

Article

Further Evidence on the Importance of Fluorous-Fluorous Interactions in Supramolecular Chemistry: A Combined Structural and Computational Study

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7 Further Evidence on the Importance of Fluorous-
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11 Fluorous Interactions in Supramolecular Chemistry:
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15 A Combined Structural and Computational Study
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34 KEYWORDS: Non-covalent interactions; fluorous-fluorous interactions; DFT; AIM
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37 ABSTRACT. The solid state structures of $\text{CF}_3(\text{CF}_2)_5\text{CH}_2\text{CO}_2\text{H}$ and a fluorous triazole are
38 reported, both of which display a wide variety and large number of non-covalent interactions in
39 their packing. The solid state structure of $\text{CF}_3(\text{CF}_2)_5\text{CH}_2\text{CO}_2\text{H}$ is stabilized by multiple F...F
40 contacts but only one C—H...F—C interaction, as well as O—H...O and C—H...O hydrogen
41 bonds. In contrast to other reported structures, the torsion angles in the fluorous chain are close
42 to 180° which means that the fluorine atoms are eclipsed. A DFT study of the interactions in
43 both compounds show that F...F interactions, along with stacking and C—H...F and C—H...O
44 contacts, are individually weakly energetically stabilizing, but collectively can give rise to
45 interaction energies of up to 13 kcal mol^{-1} . A topological approach to the interactions using
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3 Atoms-in-Molecules (AIM) theory reveals that there are bond critical points between the C—
4 F...F—C interactions as well as C—F...H—C interactions that are not recognized when only
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6 using the van der Waals distances.
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10 11 12 13 14 15 **Introduction**

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18 There are a plethora of non-covalent interactions that synthetic chemists can use to design
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20 supramolecular structures.^{1,2} Whilst hydrogen bonding continues to be a mainstay of such
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22 interactions, there is a growing realization that halogens interactions can also be utilized.
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24 Consequently there is now much interest in the halogen bond, defined recently by IUPAC,³ in
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26 fields as diverse as crystal engineering,^{4,5,6} liquid crystals,⁷ molecular conductors⁸ molecular
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28 recognition agents,^{9,10,11,12,13,14,15} catalysis^{16,17} and medicinal chemistry.^{18,19,20} Perhaps of most
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30 surprise is that F...F non-covalent interactions are known to be stabilizing and can give a
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32 significant energy contribution to the structures, as Pauling's principle²¹ state that the attractive
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34 interatomic dispersion forces would be low due to the low polarisability of fluorine.²² However,
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36 in recent years a number of studies have shown that these type of interactions do exist and are
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38 not simply due to crystal packing. There are now a growing number of examples of F...F
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40 interactions being utilized as crystal engineering for applications in materials
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42 chemistry^{23,24,25,26,27,28,29,30} or in catalysis.³¹
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50 Given the importance and potential use of C—F...F—C interactions, it is imperative to ascertain
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52 the conditions where these have a stabilizing interaction and situations where these are due only
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54 to packing forces. There are three recognized types of F...F interactions (Chart 1); Type I are the
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56 most contentious in terms of delineating between crystal packing and stabilizing,⁴ whilst Type III
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3 have recently been described in restricted geometries afforded by cyclohexane or naphthalene
4 frameworks.³² We recently reported on a systematic structural and computational study on three
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6 distinct molecules, each featuring a $\text{CF}_3(\text{CF}_2)_5$ ponytail, *vis* $\text{CF}_3(\text{CF}_2)_5\text{CH}(\text{Me})\text{CO}_2\text{H}$, **1**,
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8 $\text{CF}_3(\text{CF}_2)_5(\text{CH}_2)_4(\text{CF}_2)_5\text{CF}_3$ and $(\text{CF}_3(\text{CF}_2)_5\text{CH}_2\text{CH}_2)_3\text{P}=\text{O}$ where Type II C—F...F—C
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10 interactions were present.³³ Intriguingly we noted that in the carboxylic acid there were a number
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12 of C—H...F—C interactions but in the alkane only C—F...F—C interactions were present. This
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14 can be contrasted to the structure of 1,2,3,4-tetrafluorobenzene, where there is a preference for
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16 C—H...F—C interactions over C—F...F—C interactions.³⁴ This poses an interesting question as
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18 to which are the more stabilizing interaction. It is possible that more or stronger dipole-dipole
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20 interactions between non-fluorous neighbors, leads to segregation of the fluorous domains (a
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22 form of molecular xenophobia) or a steric dominated interaction, specifically the larger radius of
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24 F *vs.* H determines the interactions. It is noteworthy that such C—H...F—C hydrogen bonds
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26 have only recently been recognized and are developing a strong research interest by both theory
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28 and experiment^{35,36,37,38,39,40} but C—F...F—C interactions are not so well developed.

