S1) and then integrating the peak after a linear baseline correction. Integrated ranges were 1089–1123 cm<sup>-1</sup> (C3) and 781–815 cm<sup>-1</sup> (C3-F). Images were produced in the WiRE software (V5.5, Renishaw, UK) and arbitrarily scaled for comparison of the distribution of each chemical phase.

#### 2.3. Differential Scanning Calorimetry (DSC)

Thermal analysis of **C3** and **C3-F** was performed using a 204F1 Phoenix for differential scanning calorimetry (Netsch, Selb, Germany). Crystals were compared by loading 3–4 mg in a 25  $\mu$ L pierced lid aluminium crucible to examine phase change exotherms (cooling) and endotherms (heating) by cycling through the temperature range of interest (150 K to room temperature) at 10 K/min. The thermally-induced structural transition in **C3** was studied further by measuring event onset temperatures with a variable ramping rate (5, 10, and 15 K/min).

#### 2.4. Powder X-ray Diffraction (XRD)

XRD scans were performed on the equimolar mixture of **C3:C3-F** finely ground in an agate mortar and pestle, then measured in transmission mode between Kaptan foils. The XRD was collected on an Empyrean diffractometer (PANalytical, Almelo, The Netherlands) using Cu K $\alpha$  radiation ( $\lambda = 1.5406$  Å) at ambient temperature 20 between 3 and 30° with 0.01 degree/step and a measurement time of 7 s/step and 19 detector channels. A direct derivation method [14,15] with peak area extraction by Pawley fit [16] was employed in the HighScorePlus software (PANalytical, Almelo, The Netherlands) to perform a composi-

tional analysis of the phases to determine if C3:C3-F had combined into a new phase or had remained as discrete, pure phases of C3 and C3-F.

#### 2.5. X-ray Crystallography

Crystallography of C3 at 150 K and room temperature has been reported previously [7]. The structure of C3-F was determined at 100 K and 302 K, respectively. A suitable single crystal was selected under a M165Z polarising microscope (Leica, Wetzlar, Germany) and then mounted on a MicroMount (MiTeGen, Ithaca, USA) consisting of a thin polymer tip with a wicking aperture. X-ray diffraction measurements were carried out on a Bruker kappa-II CCD diffractometer (Bruker AXS, Fitchburg, USA) using IµS Incoatec Microfocus Source with Mo-K  $\alpha$  radiation ( $\lambda = 0.710723$  Å). The single crystal, mounted on a goniometer using a cryo loop for intensity measurements, was coated with paraffin oil and then quickly transferred to the diffractometer using an Cryostream 700 series (Oxford Cryosystems, Long Hanborough, UK) for the 100 K measurements. Symmetry-related absorption corrections (Multi-Scan) using the program SADABS [17] were applied, and the data were corrected for Lorentz and polarisation effects using Bruker APEX2 software [17]. The structures at both temperatures were solved by the Intrinsic Phasing method using program SHELXT [18], and full-matrix least-squares refinements were carried out using SHELXL [19] using Olex-2 [20]. The non-hydrogen atoms were refined anisotropically. A summary of the crystallographic data is given in Table 1.

CCDC Deposition No.	2291902	2291903
Temperature (K)	100	302
Chemical formula	$C_9H_6ClF_{10}N_5$	C <sub>9</sub> H <sub>6</sub> ClF <sub>10</sub> N <sub>5</sub>
$M_{ m r}$	409.64	409.64
Crystal system, space group	Triclinic, P1bar	Triclinic, P1bar
a, b, c (Å)	5.3461 (14), 9.675 (3), 13.953 (4)	5.3497 (7), 9.8933 (13), 14.1357 (19)
$\alpha, \beta, \gamma$ (°)	93.850 (11), 100.480 (9), 102.003 (10)	94.721 (6), 100.439 (4), 100.181 (4)
$V(Å^3)$	690.0 (4)	719.11 (17)
Ž	2	2
Radiation type	Μο Κα	Μο Κα
$\mu (mm^{-1})^{1}$	0.41	0.39
Crystal size (mm)	0.14 imes 0.09 imes 0.03	0.13 imes 0.11 imes 0.03
Data collection		
Diffractometer	Bruker D8Quest	Bruker APEX-II CCD
	Multi-scan	Multi-scan
	SADABS2016/2 (Bruker, 2016/2) was	SADABS2016/2 (Bruker, 2016/2) was
	used for absorption correction. wR2(int)	used for absorption correction. wR2(int)
Absorption correction	was 0.1682 before and 0.1001 after	was 0.1408 before and 0.0903 after
	correction. The Ratio of minimum to	correction. The Ratio of minimum to
	maximum transmission is 0.7922. The	maximum transmission is 0.7709. The
T T	$\lambda/2$ correction factor is not present.	$\Lambda/2$ correction factor is not present.
I min, I max	0.591, 0.746	0.575, 0.745
No. of measured, independent and	12,366, 2435, 1740	24,528, 2657, 1684
observed $[1 > 2\sigma(1)]$ reflections		
$V(A^3)$	690.0 (4)	719.11 (17)
$K_{\text{int}}$	0.105	0.159
$(\sin \theta / \lambda)_{max} (A^{-1})$	0.595	0.607
Refinement		
$R[F^2 > 2\sigma(F^2)], wR(F^2), S$	0.063, 0.137, 1.06	0.070, 0.149, 1.08
No. of reflections	2435	2657
No. of parameters	226	316
No. of restraints		102
H-atom treatment	H-atom parameters constrained	H-atom parameters constrained
$\Delta \rho_{\rm max}, \Delta \rho_{\rm min} \ ({\rm e} \ {\rm A}^{-3})$	0.44, -0.42	0.22, -0.26
R <sub>int</sub>	0.105	0.159

