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The disorder of perfluoroalkyl chains in crystals: Two case histories of interpretation and refinement

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ABSTRACT

Perfluoroalkyl chains in solids are highly disordered in a wide range of temperatures. Poor attention is typically given to this problem in crystallographic studies to the point that no attempt is frequently made in order to model the collected data and disorder remains even unmentioned in a large number of single crystal reports. This paper presents a short analysis of the problems related with this disorder. Two simple crystal structures, namely the halogen bonded adducts between *N*,*N*,*N*′,*N*′-tetramethyl-1,4-phenylendiamine and α,ω-diiodoperfluorobutane or α,ω-diiodoperfluorohexane are discussed in details in order to suggest some simple and basic principles for the refinement of perfluoroalkyl chains in single crystal structural studies.

1. Introduction

The unique properties of the fluorine atom (high ionization potential, electron affinity, and electronegativity, small atom polatizability and radius) [1] are the basis for the unique properties of perfluoroalkanes and their derivatives (high density, viscosity, and chemical stability, low surface tension, refractive index, and dielectric constants) [2]. The usefulness of these properties account for the interest for the incorporation of perfluoroalkyl moieties into small molecules and polymers when the obtainment of new materials with modified physical characteristics is pursued (e.g. visco-elastic, dielectric, and optical properties) [3]. The presence of perfluoroalkyl residues is thus becoming more and more common in organic materials. A rational use of perfluoroalkyl residues in order to tune the functional properties of a material requires a detailed knowledge of the structural characteristics of these residues, both in solution and in the solid. This knowledge has to span a wide length scale, from the Angstrom to the micrometer.

This paper gives a contribution to the full utilization of the potential of single crystal X-ray analyses for determining the structural details of perfluoroalkyl chains in the solid. An analysis of the Cambridge Structural Database (CSD Version 5.30) proves how perfluoroalkyl residues in crystals are highly disordered in a wide range of temperatures. Poor attention is typically given to this problem to the point that no attempt is frequently made in order to model the collected data and disorder remains even unmentioned in a large number of single crystal reports [4]. Some approaches to model this disorder will be discussed thus favouring a deeper insight into a key feature of perfluoroalky chains, namely their conformational preferences. The halogen bonding (the non-covalent interaction involving halogens as electrophilic species [5]) has recently allowed for the easy formation of solid adducts on self-assembly of mono- and diiodoperfluoroalkanes with a wide diversity of electron donor species [6]. Nicely crystalline materials

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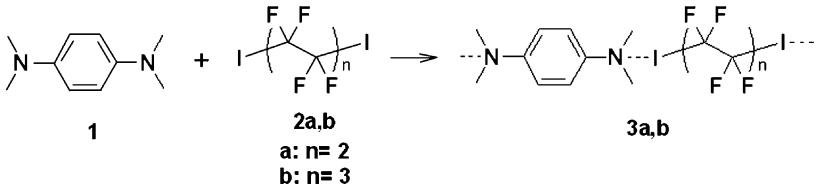

Scheme 1. Halogen bonding driven self-assembly of infinite chains **3a**,**b**.

are frequently obtained and two such adducts will be studied here. Specifically, the single crystal X-ray analyses of the infinite chains **3a**,**b** (obtained when *N*,*N*,*N*′,*N*′-tetramethyl-1,4-phenylendiamine (TMPDA, **1**) self-assembles with 1,l,2,2,3,3,4,4-octafluoro-1,4-diiodobutane (PFDIB, **2a**) or 1,1,2,2,3,3,4,4,5,5,6,6-dodecafluoro-1,6-diiodohexane (PFDIH, **2b**), respectively) will allow for the description of some simple and basic protocols for the refinement of perfluoroalkyl chains (Scheme 1).

2. Results and discussion

CSD studies. Due to the strength of C–F bond and the steric requirements of F–C–F groups, C–$C_{sp3}F_2$– groups are expected to be characterized by very limited geometric parameters variability. In order to confirm this expectation and to get an extensive overview of these parameters in the solid state, an analysis of the Cambridge Structural Database (CSD Version 5.30) was performed. The analysis reveals that most of the terminal perfluorinated chains are disordered and we will show how a fairly simple refinement can solve some of the related problems. Specifically, we searched for all structures, in the CSD, containing at least one acyclic C–$C_{sp3}F_2$– group. To limit the inclusion of inaccurate data, or to elicit biases due to different chemical environments, we imposed the following restraints: *3D coordinates, no errors, no ions, not polymeric, no powder structures*. The search provided 2753 hits, these structures becoming 2041 on adding the condition not disordered, and being further reduced to 1083 on adding the restraint $R < 0.05$. It might be expected the obtained dataset is rather accurate and characterized by a very sharp distribution of geometric parameters. On the contrary, the scatterplot of F–C–F bond angles *versus* C–F bond lengths of the 1083 structures (corresponding to 6925 datapoints) (Fig. 1a) shows clearly that the subset still contains a large number of inaccurate data. In order to eliminate the less accurate of them, we have excluded the *single datapoints* in which at least one parameter p (either C–F distance or F–C–F angle) differs, from the corresponding mean value (p_{mean}, the white dot in Fig. 1a), for more than twice the corresponding standard deviation [SD, derived by the CCDC VISTA program, $p = p_{mean} \pm 2SD(p)$]. Although the resulting intervals are quite large (0.12 Å and 9.3°), another 8% reduction of the set occurred (from 1083 to 1035 hits and from 6925 to 6339 datapoints).