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37 In order to answer this we have sought to (a) change the substitution pattern on the methylene
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39 carbons in the acid, as this is synthetically rather straightforward and (b) explore what happens
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41 when the strongly hydrogen bonded carboxylic acid is substituted for a functional group with
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43 less propensity of being involved in hydrogen bonding such as an azide function. In this work we
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45 report on the structure of the complex $\text{CF}_3(\text{CF}_2)_5\text{CH}_2\text{CO}_2\text{H}$, **2**, as the removal of the methyl
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47 group should reduce the steric demand of the compound and thus allow a closer packing of the
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49 fluorous chains. Furthermore, we have structurally characterized an unusual rearrangement
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51 product from the synthesis of $\text{CF}_3(\text{CF}_2)_5\text{CH}_2\text{CH}_2\text{N}_3$, *viz*, a 1,4-bis(perfluoroalkyl)triazole, **3**;
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53 triazoles have become a useful platform for the characterization of supramolecular interactions.⁴¹
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For instance, the 1,4-diphenyl-1,2,3-triazole fragment has been used as a scaffold to explore halogen substitution in the ortho- and para-position of the phenyl group to explore the relative strengths of the C—X...H bonding and it was concluded that the C—F...H interactions are stronger than the C—Cl...H interaction.⁴² We may be able to begin to shed light on the factors that influence C—F...F—C and C—F...H—C interactions, which would be useful in the multitude of applications of these interactions.

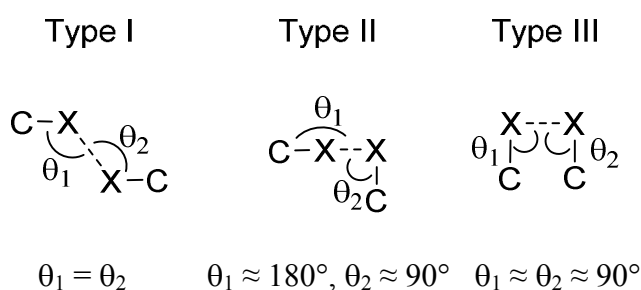
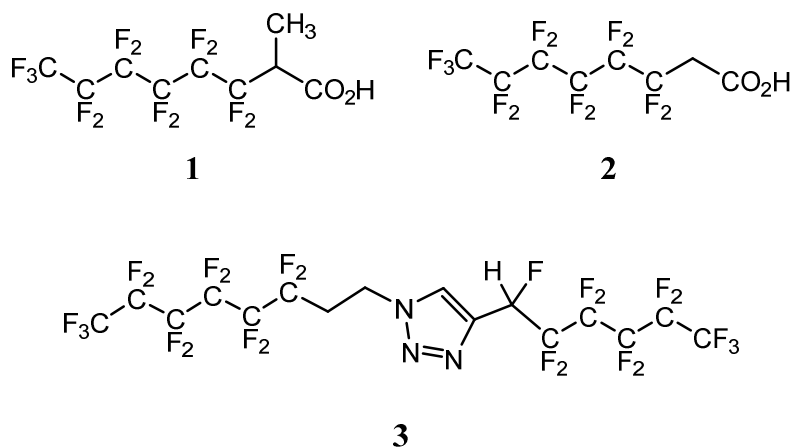


Chart 1. Classification of halogen-halogen interactions.



Results and Discussion

Synthesis and Structures of 2 and 3. The complex $\text{CF}_3(\text{CF}_2)_5\text{CH}_2\text{CO}_2\text{H}$, **2**, was prepared by oxidation of the corresponding alcohol with Jones Reagent, as described in the literature.⁴³

Crystallization from chloroform afforded X-ray quality crystals and the packing diagram is shown in Figure 1.