Table 1. Crystallographic parameters for the new structures in this study, C3-F at two temperatures.

#### 2.6. Molecular Graphics and Calculations

Molecular graphics from the crystal structure data were generated using Olex-2 [20] and Mercury (V4.0) [21]. Hirshfeld analysis and intermolecular interaction energies were

performed using the CrystalExplorer software (Version: 21.3, Revision: e9abf3f) [22]. Crystal Explorer calculates interaction energies using a CE-B3LYP model that simulates higherlevel calculations using dispersion-corrected B3LYP-D2/6-31G(d,p) calculations on a large range of dimers with a mean absolute deviation of only 1 kJ/mol [23]. The interaction energy is calculated for each molecule in a cluster of molecules surrounding a central molecule within a 3.8 Å radius. A full set of interaction energies colour-coded for each molecule is provided in the Supplementary Materials. The electrostatic potential maps for C3 and C3-F were calculated in Gausian09 [24] using B3LYP and a 6-311G basis set.

## 2.7. Time-of-Flight Secondary Ion Mass Spectrometry ToF-SIMS

Mass spectrometry of C3, C3-F, and the C3:C3-F mixture was performed on an ION.TOF5 ToF-SIMS (Ionplus, Munster, Germany). Microcrystalline powders were mounted on carbon tape and ionised by rastering a 500  $\times$  500-micrometre area with a Bi<sub>3</sub><sup>+</sup> beam at 30 keV and a lateral spatial resolution of 1 micrometre. The positive polarity mass spectrum was analysed at each point using the normalised intensity of the [M+H]<sup>+</sup> peaks for C3 and C3-F to produce images of the distribution of each molecular species across the sample.

#### 3. Results and Discussion

Crystalline **C3** is known to undergo a structural phase transition between 150 K and room temperature, occurring around 170 K. On warming through the transition point, the triclinic space group is retained, but the cell a-axis is halved as the asymmetric changes from two molecular conformers to one. The propyl chains in the low-temperature conformers straighten, leading to a single molecule in the asymmetric unit (Figure 2a). The resulting high-temperature phase has a thermal disorder in the chains (Figure 2b), leading to a tilting of the unit cell corresponding to decreases of  $4^\circ$ ,  $16^\circ$  and  $7^\circ$  in the lattice values for  $\alpha$ ,  $\beta$  and  $\gamma$ , respectively.



**Figure 2.** Thermally-induced phase transition in **C3**, (**a**) ORTEP structures (ellipsoids at 50%) showing conformation at 150 K and room temperature, (**b**) three hydrogen-bonded chains showing alternate propyl chain interaction at 150 K and room temperature (H = white, C = grey, N = blue, Cl = green, dotted lines indicate hydrogen bonds), (**c**) VT-Raman spectroscopy showing combined cooling and heating runs for **C3**. Spectra are normalised in the 500–600 cm<sup>-1</sup> region (in-plane aromatic stretching) and plotted vs. temperature showing the overlap (boxed region) where both high-temperature and low-temperature structures can be observed between 170 and 175 K, (**d**) heating and cooling DSC runs from 150 K to room temperature with exotherm (positive peak) and endotherm (negative peak).