An analysis of this reduced subset was made by plotting the two C–C–F angles of a CF_2 group (Fig. 1b). Obviously, the two angles being chemically equivalent in most cases, their mean values are nearly equal (Fig. 1b, bottom). The scatterplot of Fig. 1b begins to be sufficiently refined and shows a meaningful detail, namely the presence of two partly overlapping populations (central and bottom-left regions with high density of datapoints).

Fig. 2 is a further refinement of Fig. 1b and has been obtained by excluding *all datapoints* from a structure wherein a parameter is out of the limit $p = p_{mean} \pm 2SD(p)$ and also the datapoints from structures where the parameter p = C–C–F angle is out of the interval $p = p_{mean} \pm 3SD(p)$. The aim is to avoid the loss of the apparent bias of Fig. 1b. The CSD hits are now reduced to 866 hits and give rise to 5079 datapoints. The presence of two populations is much more evident (ellipsoids in Fig. 2), confirming that the subset is now quite clean. An analysis of this bias shows that the group of datapoints in the bottom-left ellipsoid are essentially due to –CF_2– embedded in perfluorocarbon chains, while those of the central ellipsoid contains mainly the less hindered groups, like CH_2–CF_2–C and –CF_3 moieties. It is noteworthy that, on going from the 2753 initial hits to the 'error-free' 866 hits of Fig. 2, more than 2/3 of the molecules containing the

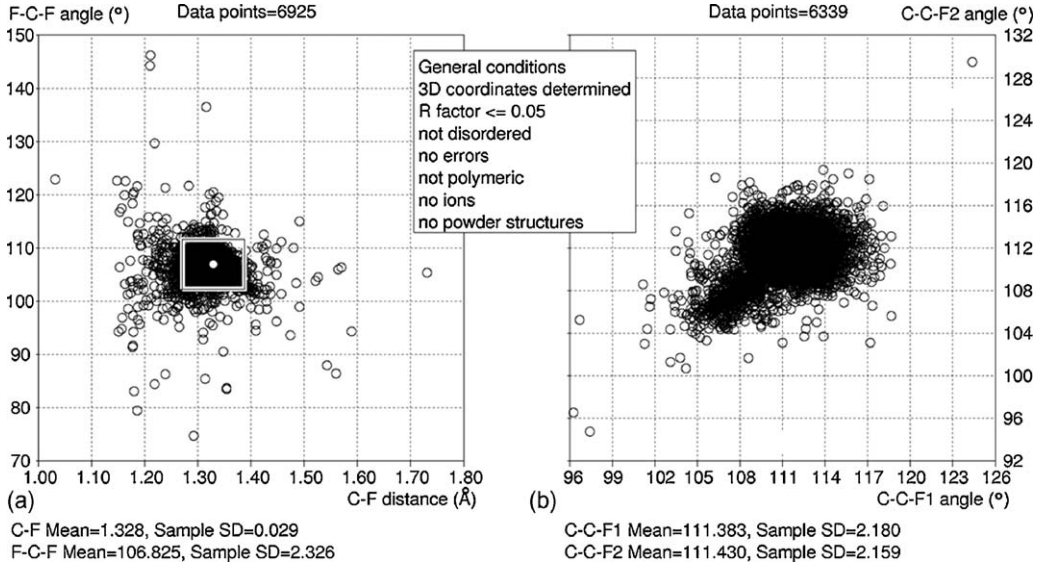

Fig. 1. (a) Scatterplot of F–C–F angle (°) *versus* C–F bond distance (Å) in a group C–$C_{sp3}F_2$; data obtained from CSD Version 5.30; no limits established for F–C–F and C–F values. The white spot represents the p_{mean} value and the box delimitates the datapoints $p = p_{mean} \pm 2SD(p)$. (b) Scatterplot of C–C–F1 angle (°) *versus* C–C–F2 angle (°) for the more accurate datapoints included in the box of (a) (namely: 102.173° < F–C–F angles < 111.477°; 1.267 Å < C–F distance < 1.387 Å).

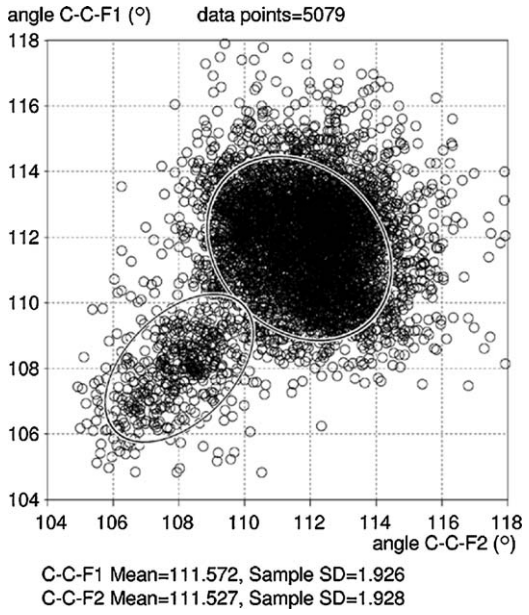

Fig. 2. Scatterplot of datapoints of Fig. 1b, with the further exclusion of *all datapoints* from a structure wherein a parameter is out of the limit $p = p_{mean} \pm 2SD(p)$ and of the datapoints from structures where the parameter p = C–C–F angle is out of the interval $p = p_{mean} \pm 3SD(p)$ (104.800° < C–C–F1 (or C–C–F2) angle < 118.000). The two ellipses evidence the bias between two groups of data with different hindrance (see text).