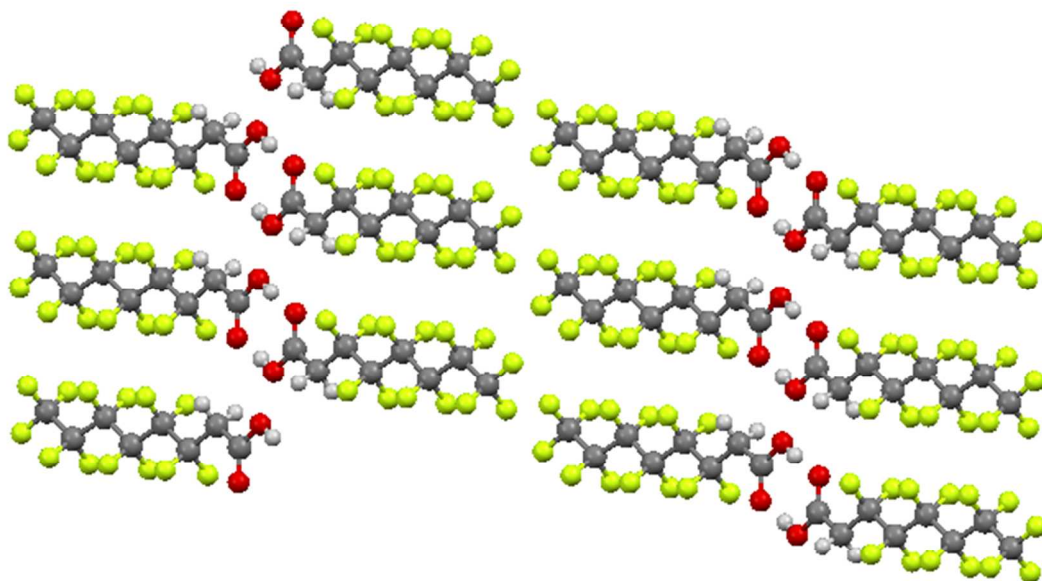


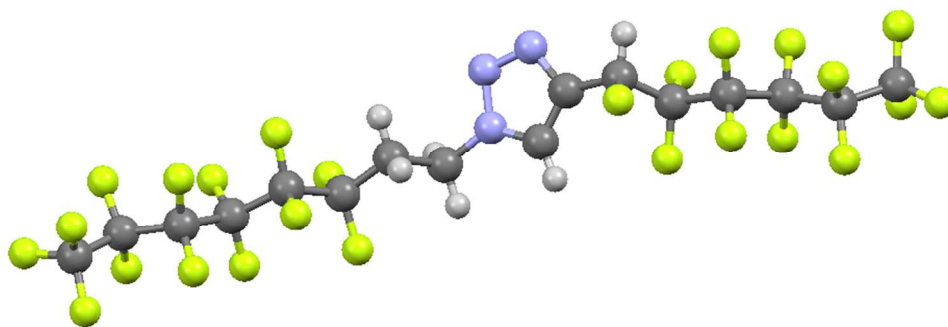
Figure 1. Packing diagram of **2** viewed down the *c* axis.

The complex exists as the typical hydrogen bonded dimer and there are a number of C—F...F—C contacts that are shorter than the van der Waals radii. There are type I interactions between the CF₃ groups on the chains which extend in the *c* plane ($d_{F...F} = 2.803$ and 2.903 Å, $\angle C-F...F = 135^\circ$ and 158°). Bifurcated “three-point interactions” ($d_{F...F} = 2.908$ and 2.923 ; $\angle F...F...F = 54^\circ$) are also present between the ponytails. In contrast to **1**, there are no short C—F...H—C interactions ($d_{F-H} < 2.66$ Å)⁴⁴ in this complex as the hydrogens are involved in C—H...O hydrogen bonding to a carboxylate group. This indicates that the C—H...O interaction is stronger than a C—H...F—C interaction, and in accord with other examples in the literature. The bond lengths within the fluorous domain are identical to that seen in **1**, but the C—C and C—O

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3 bonds of the acid fragment are slightly different {C—C: **1** – 1.595(6) Å; **2** – 1.510(3) Å; C=O: **1**
4 – 1.379(5) Å; **2** – 1.235(2) Å; C—OH: **1** – 1.381(5) Å; **2** – 1.293(2) Å} and this is also reflected
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7 in the changes in the C=O stretch in the infrared spectra (**1**: 1772 cm⁻¹; **2**: 1714 cm⁻¹;
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10 CH₃(CH₂)₇CO₂H⁴⁵: 1712 cm⁻¹). Interestingly, there is a significant difference in the F—C—C—
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13 F torsion angles, as in **1**, and indeed 148 of 149 structurally characterized examples in the
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15 Cambridge Structural Database⁴⁶ that feature at least a CF₃(CF₂)₅ chain, the torsion angles are
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17 lower compared to hydrocarbon chains. This is to relieve electrostatic interactions between two
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19 fluorine groups, although other factors may also be involved, and results in a slight twist of the
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21 fluorocarbon chain.^{47,48,49,50,51,52,53,54} However in **2** this is not the case and the fluorine atoms are
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23 in an eclipsed conformation. The only other example in the database that has eclipsed F atoms is
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25 the structure of heptyl 2-(perfluorohexyl)ethyl ketone, but no comment was made about this in
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27 the paper.⁵⁵ It has been reported that C—F...F—C interactions can be observed by small shifts in
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29 the infrared spectrum,⁵⁶ but the infrared and Raman spectra of **2** and **3** are identical in the C—F
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31 stretching and bending regions (spectroscopic data are included in the ESI). DFT calculations of
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33 **2** suggest that the twisted conformation is indeed the most stable, with the ‘untwisted’ conformer
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35 at 96 kJ mol⁻¹ higher in energy. Given the unusual nature of this compound, we have explored
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37 the weak interactions using a combination of DFT and Atoms-In-Molecules (*vide infra*).
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45 The triazole, **3**, was synthesized as a minor byproduct from the treatment of
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47 CF₃(CF₂)₅CH₂CH₂I with NaN₃ in DMF, according to the literature.⁵⁷ Cooling the crude mixture
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49 to -35 °C afforded a few crystals that were structurally characterized. Careful ¹H NMR
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51 spectroscopic analysis of the reaction mixture showed that **3** is consistently formed in low yield;
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53 the spectroscopic data confirm the formulation of **3**, particularly the unique CHF group. The
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55 mechanism of formation is rather unclear but dissolution of CF₃(CF₂)₅CH₂CH₂I in DMF affords
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3 a number of products,⁵⁸ one of which we can also identify as the alcohol $\text{CF}_3(\text{CF}_2)_5\text{CH}_2\text{CH}_2\text{OH}$.
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5 It is also possible that a dehydrohalogenation step occurs upon reaction of the perfluoroalkyl
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7 halide with DMF;⁵⁹ this may give rise to the unique CHF moiety. Clearly the reaction is more
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9 complex than described, and presumably an alkyne must be eventually generated to form the
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11 triazole via a Huisgen 1,3-dipolar cycloaddition reaction. It's also worth noting that similar azide
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13 has been reported to form triazoles via the copper catalyzed click reaction in good yield and with
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15 an intact fluororous group.^{60, 61} The structure of **3** is shown in Figure 2. The most notable feature is
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17 the replacement of one C—F bond for a C—H bond in one of the R_f chains. The metric
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19 parameters within the heterocyclic ring are as expected from a survey of the Cambridge
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21 Structural Database and the bond lengths within the ponytails are also normal, apart from the
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23 CHF group, where the C—F bond is the longest at 1.401(6) Å. It is also noteworthy that the F—
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25 C—C—F torsion angles are as expected for a fluororous chain, imparting a twist to the chain.
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49 **Figure 2.** The molecular structure of **3**.
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52 The packing of **3** is shown in Figure 3, and a plethora of non-covalent interactions are clear.
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54 There are number of C—F...F—C interactions that segregate the fluororous and non fluororous
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56 domains. There are long contacts between the ends of the molecule ($d_{\text{F...F}} = 2.915$ Å) and
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3 bifurcated “three-point interactions” ($d_{F...F} = 2.679$ and 2.781 Å; $\angle F...F...F = 99.2^\circ$) that connect
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6 the chains. There are C—F...H—C interactions present from the CHF carbon ($d_{H...F} = 2.463$ and
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8 2.503 Å) which unusually exist in a bifurcated arrangement between three chains. C—H...N
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10 hydrogen bonds between the triazole backbone and a second triazole N² nitrogen ($d_{C...N} = 3.235$)
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12 are also present; it has been noted that this C—H bond is highly polarized and can be as strong as
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14 as amides.⁴¹ The CH₂ groups on the ‘normal’ Rf chain are also involved in hydrogen bonding to
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16 the other triazole nitrogen ($d_{C...N} = 3.662$) to form chains perpendicular to the plane depicted in
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Figure 3.