Raman spectroscopy is a useful tool to distinguish between organic crystallographic phases and was used to better understand the structural phase transition of C3. There are distinct Raman peaks for each crystal phase (Supplementary Materials Figure S2). The effect of the thermal phase transition on the Raman spectrum is subtle but very clear in certain regions of the spectrum representing vibrations from, or coupling to, the alkyl chains. The two alternate alkyl chain conformations in the low-temperature form lowers the vibrational frequencies of the triazine ring breathing modes found at 620-635 cm<sup>-1</sup>, ring deformation modes at 900–913 cm<sup>-1</sup> and 1013–1023 cm<sup>-1</sup>, and methyl CH stretching at 2965–2974 cm<sup>-1</sup>. The triazine in-plane stretching region between 550 and 600 cm<sup>-1</sup> has relatively few peaks with minimal overlap and is coupled to the alkyl chains. This coupling renders the triazine in-plane peak sensitive to the alkyl chain conformation, so it is an especially useful probe to monitor the structural phase change during variable temperature measurements. There are two peaks for the low-temperature structure corresponding to the two independent molecules in the asymmetric unit. On transition to the high-temperature phase, the doublet is replaced by a singlet in this region corresponding to a single molecule in the asymmetric unit. This behaviour is reversible and repeatable when moving between high-temperature and low-temperature structures.

Prior variable temperature studies using crystallography and XRD data have demonstrated that there are only two phases present in the temperature range of interest for this study (150 K to room temperature) [10]. More detailed VT-Raman measurements around the transition point show that the structural transition has a temperature overlap (Figure 2c) where, on cooling, the high-temperature structure persists until 170 K, then immediately transitions to the low-temperature structure. Conversely, on warming, the low-temperature structure persists until 175 K and then transforms to the high-temperature structure, so there is a 5 K overlap where molecular reorganisation occurs. The Raman spectroscopy is supported by DSC (Figure 2d), where an exotherm (positive peak, 9.0 J/g) is observed at 172–176 K on cooling and a corresponding endotherm (negative peak, -8.2 J/g) at 183–185 on heating. The transition onset temperatures are relatively unchanged when the ramping rate is varied from 5, 10, and 15 K/min (Supplementary Materials, Figure S3), a property that is characteristic of a kinetically reversible enantiotropic transition [25].

The aim of this study was to investigate an analogue that would adopt similar layered packing as that found in the C3 crystals yet would suppress the temperature-induced structural phase transition. The N-alkyl groups in these triazines are readily modified by reacting an appropriate alkylamine with cyanuric chloride, and there are several alkylamines that could be used to produce analogues that should adopt the same packing as C3. For example, longer side chains might align and enforce more ordering. However, prior studies have shown that, while the bilayer packing persists, thermally-induced phase transitions still occur in the N-butyl, N-pentyl, and N-hexyl analogues of C3 [10]. A bulkier, branched side chain may improve packing, as in the herbicide atrazine that is functionalised with N-isopropyl and N-ethyl chains. However, atrazine has been shown to exhibit multiple structural phases at room temperature in the form of polymorphism [7]. From these studies, it seems that stabilising the crystal structure through longer or larger alkyl chains is not a solution for avoiding thermally-induced phase transitions. For this reason, we investigated using functionalised alkyl chains that might develop stronger interactions. Incorporation of a fluorinated chain into the triazine can be achieved using 2,2,3,3,3-pentafluoropropylamine and cyanuric chloride to produce **C3-F**. This analogue of C3 combines the benefits of a slightly bulkier structure for more efficient packing as well as the capability to form fluorine-based attractive interactions.

The crystal structure of the fluorinated analogue C3-F was measured at 100 K and at room temperature. The crystal structure packing was effectively the same at each temperature; both structures are triclinic, P1bar, with small increases in the length of the b and c-axes to accommodate increased disorder in the fluorinated chains at room temperature (Figure 3a and Table 1). Like C3, C3-F also comprised stacked chains of hydrogen-bonded triazines interacting via propyl chains, so fluorine in the propyl chain

did not disrupt the major features of molecular assembly. Preserving polymeric hydrogenbonded chains is essential in such materials as covalent organic frameworks designed with pore surface modification [26]. In this case, the hydrogen-bonded chains are preserved in **C3-F**, with N...N and triazine stacking distance within around 1% (Supplementary Materials, Table S1). Crystallography demonstrates that the "unwanted" alkyl chain flipping present in **C3** is successfully suppressed in **C3-F**, and this is supported by the consistency of the Raman data at room temperature and at 150 K (Supplementary Materials, Figure S2) and the lack of any features in DSC runs between room temperature and 150 K (Supplementary Materials, Figure S3).