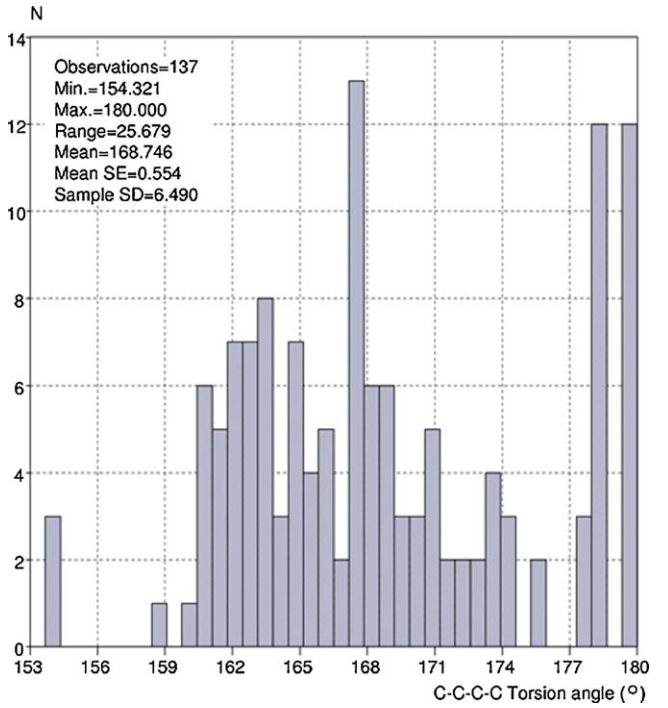

Fig. 3. Histogram of the numbers of C–C–C–C torsion angles with a given absolute value (°) for the structures subset of Fig. 2 without any *gauche* conformation (mean value = 168.746°).

corresponding 5079 $-CF_2-$ groups are probably disordered or at least have very high anisotropic thermal parameters. In fact, the C–C–F1 and C–C–F2 angles are usually chemically equivalent, and they are thus expected to be dispersed strictly along the diagonal of the plot. Differently, this is not the case here and the dispersion of the data is still very high despite the subset seems to be free from inaccurate data. This observation indicates that perfluorinated residues are frequently affected by disorder and that attempts are rarely made to accurately refine these residues [4].

Fluorine atoms typically do not provide strong intermolecular interactions with any atomic species situated at the periphery of organic molecules (e.g. H, O, halogen atoms) [7]. In fact, at the bulk materials level, perfluorinated chains impart hydrophobicity, lipophobicity, and, even more remarkable, also the F···F interactions are very weak [1]. As their hydrocarbon counterparts, perfluorinated residues can assume different conformations by rotating around C–C single bonds, whenever possible. This is particularly the case for trifluoromethyl groups [8]. In contrast, residues with at least three consecutive $-CF_2-$ groups are stiffer than the equivalent hydrocarbon chains and show ground state C–C–C and F–C–F angles which are greater and smaller than the tetrahedral angle, respectively. Few structures reported in the CSD display a *gauche* conformation [9] as the *trans* arrangement is largely preferred. In details, the distorted *trans* conformation is favoured over the exact *trans* conformation due to the short contacts and electrostatic repulsions between 1,3 positioned CF_2 groups [10] (Fig. 3). If no severe packing constrains are present in the crystal, the energy barrier between the conformation with all positive (t^+) and all negative (t^-) deviations from the exact *trans* arrangement of the perfluoroalkyl chain is low and both conformers of the perfluorocarbon chains are present, dynamically or statically. This is often the case also at low temperature.

Generalities on the refinement of perfluoroalkyl chains. In most cases an interpretation of perfluoroalkyl residues disorder less inaccurate than that routinely practised is not time demanding and is also very easy. It produces more accurate geometric parameters, lower R values and residual electron density, and, more importantly, it may give the correct molecular connectivity and conformation, as we will see in one of the examples presented below. In some cases, when the perfluorinated chain is short and the deviation from the exact *trans* C–C–C–C torsion angles are small, exclusively the *ordered* anisotropic standard refinement is possible. The method gives good results and the only problem encountered in these cases are the high values of the anisotropic displacement parameters which causes an apparent small shortening of C–F covalent bonds and a wrong C–C–C–C torsion angle. In contrast, when the perfluoroalkyl chain is long or the C–C–C–C torsion angles markedly differ from 180°, or 60°, the split model refinement becomes essential as well as the use of restraints.