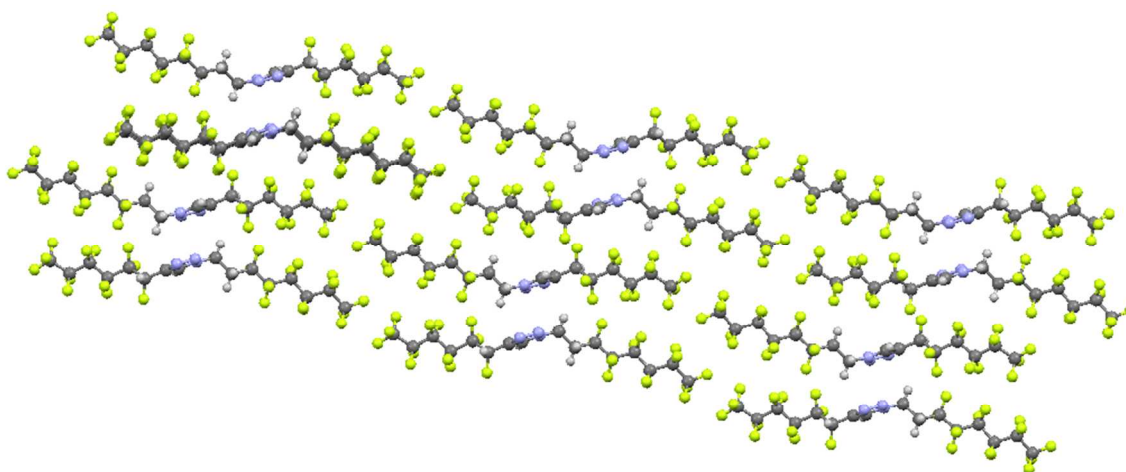


Figure 3. Packing diagram of **3** viewed down the *ab* plane.

Given the unusual structure of **2** compared to **3** we were interested to see if there were any differences in the solid state ¹⁹F NMR spectra that may be related to the C—F...F—C interactions (spectroscopic data are included in the ESI). The spectrum recorded for **2** was very broad, likely due to extensive dipolar couplings,⁶² but in **1** the signals were quite sharp. However as noted previously,⁶³ further work is required to attain a level of accuracy on a par with NMR crystallography.⁶⁴

Computational studies on **2** and **3**.


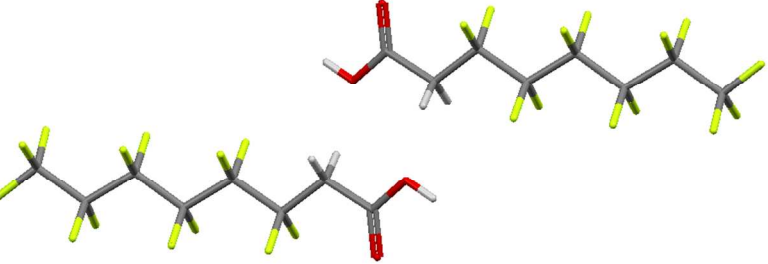

One method of quantifying the interactions in the solid state is to calculate the interaction energies between individual molecules. We have recently studied some examples via this technique³³ so include a DFT and QTAIM description of the two complexes herein. A series of dimers was extracted from the crystal structures of **2** and **3** by applying individual symmetry operations to the entire molecule, with interaction energies (calculated without altering geometry) reported in Tables 1 and 2. Using this methodology, five dimers were extracted from the crystal structure of **2**. The first, **2a**, contains two hydrogen bonds linking carboxylic acid groups and no close C—F...F—C contacts. **2b** contains only C—H...O hydrogen bonds between the carboxylic acid and the methylene group. **2c** however does exhibit C—F...F—C contacts of length 2.854, 2.922, and 2.861 Å, while **2d** and **2e** contains just one C—F...F—C contact at 2.913 Å and 2.803 Å respectively. As expected the hydrogen bonded dimer **2a** is very strongly stabilised; for comparison the interaction energy for the same dimer in **1** was -13.23 kcal mol⁻¹. **2c** is only weakly stabilised despite its numerous close contacts, but this data confirms that the three-point interaction motif discussed above is stable; the comparable energies for **1** was -1.69 kcal/mol. Binding of **2d** and **2e** is very weak indeed with a binding energy close to that we previously calculated for (CF₄)₂.³³