**Figure 3.** (a) ORTEP structures (50%) of **C3-F** at 100 K and room temperature (H = light blue, C = grey, N = Blue, halogens=green, dotted lines indicate hydrogen bonds), and (b) packing showing a small increase in cell axis dimensions with an increase to room temperature (H = white, C = grey, N = blue, Cl = green, F = yellow, dotted lines indicate hydrogen bonds).

Intermolecular interactions in both structures are visualised by mapping the normalised contact distance (d<sub>norm</sub>) onto the Hirshfeld surface for each molecule (upper image Figure 4a) [22]. In **C3** and **C3-F**, both classical N-H...N hydrogen bonds and non-classical C-H...Cl hydrogen bonds are observed. The nature of the side chains obviously changes the nature of the weaker interactions in each structure. This can be seen in the plot of the percentage of the molecular Hirshfeld surface area interacting with external elements (Figure 4b and Supplementary Materials Table S2). In **C3**, interactions between C-Cl...H-C and C-H...H-C can be seen, with the latter dominating, occupying 78% of the Hirshfeld surface. In **C3-F**, there are C-H...H-C interactions on the Hirshfeld surface (25%) and also numerous C-F...F-C and C-H...F-C interactions (54%), so the total contribution of the side



chain interactions with the surface is 79%, similar to the C-H...H-C side chain interaction surface in **C3**.

**Figure 4.** Comparison of the **C3** and **C3-F** room temperature crystal structures, (**a**) upper image shows contacts at or below the VDW radii (red) identified using the normalised contact distance ( $d_{norm}$ ) mapped onto the Hirshfeld surface, lower image, electrostatic potential maps showing electronegative regions (red-yellow) and electropositive regions (blue), (**b**) Hirshfeld surface occupancy (%) involved in interactions from each external element, (**c**) calculated interaction energies for interaction types in each crystal (H = white, C = grey, N = blue, Cl = green, F = yellow, dotted lines indicate hydrogen bonds).

The electrostatic potential map of each structure (lower images Figure 4a, Table S3) shows electronegative (red-yellow) surface regions from the triazine nitrogen lone pairs and electropositive regions (blue) for the surface of the N-H bond that engage in hydrogen bonding in each molecule. The fluorine atoms indicated in C3-F show relatively higher electronegativity (yellow) than the surface of the C-H bond in C3. The fluorine atoms in the  $CH_2CF_2CF_3$  chain of C3-F appear to induce a more electropositive surface at the  $CH_2$ 

groups compared to the equivalent region in **C3**, suggesting these groups would engage in stronger CH...F interactions (Figure S4).

The suppression of the structural phase transition in **C3-F** is clearly associated with the presence of fluorine in the molecule. Fluorinated alkyl chains can significantly change a crystal structure from the equivalent hydrogenated analogue; for example, longer fluorinated carbon chains have been observed to adopt a helical structure in solution, although perfect helicity was disrupted by packing forces in the solid state [27]. Increased disorder has been observed in fluorinated octane chains in thin films compared to the hydrogenated equivalent [28]. Fluorinated *n*-alkane thiols on an Au(111) substrate show subtly different packing compared to *n*-alkane thiols, as shown by atomic force microscopy and grazing incidence XRD [29]. Significant melting point increases in fluorinated vs. non-fluorinated compounds have also been observed [30,31].

The electrostatic component of a C-H...F-C interaction in a trifluoromethyl group has been calculated at -6 kJ/mol up to -22 kJ/mol, which is a significant fraction of much stronger classical hydrogen bonds such as N-H...O at -70 kJ/mol [32]. It seems conceivable that the accumulated fluorine-based interactions in the C3-F crystal would change the behaviour of the system compared to C3. The similarity of the crystal structures of C3 and C3-F can be seen in the selection of intermolecular interactions shown in Figure 4c. Examples of each type of interaction are given, with the strength of the interaction estimated from electron densities using the CE-B3LYP model in CrystalExplorer that models higher level calculations at B3LYP/6-31G(d,p) level (Supplementary Materials Tables S4 and S5) [23]. As expected, hydrogen bonding is the strongest interaction with an attractive energy of ca.-70 kJ/mol for each self-complementary N-H...N bond in the hydrogenbonded tape that persists in these structures. This hydrogen bond interaction energy is effectively the same for both C3 and C3-F. Similarly, the interaction between the hydrogenbonded tapes via triazine ring stacking has an attractive energy of ca.-37 kJ/mol. Where we see clear differences is in the weaker interactions where the alkyl chains interact. In C3, the C-H...H-C interactions lead to an attractive energy of -7 to -10 kJ/mol, whereas, by comparison, in C3-F, the C-F...F-C close contacts lead to a significantly higher attractive interaction energy of -12 to 14 kJ/mol. Accumulated low-energy interactions of this type lead to a larger total attractive interaction energy of -267 kJ/mol in C3-F compared to -245 kJ/mol in C3 around each molecule.