The modern codes for crystal structures refinement provide facilities for refinement with restraints and constraints, easy to use and very powerful. In the following discussion we will refer to SHELX-97 and its facilities [11], the standard refinement program in our laboratory, but procedures similar to those discussed here may be found in other programs.

The single crystal X-ray structure determination, and a simple refinement procedure, of the infinite chains **3a**,**b** (Scheme 1) (obtained on halogen bonding driven self-assembly of *N*,*N*,*N*′,*N*′-tetramethyl-1,4-phenylendiamine (TMPDA, **1**) with 1,4-diiodoperfluorobutane (PFDIB, **2a**) or 1,6-diiodoperfluorohexane (PFDIH, **2b**), respectively) is discussed below. These two case histories will allow for the description of some simple and basic rules for the refinement of perfluoroalkyl chains.

The case histories of **3a**,**b**. Partial evaporation of equimolar solutions of TMPDA **1** and PFDIB **2a**, or PFDIH **2b**, affords colourless crystals **3a**,**b** where starting modules are present in 1:1 ratio (as confirmed with $^1H/^{19}F$ NMR analyses in the presence of 2,2,2-trifluoroethyl ether as external standard [12]). Single crystal X-ray analyses of these solids (Fig. 4) confirm the stoichiometry, reveal that both TMPDA **1** and α,ω-diiodoperfluoroalkanes **2a**,**b** behave as bidentate and telechelic modules and lie on crystallographic symmetry centres. Short N···I halogen bonds (2.862(5) Å in **3a** and 2.845(3) Å in **3b**) are present, which drive the self-assembly and

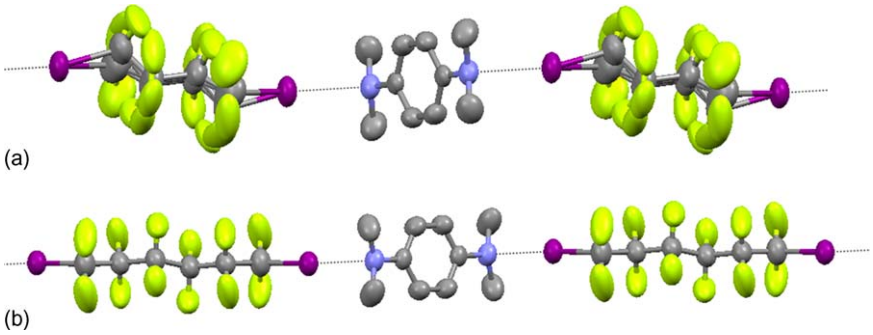

Fig. 4. Ellipsoid representation of 1D unlimited linear chains of **3a** (top) and **3b** (bottom). Colours are as follow: carbon, grey; fluorine, green-yellow; nitrogen, light blue; iodine, purple. Hydrogens are omitted for clarity. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of the article.)

give rise to unlimited chains where the complementary modules alternate.

While the supramolecular arrangements of **3a**,**b** are quite standard, these co-crystals present two significant and educational aspects in terms of crystallographic resolution and refinement. The ordinary refinement of **3a** leads to incorrect molecular connectivity and the splitting model of **3b** into two subsets, in spite of SHELXL-97 suggestion, is not supported by the experimental data.Fig. 5(top) shows the resulting peaks from *SIR*2002 resolution [13] of **3a** (purple circles for iodine and black circles for undefined atoms), together with some peaks from the subsequent difference Fourier map (green circles). Clearly, the TMPDA **1** moiety is well defined and not disordered, but this is not the case for PFDIB **2a**. A quick and simple analysis based on geometrical considerations provides the starting system for the refinement of **3a** (Fig. 5, bottom).

The four different refinement models **M1**–**M4** are tested to refine the perfluorinated chains. In the Model 1 (**M1**) the standard anisotropic refinement was carried out to the end, but some problems occurred with the PFDIB moiety (Table 1). In spite of the reasonable disagreement factors, large correlation factors are present, especially between anisotropic displacement parameters (ADPs) components of fluorine atoms. This approach leads to poor

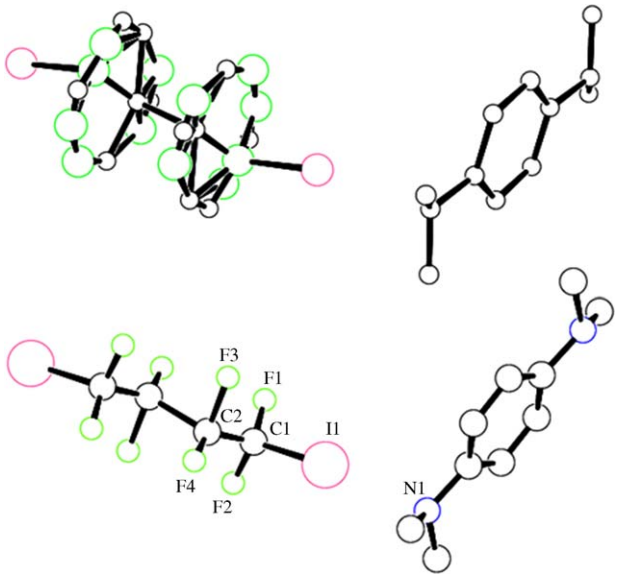

Fig. 5. Top: ball and stick model plot by *SIR*2002 solution of **3a** (purple circles for iodine, black circles for undefined atoms) and difference map residues (green circles). Bottom: initial structure to be refined, obtained by elimination of some peaks based on pure geometric considerations. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of the article.)

geometrical connection around the two independent C atoms of PFDIB molecule, in fact C1–F2 and C2–F2 distances are 1.61(3) and 1.91(3) Å, respectively.