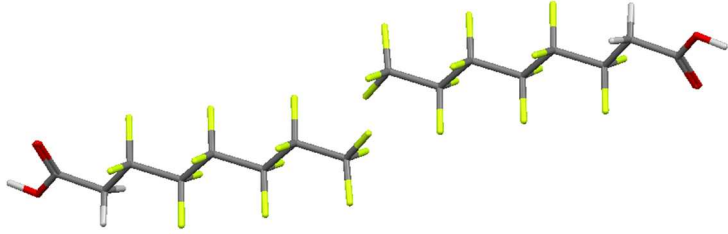
Topological analysis using an Atoms-in-molecules approach have also been conducted and the results are shown in Table 1. Strictly speaking, since the dimers considered here are not at their optimal geometry, the presence of a bond critical point and associated atomic interaction line cannot be used as evidence of bonding. However, we prefer this approach here as it should better preserve the interactions present in the solid state. Dimer **2a** displays only the hydrogen bonds of the acid function, and the electron density at the bond critical point ρ_{bcp} is slightly smaller than

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3 that seen in **1** (0.048 au), in line with the slightly smaller interaction energy. C—F...F—C
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5 interactions are observed in dimer **2c**, and again the electron density at the bond critical point
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7 ρ_{bcp} is of the same order of magnitude as in **1**, indicating that these interactions are not due to
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9 crystal packing effects and do have an important contribution to the stabilization of the dimers.
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11 Interestingly, AIM analysis finds one C—H...F—C interaction that was not observed by
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13 consideration of the van der Waals radii analysis, although it is rather weak (c.f. $\rho_{\text{bcp}} = 0.0045$ in
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18 **1**). Dimers **2d** and **2e** on the other hand are likely due to Type I interactions.
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23 Recent work⁶⁵ has shown that intramolecular X...X interactions in perhaloethanes are
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25 destabilizing, despite the presence of a bond critical point and bond path, through use of the
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27 Interacting Quantum Atoms (IQA) approach, although no such critical points were found for
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29 fluoro- compounds. Unfortunately, the computational requirements of this approach prohibit its
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31 use for the dimers we consider here. However, our data suggest that the intermolecular F...F
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33 contacts seen here are stabilizing, since dimers **2d** and **2e** are predicted to be weakly bound and
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35 contain only F...F contacts between molecules. Further detail on the origin of this stabilization
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37 comes from data reported in Table S1 (see ESI), which reports the contribution of dispersion to
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39 the overall interaction energy. For the purely F...F contacts in **2d** and **2e**, the dispersion
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41 contribution is larger than the overall interaction energy, such that it accounts for all
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43 stabilization: presumably electrostatic and exchange effects are weakly repulsive in the crystal
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45 geometry. The same pattern is observed for dimers **2b** and **2c**, and only in the hydrogen bonded
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47 dimer **2a** do we observe dispersion contribution smaller in magnitude than the overall interaction
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60 energy.

Table 1. Interaction energies (kcal mol⁻¹) and ρ_{bcip} values (au) of dimers of **2** taken from the crystal structure.

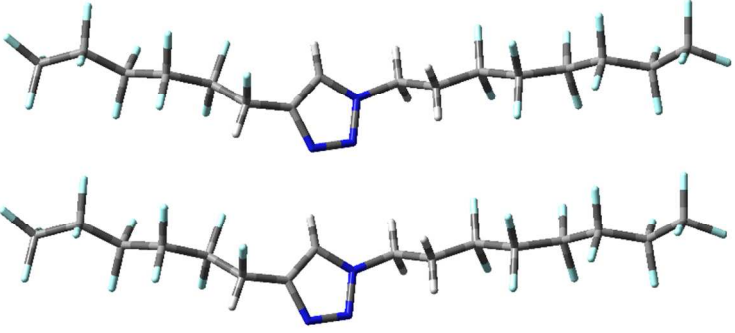

 <p style="text-align: center;">2a</p>	IE = -14.7 O-H...O: 0.038 (x2)
 <p style="text-align: center;">2b</p>	IE = -2.9 C-H...O: 0.008 H...H: 0.003 F...O: 0.003
 <p style="text-align: center;">2c</p>	IE = -4.0 F...F: 0.006 0.005 (x5) C-H...F: 0.002 F...O: 0.002 (x2)