Given the similarity in packing between the room-temperature crystal structures of **C3** and **C3-F**, we explored the possibility of producing a mixed crystal as an additional tool for crystal engineering in this system [33]. There is precedence for producing molecular mixtures of these *N*-hydrocarbon triazines, and they have been shown to form larger, highly ordered bilayers on mica than pure molecular crystals [9]. Hence, preparing mixed molecular crystals could be a useful tool to tune the structural properties of this crystal system. However, the preparation of a mixed molecular crystal was not possible using solution crystallisation or mechanical mixing. Crystallisation from an equimolar solution of **C3** and **C3-F** in ethanol produced rapid formation of large **C3-F** prisms (Supplementary Materials Figure S5a) with no trace of incorporation of the more soluble **C3**, as confirmed by single crystal XRD measurements. An alternative approach was a thorough mechanical grinding in an agate mortar and pestle to produce an intimate mixture of crystallites sized at less than 10 micrometres by optical microscopy (Supplementary Materials Figure S5b).

The degree of mixing was confirmed using two chemical mapping techniques, ToF-SIMS and Raman spectroscopy. Mapping experiments using ToF-SIMS (Figure 5a) clearly showed the co-location of **C3** and **C3-F** molecules down to length scales of 1 micrometre, and this co-location was also seen in Raman maps of the mixture (Supplementary Materials, Figure S6). However, despite the high degree of mixing of the two compounds, the room temperature powder XRD data can be completely described using the room temperature crystal structures of pure **C3** and **C3-F** when simulated using a Pawley analysis [16]. The molar proportion of **C3** (43 wt.%) to **C3-F** (57 wt.%) was 1:1.3, approximately simulating the expected 1:1 ratio of the mixture (Figure 5b). No new XRD peaks are observed that require

a new crystallographic phase for a hypothetical **C3:C3-F** co-crystal in this mechanically ground mixture. We speculate that the extensive network of fluorine-based interactions present in **C3-F** would be disrupted by the presence of propyl triazine in the structure, resulting in a less stable crystal.



**Figure 5.** (a) ToF-SIMS map of equimolar **C3:C3-F** showing co-location of **C3** (red) and **C3-F** (green) protonated molecular ions resulting from grinding, (b) powder XRD analysis of **C3:C3-F** mixture (red) showing Pawley fit in wt% (blue, Rwp = 5.62) to experimental data (red).

The behaviour of long perfluorinated alkyl chains has been extensively explored in the production of functional materials, including in the solid state [34]. However, short-chain fluoroalkanes are less well-studied in this regard. Replacement of the propyl group in C3 with the pentafluoropropyl group in C3-F successfully eliminated the structural phase transition in hydrocarbon-layered crystal structures. However, a CCDC search produced relatively few examples utilising the pentafluoropropyl group for similar structural chemistry studies. The pentafluoropropyl group has been incorporated into a steroidal host to compare the guest behaviour in aliphatic, aromatic, and fluorocarbon nanopores [35]. A water-repellent pillar [5] arene substituted with pentafluoropropyl groups demonstrated reversible transitions between amorphous and crystalline states by uptake and release of *n*-alkane guest vapours [36]. The introduction of pentafluoropropyl groups into the side chains of benzothiophene semiconductors successfully prevented unwanted chain interdigitation [37], and the role of attractive intermolecular interactions between the fluor

rinated segments was similar to that seen in **C3-F**. These studies suggest that short-chain fluoroalkanes may have more potential for engineering new behaviour in organic materials.