Additionally, in **M1** the ratios between maximum (U_{max}) and minimum (U_{min}) principal mean square atomic displacements for some atoms in the perfluorinated chain are very large, particularly those of F atoms and C1 (Fig. 6a). If the displacements anisostropy are only due to the libration around the molecular inertial axes, the U_{max}/U_{min} ratios of I1, C1, and C2 are expected to be almost the same, as their distance from the longest molecular axis is small and nearly the same. On the contrary, C1 carbon shows an extremely higher ratio than I1 and C2 (Table 1, second column). Only by the superposition of the t^+ and t^- conformers or of two opposite conformers may explain this difference. Obviously, SHELXL97 suggests the splitting of C1 and all F atoms.

The second refinement model (**M2**) is slightly more sophisticated than **M1**. Atoms are split as suggested by SHELXL97 but no constraint is applied (Table 1, Fig. 6b and c). The correlations between refined parameters given by **M2** are higher than those of **M1** (0.893 *vs* 0.804) and the dispersion of the geometric parameters in the perfluorinated chain is still very high (the intramolecular C2-F2B distance is as short as 1.85(3) Å). The F4A–F4B distance (3.005 Å) is much longer than two times the expected value for the canonical C–F distance (1.34 Å) thus proving further the presence of some problems in **M2**. This suggests that also the C2 carbon atom must be split.

Clearly, the constrained refinement becomes mandatory and new refinement models must be developed. The choice of the restraints is somehow problematic as it does not follow strict, well-defined, and pre-established rules and largely depends on crystallographer's preferences. In **3a**, also C2 carbon atom has to be split for imposing the correct restraints (Fig. 6d and e) and the ambiguity problem of choosing the right model to describe the perfluorinated chain has to be solved. PFDIB **2a** can be interpreted as the four different conformers C1A–C2A–C2B–C1B, C1A–C2A–C2A′–C1A′, C1A–C2B′–C2B–C1A′, or C1A–C2B′–C2A′–C1B (Fig. 7). The last two models can be excluded since the distance between C1A–C2B′ is too short. C1A–C2A–C2B–C1B Sequence is treated with the third method (**M3**) and C1A–C2A–C2A′–C1A′ sequence with the fourth method (**M4**). The choice of the carbon atoms sequence is a crucial factor and influences both the definition of the geometric restraints and the modelling of the molecular conformation.

The conformation is not the only difference in the two backbone sequences. In fact, the C1A–C2A–C2B–C1B chain (**M3**) is related to C1A′–C2A′–C2B′–C1B′ by a crystallographic centre of symmetry, this means that the population factor must be fixed to 0.5, while for **M4** chain the two split models are not correlated by any symmetry element and their complementary population factors could need an optimization parameter.

Table 1
Proposed refinement models for **3a**.

	M1		M2		M3		M4	
No. ref. parameters	118		164		168		169	
No. restraints	0		0		170		181	
R_1 [$I_o > 2\sigma(I_o)$]	0.0576		0.441		0.495		0.485	
wR^2 [$I_o > 2\sigma(I_o)$]	0.1484		0.1107		0.1336		0.1277	
Max. correlation factors	0.804		0.893		0.770		0.806	
No. correlation factors >0.7	9		23		4		5	
$\Delta\rho_{min,max}$ e Å^{-3}	−0.86, 1.52		−0.50, 1.52		−0.57, 1.52		−0.50, 1.52	
No. reflections		Part A	Part B	Part A	Part B	Part A	Part B	
C1–I1	2.148(14)	2.20(2)	2.18(3)	2.180(16)	2.180(17)	2.192(15)	2.196(17)	
C1-F1	1.201(19)	1.49(3)	1.38(4)	1.362(11)	1.356(11)	1.348(10)	1.345(10)	
C1-F2	1.61(3)	1.17(2)	1.43(4)	1.339(10)	1.348(11)	1.327(10)	1.339(10)	
C1–C2	1.301(17)	1.40(2)	1.30(3)	1.519(11)	1.523(12)	1.519(11)	1.541(12)	
C2–C2[a]	1.577(19)	1.590(14)	–	1.515(11)	–	1.530(11)	1.523(12)	
C2–F3	1.305(13)	1.41(2)	1.278(18)	1.355(10)	1.347(10)	1.351(9)	1.343(10)	
C2–F4	1.539(16)	1.398(16)	1.67(2)	1.352(10)	1.363(10)	1.344(9)	1.344(10)	
F1–C1–F2	105(2)	118(2)	98.9(16)	117.6(19)	123(2)	119.7(17)	123(2)	
F1–C1–C2	120.7(16)	97(2)	125(3)	101.2(11)	100.3(12)	102.9(10)	102.0(11)	
F2–C1–C2	78.0(15)	109.8(2)	85(2)	105.0(11)	101.4(12)	103.1(10)	103.2(12)	
F3–C2–F4	99.8(12)	103.6(18)	98.9(16)	109.9(16)	110.4(17)	110.8(13)	112.0(17)	
F3–C2–C1	119.3(12)	104.5(16)	117.3(18)	105.6(10)	105.2(11)	106.1(9)	104.6(11)	
F4–C2–C1	84.4(16)	112.1(14)	94(2)	103.7(10)	104.7(11)	103.8(9)	104.6(10)	
F3–C2–C2[a]	112.5(12)	111.2(14)	113.2(12)	114.1(11)	114.0(11)	111.8(10)	111.3(11)	
F4–C2–C2[a]	103.8(11)	105.0(11)	98.1(9)	103.4(9)	104.7(10)	111.7(10)	111.7(12)	
C1–C2–C2[a]	125.3(14)	119.4(13)	125.2(17)	119.4(12)	118.3(13)	112.2(12)	112.4(14)	
U_{max}/U_{min} (I1)	2.48	2.49	2.49	2.49				
U_{max}/U_{min} (C1)	9.21	2.88	3.48	2.71	2.23	2.38	2.37	
U_{max}/U_{min} (C2)	1.82	2.33	–	2.38	–	2.19	–	
U_{max}/U_{min} (F1)	8.44	10.12	16.00	5.85	6.02	5.68	18.11	
U_{max}/U_{min} (F2)	12.55	7.72	4.48	7.84	4.28	7.63	4.58	
U_{max}/U_{min} (F3)	8.24	4.49	7.86	3.39	5.09	4.02	4.76	
U_{max}/U_{min} (F4)	8.27	7.15	5.28	5.31	3.74	5.53	3.96	