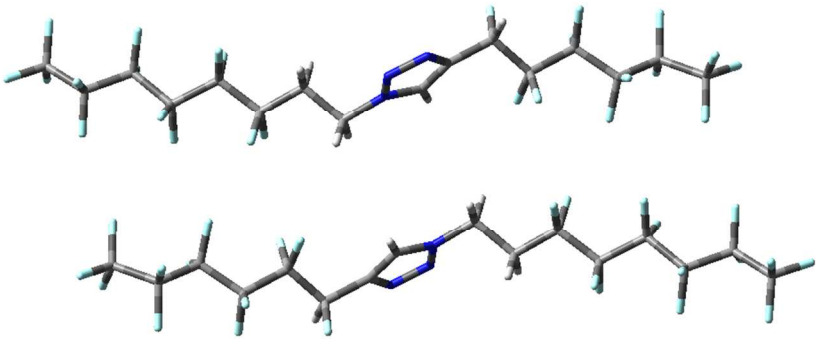
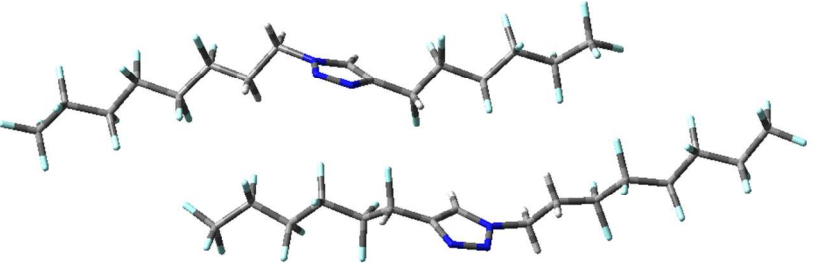
 <p style="text-align: center;">2d</p>	<p>IE = -0.6</p> <p>F...F: 0.004</p>
 <p style="text-align: center;">2e</p>	<p>IE = -1.5</p> <p>F...F: 0.006</p>

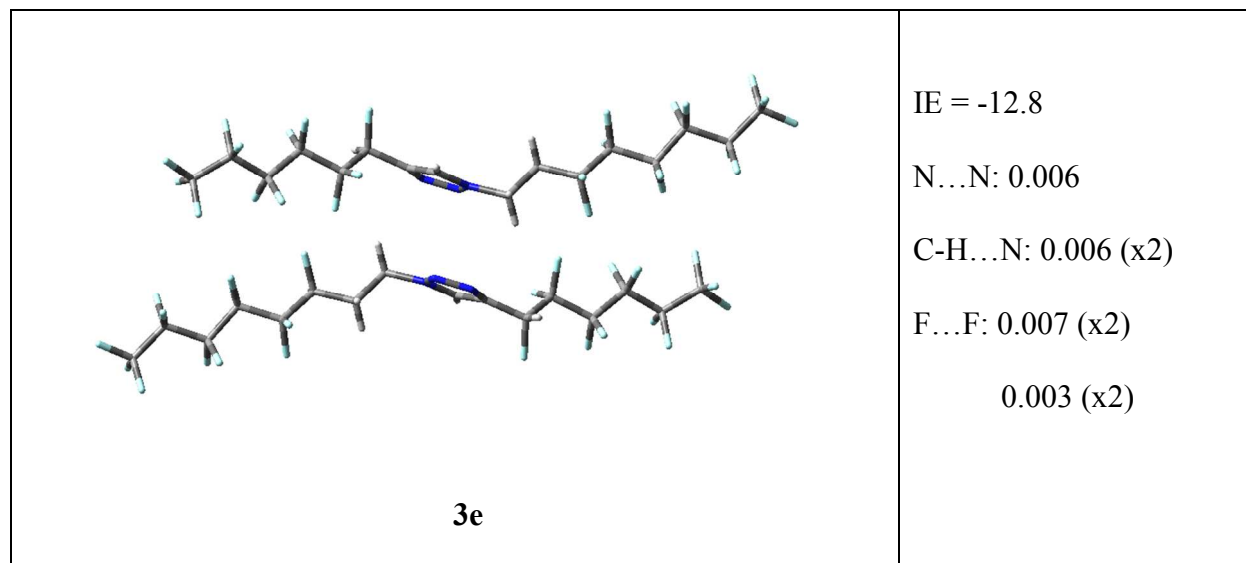
The same process applied to **3** results in 5 dimers generated by symmetry operations: interaction energy and ρ_{bcp} values for each are reported in Table 2. It is immediately apparent that dimer **3a**, which contains a C—H...N hydrogen bond between triazole rings, is almost as strongly stabilized as the dimer **2a**, which has two classical O—H...O H-bonds. Topological analysis indicates that the C—H...N has substantial electron density, but that this is only one-third of that seen in O—H...O in **2a**. Instead, the large stabilization of this dimer arises just as much from numerous other interactions, including a weaker C—H...N contact between methylene and triazole, two C—H...F contacts and 12 F...F ones. Collectively, ρ_{bcp} values of all contacts sum to 0.050 au, less than that in **2a** but of similar magnitude.

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3 Dimer **3b** contains just one F...F contact, and its interaction energy of just 1.1 kcal/mol
4 reflects this fact. In contrast, **3c** is strongly stabilized, but despite the short distance between and
5 parallel orientation of triazole rings, there is little contribution of stacking interactions to the
6 overall interaction. Two C...C contacts are present, but these connect methylene with triazole
7 and exhibit small ρ_{bcp} values. Instead, C—H...F and especially F...F contacts dominate **3c**. It is
8 notable that analysis based on the geometry of the crystal structure, using the default setting of
9 Mercury,⁶⁶ picks out only two F...F contacts in this structure, assigns stacking as C—H... π
10 interactions, and present no evidence for C—H...F contacts. **3d** and **3e** are also strongly
11 stabilized, in both cases through a combination of π -stacking, C—H...F and F...F interactions.
12 The former contains F...N contacts as well as numerous F...F, whereas the latter is the only one
13 found here that exhibits the pattern of critical points expected of π -stacking as seen in the
14 benzene dimer and related complexes.⁶⁷ Once again, dispersion dominates these dimers, since in
15 each dimer this is larger in magnitude than the overall interaction energy (Table S1).
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Table 2. Interaction energies (kcal mol⁻¹) and ρ_{bcP} values (au) of dimers of **3** taken from the crystal structure.