#### 4. Conclusions

An *N*-propyl chlorotriazine model was used to examine if a fluoroalkane analogue would suppress a thermally-induced phase transition. This well-studied crystal system comprises a 1-dimensional molecular tape made up of self-complementary N-H...N hydrogen bonds. The tapes interact through aromatic stacking to produce a 2-dimensional layer, with stacked layers interacting via the alkyl side chains to produce the 3-dimensional structure of the crystal. When the triazine is functionalised with short propyl chains, these remain partially folded and ordered below 170 K, while above 175 K, a temperature-induced structural phase transition occurs where the propyl chains extend and become disordered. Replacing the propyl chains with pentafluoropropyl groups produces multiple fluorine-based interactions that stabilise the crystal and suppress the phase transition, although this stability prevents the formation of a co-crystal with the propyl derivative. Self-aggregation of long perfluoroalkanes in the solid state is well known, but the use of shorter, semi-fluorinated chains is unusual. Short, fluorinated alkanes, when used in conjunction with an organising element such as classical hydrogen bonds, show great promise as a tool for controlling organic assembly in the solid state.

**Supplementary Materials:** The following supporting information can be downloaded at https://www. mdpi.com/article/10.3390/cryst13101425/s1, CIF and CheckCIF files; Table S1: Significant intermolecular distances in the crystal structures in this study; Table S2: Percent coverage of the Hirshfeld intermolecular interactions; Table S3: Parameters for DFT calculation of electrostatic potential surfaces; Table S4: Interaction Energies (kJ/mol) for the room temperature crystal structure of C3; Table S5: Interaction Energies (kJ/mol) for the room temperature crystal structure of C3-F; Figure S1: Comparison of Raman spectra of C3 and C3-F; Figure S2: Raman spectra of C3 at low temperature (175 K) and room temperature; Figure S3: DSC of C3 and C3-F between 150 K and room temperature; Figure S4: Electrostatic potential maps of three orientations of C3 and C3-F; Figure S5: micrographs of crystal mixtures of C3:C3-F; Figure S6: Raman maps of C3:C3-F. Reference [38] has been explained in the Supplementary Materials.

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## References

- Hoffman, J.D. Hindered Intermolecular Rotation in the Solid State: Thermal and Dielectric Phenomena in Long-Chain Compounds. J. Chem. Phys. 1952, 20, 541–549. [CrossRef]
- Wildfong, P.L.; Morris, K.R.; Anderson, C.A.; Short, S.M. Demonstration of a shear-based solid-state phase transformation in a small molecular organic system: Chlorpropamide. *J. Pharm. Sci.* 2007, *96*, 1100–1113. [CrossRef] [PubMed]