[a] -*x*, -*y*, -*z* for **M3**, C2A–C2A and C2B–C2B bonds; for **M4**, C2A–C2B.

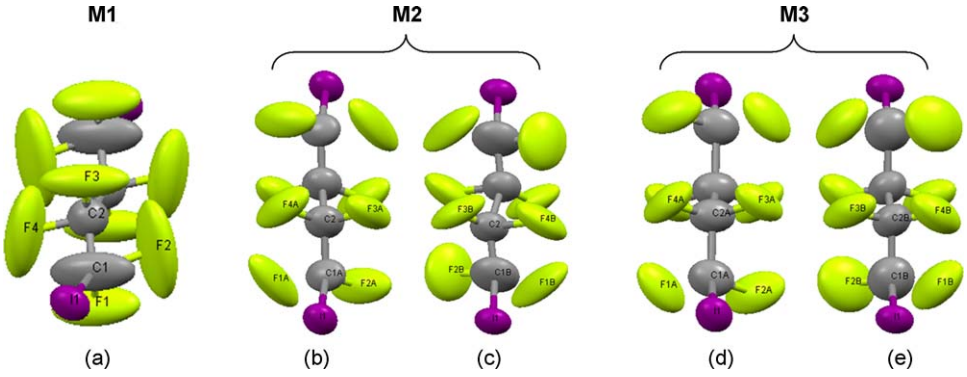

Fig. 6. The three different models of PFDIB refinement: (a) standard anisotropic **M1**; (b) and (c) unrestrained **M2**; (d) and (e) restrained **M3**.

In this case the chosen starting geometry was based on the techniques summarized in Section 4.3. To refine appropriately the **3a** system we decided to restrain the C–F and C–C distances to 1.34 and 1.54 Å, respectively, using a 0.01 Å estimated standard deviation (e.s.d.). Moreover, considering that a 1,3 distance, corresponding to a bond angle, is less rigid than a bond distance, we have imposed the same values for chemically equivalent angles with a 0.03 Å e.s.d. Additional restraints were adopted to describe the perfluorobutane chain motion assuming similar ADPs with e.s.d.s of 0.015. For C1A and C1B only, whose separation was lower that the resolution data, we imposed equal ADPs. The applied constraints and restraints were the same in both models **M3** and **M4**, apart from minor details due to the different symmetry of the two models.

Both the **M3** and **M4** models provide a better geometrical description of the perfluorinated chain than **M1** and **M2**. The refinement of **M3** and **M4** gives smaller correlation factors and U_{max}/U_{min} ratios compared with standard anisotropic and unrestrained models, a single exception is observed for F1B for **M4**. Indeed, in our opinion the real situation, at room temperature, has not to be ascribed to one single model but is a dynamic equilibrium

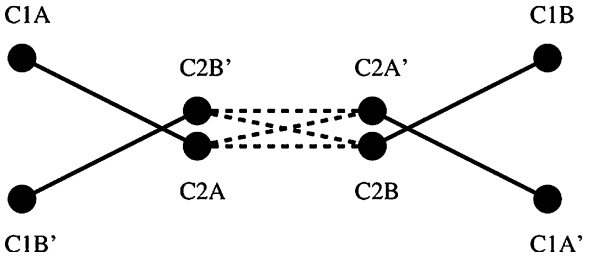

Fig. 7. Possible interpretations of molecular split: the *exact trans* conformation is C1A–C2A–C2A′–C1A′, the *distorted trans* conformation is C1A–C2A–C2B–C1B.

of the two models, despite **M3** seems to be better on the basis of geometric values, ADPs, and correlations as reported in Table 1.