 <p style="text-align: center;">3a</p>	<p>IE = -14.2</p> <p>C-H...N: 0.013</p> <p>0.006</p> <p>C-H...F: 0.005, 0.003</p> <p>F...F: 0.003 (x2)</p> <p>0.002 (x7)</p> <p>0.001 (x3)</p>
 <p style="text-align: center;">3b</p>	<p>IE = -1.11</p> <p>F...F: 0.005</p>

 <p style="text-align: center;">3c</p>	<p>IE = -7.8</p> <p>C...C: 0.001 (x2)</p> <p>C-H...F: 0.002 (x2)</p> <p>F...F: 0.008 (x2)</p> <p>0.004 (x2)</p> <p>0.003 (x4)</p> <p>0.002 (x6)</p> <p>0.001 (x2)</p>
 <p style="text-align: center;">3d</p>	<p>IE = -11.5</p> <p>F...N: 0.004, 0.003, 0.002, 0.001</p> <p>C-H...F: 0.008, 0.004</p> <p>0.002 (x3)</p> <p>F...F: 0.007 (x2)</p> <p>0.003 (x4)</p> <p>0.002 (x3)</p> <p>0.001</p>



Conclusion

In conclusion we have isolated and structurally characterized two examples of compounds that feature fluorinated ponytails and have characterized the non-covalent interactions that are present. In the perfluorinated carboxylic acid, $\text{CF}_3(\text{CF}_2)_5\text{CH}_2\text{CO}_2\text{H}$, X-ray and computational data show that the order of stabilizing interactions are O—H...O , C—H...O , C—F...F—C and no C—F...H—C interactions are present. However, a topological analysis does find one weak C—F...H—C interaction. There is an unusual ‘untwisting’ of the perfluorochain that has not been commented upon previously and it may be that the untwisting increases the number of C—F...F—C interactions at the expense of C—F...H—C electrostatic interactions; clearly further work is required to fully understand this, but the energies of these interactions could be of the same order of magnitude. The structure of a triazole, synthesized as a minor byproduct shows the normal twisted perfluorinated chain with a cornucopia of weak interactions. Computational studies reinforce previous work from us and others that the C—F...F—C interactions are present

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3 and stabilizing. Finally this work adds some credence to the idea that steric interactions do play a
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5 role in the non-covalent interactions present in these compounds.
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10 11 **Experimental**