- 3. Swoboda, T.; Klinar, K.; Yalamarthy, A.S.; Kitanovski, A.; Munoz Rojo, M. Solid-State Thermal Control Devices. *Adv. Electron. Mater.* **2021**, *7*, 2000625. [CrossRef]
- Chen, J.; Anthony, J.; Martin, D.C. Thermally-induced solid-state phase transition of bis (triisopropylsilylethynyl) pentacene crystals. J. Phys. Chem. B 2006, 110, 16397–16403. [CrossRef]
- 5. Xie, R.; Bui, C.T.; Varghese, B.; Zhang, Q.; Sow, C.H.; Li, B.; Thong, J.T. An Electrically Tuned Solid-State Thermal Memory Based on Metal–Insulator Transition of Single-Crystalline VO2 Nanobeams. *Adv. Funct. Mater.* **2011**, *21*, 1602–1607. [CrossRef]
- Chandra, D.; Chellappa, R.; Chien, W.M. Thermodynamic assessment of binary solid-state thermal storage materials. J. Phys. Chem. Solids 2005, 66, 235–240. [CrossRef]
- Le, T.; Bhadbhade, M.; Gao, J.; Hook, J.M.; Marjo, C.E. Persistence of a self-complementary N–H...N tape motif in chloro-s-triazine crystals: Crystal structures of simazine and atrazine herbicides and their polymorphic and inclusion behaviour. *CrystEngComm* 2016, *18*, 962–970. [CrossRef]
- Aldilla, V.R.; Bhadbhade, M.; Bhattacharyya, S.; Kumar, N.; Rich, A.M.; Marjo, C.E. Controlling the distance between hydrogenbonded chloro-s-triazine tapes: Crystal engineering using N-alkyl chains and the influence of temperature. *CrystEngComm* 2017, 19, 4749–4758. [CrossRef]
- 9. Yao, Y.; Aldilla, V.R.; Bhadbhade, M.; Bhattacharyya, S.; Gong, B.; Kumar, N.; Rich, A.M.; Sando, D.; Cheong, S.; Tilley, R.; et al. Synthetic Bilayers on Mica from Self-Assembly of Hydrogen-Bonded Triazines. *Langmuir* **2020**, *36*, 13301–13311. [CrossRef]
- 10. Rich, A.M.; Bhattacharyya, S.; Aldilla, V.R.; Beves, J.E.; Bhadbhade, M.; Kumar, N.; Luis, E.T.; Marjo, C.E. Quantifying alkyl chain disorder in crystalline models of lipid bilayers using Raman spectroscopy. *J. Raman Spectrosc.* **2019**, *50*, 63–73. [CrossRef]
- 11. Yuan, Q.; Mannsfeld, S.C.; Tang, M.L.; Roberts, M.; Toney, M.F.; DeLongchamp, D.M.; Bao, Z. Microstructure of oligofluorene asymmetric derivatives in organic thin film transistors. *Chem. Mater.* **2008**, *20*, 2763–2772. [CrossRef]
- 12. Duan, L.; Hou, L.; Lee, T.W.; Qiao, J.; Zhang, D.; Dong, G.; Wang, L.; Qiu, Y. Solution processable small molecules for organic light-emitting diodes. *J. Mater. Chem.* **2010**, *20*, 6392–6407. [CrossRef]
- 13. Welhouse, G.J.; Bleam, W.F. NMR spectroscopic investigation of hydrogen bonding in atrazine. *Environ. Sci. Technol.* **1992**, 26, 959–964. [CrossRef]
- 14. Toraya, H. A new method for quantitative phase analysis using X-ray powder diffraction: Direct derivation of weight fractions from observed integrated intensities and chemical compositions of individual phases. *J. Appl. Crystallogr.* **2016**, *49*, 1508–1516. [CrossRef]
- 15. Toraya, H. Accurate and time-saving quantification of a component present in a very small amount in a mixture by the direct derivation method. *J. Appl. Crystallogr.* **2020**, *53*, 1225–1235. [CrossRef]
- 16. Pawley, G.S. Unit-cell refinement from powder diffraction scans. J. Appl. Crystallogr. 1981, 14, 357–361. [CrossRef]
- 17. Bruker. APEX2, SAINT and SADABS, Version 3; Bruker AXS Inc.: Madison, WI, USA, 2009.
- 18. Sheldrick, G.M. SHELXT—Integrated space-group and crystal-structure determination. Acta Crystallogr. 2015, A71, 3–8. [CrossRef]
- 19. Sheldrick, G.M. Crystal structure refinement with SHELXL. *Acta Crystallogr.* **2015**, *C71*, 3–8. [CrossRef]
- Dolomanov, O.V.; Bourhis, L.J.; Gildea, R.J.; Howard, J.A.K.; Puschmann, H. OLEX2: A complete structure solution, refinement and analysis program. J. Appl. Crystallogr. 2009, 42, 339–341. [CrossRef]
- Macrae, C.F.; Sovago, I.; Cottrell, S.J.; Galek, P.T.A.; McCabe, P.; Pidcock, E.; Platings, M.; Shields, G.P.; Stevens, J.S.; Towler, M.; et al. Mercury 4.0: From visualization to analysis, design and prediction. *J. Appl. Crystallogr.* 2020, 53, 226–235. [CrossRef]
- Spackman, P.R.; Turner, M.J.; McKinnon, J.J.; Wolff, S.K.; Grimwood, D.J.; Jayatilaka, D.; Spackman, M.A. CrystalExplorer: A program for Hirshfeld surface analysis, visualization and quantitative analysis of molecular crystals. *J. Appl. Crystallogr.* 2021, 54, 1006–1011. [CrossRef] [PubMed]
- 23. Turner, M.J.; Grabowsky, S.; Jayatilaka, D.; Spackman, M.A. Accurate and efficient model energies for exploring intermolecular interactions in molecular crystals. J. Phys. Chem. Lett. 2014, 5, 4249–4255. [CrossRef] [PubMed]
- 24. Frisch, M.J.; Trucks, G.W.; Schlegel, H.B.; Scuseria, G.E.; Robb, M.A.; Cheeseman, J.R.; Scalmani, G.; Barone, V.; Petersson, G.A.; Nakatsuji, H.; et al. (Eds.) *Gaussian 09, Revision A.01*; Gaussian, Inc.: Wallingford, CT, USA, 2016.
- 25. Kawakami, K. Reversibility of enantiotropically related polymorphic transformations from a practical viewpoint: Thermal analysis of kinetically reversible/irreversible polymorphic transformations. J. Pharm. Sci. 2007, 96, 982–989. [CrossRef] [PubMed]
- Geng, K.; He, T.; Liu, R.; Dalapati, S.; Tan, K.T.; Li, Z.; Tao, S.; Gong, Y.; Jiang, Q.; Jiang, D. Covalent organic frameworks: Design, synthesis, and functions. *Chem. Rev.* 2020, 120, 8814–8933. [CrossRef] [PubMed]
- 27. Monde, K.; Miura, N.; Hashimoto, M.; Taniguchi, T.; Inabe, T. Conformational analysis of chiral helical perfluoroalkyl chains by VCD. *J. Am. Chem. Soc.* **2006**, *128*, 6000–6001. [CrossRef]
- Chen, L.; Li, N.; Yang, B.; Zhang, J. A comparative study of the tribological behaviors of CH3-and CF3-terminated bilayer films. J. Adhes. Sci. Technol. 2016, 30, 677–689. [CrossRef]
- 29. Liu, G.Y.; Fenter, P.; Chidsey, C.E.; Ogletree, D.F.; Eisenberger, P.; Salmeron, M. An unexpected packing of fluorinated n-alkane thiols on Au (111): A combined atomic force microscopy and x-ray diffraction study. *J. Chem. Phys.* **1994**, *101*, 4301–4306. [CrossRef]
- 30. Qiu, W.; Raghavanpillai, A.; Brown, P.A.; Atkinson, W.R.; Vincent, M.F.; Marshall, W.J. Ethylene-tetrafluoroethylene (ETFE) cotelomer iodides and their transformation to surface protection intermediates. *J. Fluor. Chem.* **2015**, *169*, 12–23. [CrossRef]