The refinement of **3b** is much simpler than of **3a**. For **3b**, we applied a refinement based on a standard anisotropic model, imposing very soft restraints only on C–F, C–C distances and F–C–F and C–C–C angles. All the correlation parameters are smaller than 0.5 and the *R* and *wR* values are 0.0386 and 0.1120. The geometry thus obtained for DIPFH is reasonable, with C–F and C–C–F distances and angles in the range 1.298–1.342 Å and 107.1°–110.4°, respectively. Notwithstanding this, SHELXL97 suggests to split five of the six independent fluorine atoms, which we did. The suggested separation between couples of split atoms is very low and we constrained their ADPs to be equal. The results were very disappointing as *R* and *wR* converged at 0.0387 and 0.1125, respectively, these values being larger than the previous values. No improvement in the description of the geometry was obtained: a very large number of correlations between geometric parameters were in the range 0.90–0.99 and, due to the increment of the number of refined parameters, a substantial worsening of geometric parameters' e.s.d.s occurred. Besides, the maximum separation between split atoms was 0.35 Å, below the resolution of our data. It is thus possible to conclude that the standard refinement is completely adequate for **3b** and that the large anisotropy of fluorine atoms in the chain only reflects the large thermal motion of these atoms.

3. Conclusions

The complete analysis of the structure **3a**, the refinement of the various models included, did not require more than five working hours. The analysis of **3b** was even less time demanding. While only few minutes are required to define the restraints on a disordered difluoromethylene group and to set up an initial model to be refined, the resulting improvements are substantial, as presented for **3a**. The approach does not allow for well refined structures in all cases and sometimes the work must be very hard and time consuming (as was the case for a calix[5]arene bonded to five disordered $-C_7F_{15}$ chains [14]). Nevertheless, the disordered refinement models should be adopted whenever needed, at least for the simplest cases, in order to provide the scientific community with much more information and consistent data.

4. Experimental

Commercially available chemicals were used without further purification. Chemicals were purchased from *Sigma–Aldrich* and *Apollo Scientific*. IR spectra were recorded with a Nicolet Nexus FT-IR spectrophotometer equipped with the Smart Endurance system (UATR). The thermal analysis was recorded with a Linkam DSC600 Stage (temperature range: −196 °C to 600 °C) coupled with the LN94 cooling system.

4.1. Formation of the co-crystals 3a and 3b

Equimolar amounts of *N*,*N*,*N*′,*N*′-tetramethyl-1,4-phenylendiamine (TMPDA, **1**) and 1,l,2,2,3,3,4,4-octafluoro-1,4-diiodobutane (PFDIB, **2a**) or 1,1,2,2,3,3,4,4,5,5,6,6-dodecafluoro-1,6-diiodohexane (PFDIH, **2b**) were dissolved with chloroform in a vial of clear borosilicate glass at room temperature. The open vial was placed in a closed cylindrical wide-mouth bottle containing CCl_4. $CHCl_3$ was allowed to diffuse at room temperature and after 24 h yellowish co-crystals of **3a** and **3b** were obtained. ^1H and ^{19}F NMR spectra of both adducts showed the signals of pure starting compounds with minor chemical shifts changes, if any. **3a**: M.p. ($CHCl_3$, onset temperature): 112 °C. **IR** (cm^{-1}, selected bands): 2890.5 (w), 2851.1 (w), 1516.5 (s), 1476.0 (m), 1301.7 (m), 1175.9 (s), 1116.5 (s), 1042.5 (s), 934.6 (s), 817.3 (s), 763.4(s). **3b**: M.p. ($CHCl_3$, onset temperature): 103 °C. **IR** (cm^{-1}, selected bands): 2894.4 (w), 2854.4 (w), 1514.6 (s), 1473.9 (m), 1301.2 (m), 1208.7 (s), 1171.0 (s), 1137.2 (s), 1078.8 (s), 936.3 (s), 819.8 (s), 819.8(s), 784.04 (m), 653.5 (s).

4.2. X-ray crystal structure determination

Crystal data for **3a**: $C_{10}H_{16}N_2.C_4F_8I_2$, $M = 618.09$, monoclinic, $C_{2/c}$, $a = 22.340(4)$, $b = 6.0763(10)$, $c = 16.203(3)$ Å, $\beta = 113.46(3)$, $V = 2017.7(6)$ Å^3, $Z = 4$, $\rho(\text{calc}) = 2.035$ g/cm^3, $F_{000} = 1168$, dimension: $0.06 \times 0.34 \times 0.40$. Data collected by a Bruker SMART APEX diffractometer Mo-Kα radiation, $\lambda = 0.71073$ Å, $\mu = 3.188$ mm^{-1}, $T = 295(2)$ K; 16585 reflection collected, 1990 independent, 1575 with $I_o > 2s(I_o)$, absorption corrections $T_{min}/T_{max} = 0.724$, $R_{int} = 0.038$, $2\theta_{max} = 52°$. Structure solved by SIR2002 and refined on F^2 by SHELX-97. CCDC M1: 726920; M2:726921; M3: 726922; M4: 726923.