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14 ^1H , $^{13}\text{C}\{^1\text{H}\}$ and ^{19}F NMR spectra were recorded on a Bruker AV400 spectrometer operating at
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16 400.23 MHz, 155.54 MHz and 376.55 MHz respectively, or a Bruker Avance II 600 NMR with
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18 a TCI cryoprobe spectrometer operating at 150.92 MHz (^{13}C) and were referenced to the residual
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20 ^1H and ^{13}C resonances of the solvent used or external CFCl_3 . ^{19}F NMR assignments were
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22 confirmed using COSY experiments. IR spectra were recorded on a Perkin Elmer Spectrum One
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24 spectrometer with attenuated total reflectance (ATR) accessory. Raman spectra were obtained
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26 using 785-nm excitation on a Renishaw 1000 micro-Raman system in sealed capillaries. Mass
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28 spectra were measured on a MALDI QTOF Premier MS system. X-ray crystallography data were
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30 measured on a Rigaku Saturn and on a Bruker Apex diffractometer. The structure was solved by
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32 direct methods and refined by least squares method on F^2 using the SHELXTL program
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34 package.⁶⁸ Crystal data, details of data collections and refinement are given in Table 3. All
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36 compounds and solvents were obtained from commercial sources and used as received.
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46 DFT calculations were carried out in Gaussian09⁶⁹ with the dispersion corrected B97D
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48 functional⁷⁰ and def2-TZVP basis set⁷¹ used in previous work, and taking advantage of density
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50 fitting to make larger calculations viable where possible. All calculations of interaction energy
51
52 used the counterpoise method to account for basis set superposition energy.⁷² Converged
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54 molecular orbitals were obtained from these calculations and used for topological analysis of the
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56 resulting electron density using the AIMAll package.⁷³
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6 **1H,1H-perfluorooctanoic acid, 2.** The crude product was recrystallized from DCM to yield the
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8 colorless plate-like crystals. (0.90 g, 53%). Spectroscopic data are in accord with the literature
9
10 (ESI).⁷⁴
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17 **4-(1,2,2,3,3,4,4,5,5,6,6,6-dodecafluorohexyl)-1-(3,3,4,4,5,5,6,6,7,7,8,8,8-tridecafluorooctyl)-**
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19 **1H-1,2,3-triazole, 3.** 1H,1H,2H,2H-perfluorooctyl iodide (5.82 g, 12 mmol) was dissolved in
20 DMF (60 ml). NaN₃ (1.6 g, 25 mmol) was added and refluxed for 12 h. The mixture was filtered
21 and the filtrate was extracted with ether (3 x 40 ml). The organic extracts were combined and
22 dried with MgSO₄ and concentrated to afford a brown oil. Recrystallization from DCM resulted
23 in X-ray quality crystals of **3** as a side product. (1.20 g, 15 %). M.Pt. = 90-92 °C. IR $\tilde{\nu}$ (cm⁻¹) =
24 3121 (s, C=C); 2920 (w, C-H), 1553 (s, N-H), 1468, 1363 (w, C-H), 1320 (s, C-N), 1230, 1187,
25 1139, 1107 (s, C-F), 1080, 1047, 1028, 991, (m, C-F), 870, 816, 723, (w, C-H), 692 646 (m, C-
26 H). ¹H NMR (400 MHz, CDCl₃) δ (ppm) 7.91 (s, 1H, HC=C); 6.20 (ddd, ²J_{H-F} = 25 Hz, ³J_{H-F} =
27 18 Hz, J_{H,H} = 7 Hz, CHF); 4.77 (t, 2 H, J_{H-H} = 7 Hz, CH₂CH₂N); 2.88 (m, 2 H, J_{H-F} = 19 Hz, J_{H,H}
28 = 7 Hz, CH₂CF₂) ¹³C NMR (100 MHz, CDCl₃) δ (ppm) 137.8 (1C, NC=C); 124.6 (1C, NC=C);
29 118.8 (2C, CF₃) 116.8, 115.3, 110.2, 107.9, (10C, CF₂); 83.2-81.3 (1C, CHF); 43.0 (1 C, CH₂N);
30 32.5 (CH₂CF₂); 31.3 (CH₂CF₂). ¹⁹F NMR [377 MHz, CDCl₃]: δ -81.45 (s, CF₃); -114.59 (s,
31 CF₂CH₂); -120.3 (s, CF₂CHF); -121.1 (s, CF₂CHF); -122.60 (m, CF₃CF₂CF₂); -123.54 (m,
32 CF₃CF₂CF₂CF₂); 124.11 (s, CF₃CF₂CF₂CF₂CF₂); 125.76 (s, CHF); 126.74 (m, CF₃CF₂). MS
33 (ESI-) m/z: 715.0163 [M+H, 100%]; HRMS (ESI+) calculated for C₁₆H₆F₂₅N₃: 715.0163, found:
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Table 3. Crystal Data and Refinement Parameters for Complexes **2** and **3**

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CCDC Number	1045079	1045080
Empirical formula	C ₈ H ₃ F ₁₃ O ₂	C ₁₆ H ₆ F ₂₅ N ₃
Formula weight	378.10	715.24
Crystal system	Triclinic	Monoclinic
Space Group	P -1	C2/c
a (Å)	5.1220(10)	45.931(3)
b (Å)	6.1827(12)	5.4147(4)
c (Å)	18.005(4)	19.6834(16)
α (°)	88.91(3)	90
β (°)	87.15(3)	108.222(5)
γ (°)	80.56(3)	90
V (Å ³)	561.7(2)	4649.8(6)
Z	2	8
Density (calculated) (Mg/m ³)	2.235	2.043
Absorption coefficient (mm ⁻¹)	0.295	2.479
F(000)	368	2784
Crystal size	0.300 x 0.240 x 0.100	0.190 x 0.160 x 0.060
Theta range for data collection	2.265 to 27.489	2.025 to 64.272
Limiting Indices	-6 ≤ h ≤ 6	-53 ≤ h ≤ 48
	-6 ≤ k ≤ 7	-6 ≤ k ≤ 6
	-23 ≤ l ≤ 23	-22 ≤ l ≤ 22
Reflections collected	8368	20881
Independent reflections	2412 [R(int) = 0.0284]	3868 [R(int) = 0.0659]

Completeness to theta (%)	95.3	91.6
Refinement method	Full-matrix least-squares on F ²	Full-matrix least-squares on F ²
Data / restraints / parameters	2412 / 0 / 212	3868 / 0 / 397
Goodness-of-fit on F ²	1.171	1.040
Final R indices [I>2sigma(I)]	R1 = 0.0479, wR2 = 0.1398	R1 = 0.0672, wR2 = 0.1736
R indices (all data)	R1 = 0.0496, wR2 = 0.1415	R1 = 0.1013, wR2 = 0.1949
Largest diff. peak and hole (e.Å ⁻³)	0.425 and -0.307	0.668 and -0.305

ASSOCIATED CONTENT

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Author Contributions

The manuscript was written through contributions of all authors. All authors have given approval to the final version of the manuscript.

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Supporting Information. Full crystallographic descriptions (CIF) and spectroscopic details. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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For TOC only

Further Evidence on the Importance of Fluorous-Fluorous Interactions in Supramolecular Chemistry: A Combined Structural and Computational Study

*Harrison Omorodion, Brendan Twamley, James A. Platts and Robert J. Baker**

Synopsis: The crystal structures of two compounds featuring a $\text{CF}_3(\text{CF}_2)_5\text{CH}_2\text{CH}_2$ fluorous ponytail shows a number of stabilizing $\text{C}-\text{F}\cdots\text{F}-\text{C}$ interactions that have also been characterized by computational methods.