- 31. Mohammed, A.I.; Ahmed, A.M.; Bhadbhade, M.M.; Ho, J.; Read, R.W. Sugar-substituted fluorous 1, 2, 3-triazoles: Helical twists in fluoroalkyl chains and their molecular association in the solid state and correlations with physicochemical properties. *J. Fluor. Chem.* **2020**, *236*, 109536. [CrossRef]
- 32. Hathwar, V.R.; Chopra, D.; Panini, P.; Guru Row, T.N. Revealing the polarizability of organic fluorine in the trifluoromethyl group: Implications in supramolecular chemistry. *Cryst. Growth Des.* **2014**, *14*, 5366–5369. [CrossRef]
- Lusi, M. A rough guide to molecular solid solutions: Design, synthesis and characterization of mixed crystals. *CrystEngComm* 2018, 20, 7042–7052. [CrossRef]
- 34. Gladysz, J.A.; Jurisch, M. Structural, physical, and chemical properties of fluorous compounds. *Fluorous Chem.* **2012**, 1–23. [CrossRef]
- Natarajan, R.; Bridgland, L.; Sirikulkajorn, A.; Lee, J.H.; Haddow, M.F.; Magro, G.; Ali, B.; Narayanan, S.; Strickland, P.; Charmant, J.P.; et al. Tunable porous organic crystals: Structural scope and adsorption properties of nanoporous steroidal ureas. *J. Am. Chem. Soc.* 2013, *135*, 16912–16925. [CrossRef] [PubMed]
- Onishi, K.; Ohtani, S.; Kato, K.; Fa, S.; Sakata, Y.; Akine, S.; Ogasawara, M.; Asakawa, H.; Nagano, S.; Takashima, Y.; et al. State-and water repellency-controllable molecular glass of pillar [5] arenes with fluoroalkyl groups by guest vapors. *Chem. Sci.* 2022, 13, 4082–4087. [CrossRef] [PubMed]
- Ruzié, C.; Karpinska, J.; Laurent, A.; Sanguinet, L.; Hunter, S.; Anthopoulos, T.D.; Lemaur, V.; Cornil, J.; Kennedy, A.R.; Fenwick, O.; et al. Design, synthesis, chemical stability, packing, cyclic voltammetry, ionisation potential, and charge transport of [1] benzothieno [3, 2-b][1] benzothiophene derivatives. J. Mater. Chem. C 2016, 4, 4863–4879. [CrossRef]
- Mackenzie, C.F.; Spackman, P.R.; Jayatilaka, D.; Spackman, M.A. *CrystalExplorer* model energies and energy frameworks: Extension to metal coordination compounds, organic salts, solvates and open-shell systems. *IUCrJ* 2017, 4, 575–587. [CrossRef] [PubMed]

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