Crystal data for **3b**: $C_{10}H_{16}N_2.C_6F_{12}I_2$, $M = 718.11$, triclinic, P-1, $a = 5.8258(10)$, $b = 8.1756(14)$, $c = 12.592(2)$ Å, $\alpha = 96.16(2)$, $\beta = 98.02(2)$, $\gamma = 98.77(2)$ $V = 581.85(17)$ Å^3, $Z = 1$, $\rho(\text{calc}) = 2.049$ g/cm^3, $F_{000} = 340$, dimension: $0.05 \times 0.08 \times 0.38$. Data collected by a Bruker SMART APEX diffractometer Mo-Kα radiation, $\lambda = 0.71073$ Å, $\mu = 2.80$ mm^{-1}, $T = 295(2)$ K; 18464 reflection collected, 2682 independent, 2270 with $I_o > 2s(I_o)$, absorption corrections $T_{min}/T_{max} = 0.790$, $R_{int} = 0.031$, $2\theta_{max} = 55.2°$. Structure solved by SIR2002 and refined on F^2 by SHELX-97, 145 parameters, 13 restraints. Final $R = 0.0455$ (0.0386 on observed reflections), $wR = 0.1179$ (0.1120), g.o.f. = 1.051, $-0.49 < \Delta\rho < 1.48$ e Å^{-3}. CCDC 726919.

Copies of the **3a** (all models **M1**–**M4**) and **3b** data can be obtained, free of charge via www.ccdc.cam.ac.uk/conts/retrieving.html (or from the Cambridge Crystallographic Data Centre, CCDC, 12 Union Road, Cambridge CB2 1EZ, UK; fax: 44 1223 336033 or e mail: deposit@ccdc.cam.ac.uk.

4.3. General technicalities for refining disordered perfluorated chains

As shown in the refinement of **3a**, the presence of disorder in perfluorinated chains may often be noticed from the very initial stages. For example, SHELX resolution programs output a number of peaks much greater than the independent atoms number, and when disorder is present the excess often corresponds to disordered fluorine atoms.

The definition of the starting model may follow different protocols. The first protocol is suitable for the simplest cases (such as the disorder in $-CF_3$ groups) and simply requires all the F atoms are refined anisotropically, the atoms are split (as suggested by SHELXL), dividing the split peaks into two models as similar as possible to an ideal geometry, and assigning a complementary population factor to the two models.

A second protocol is to start directly from the peaks derived from the structure resolution, possibly by adding the right peaks derived from a Fourier map (calculated before starting the refinement) as in the case shown for **3a** structure. The peaks are attributed to the two conformers (or parts in SHELXL terminology) by simply resorting to geometric consideration, while the population factor of each part may be initially the same also when symmetry considerations does not add specific constrains.

Sometime, the initial model may be complete, as in the case of a $-CF_3$ split, where not only the disordered atoms are all defined, but also the restraints may be imposed without ambiguity. In other cases the initial model may be incomplete, due to the difficulty to define the position of all the disordered atoms or to establish adequate restraints. In any case, it is convenient to start the refinement with isotropic atoms, and, above all, with a large

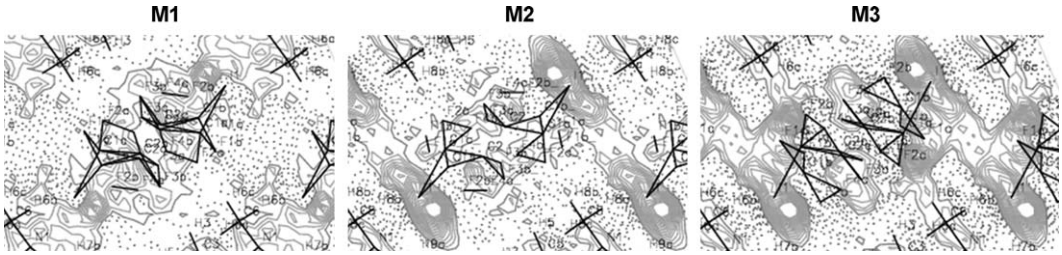

Fig. 8. Three different Fourier maps for the structure **3a**: **M1**, **M2** and **M3** (projection down b^*, a-axis vertical and c-axis horizontal).

damping factor, especially if the population factors are simultaneously refined with displacement parameters. In fact, at the beginning, the least squares matrix may be very ill-conditioned with very large correlation parameters. In our experience, 8 cycles of refinement with a damping factor that reduces the parameters changes by 0.5 is normally much better than 4 cycles without damping factor.

After the initial cycles, the analysis of the results is mandatory. Refined atoms with a too low population factor are probably to be deleted and the same has to be done for atoms with very large displacement parameter U_{iso}. Some caution is required for these latter atoms as a large U_{iso} of an atom with a large population factor may simply indicate that the atom must be split. In that case the anisotropic refinement of this atom may help to decide how to proceed. An initial, complete, and coherent model of disorder could normally be found after some cycles of refinement and elimination of incorrect atoms.

At this point the model restraints may be defined. Firstly, we have to assign the molecular part: any atoms must be attributed to a part and any part must have its own population factor that may be fixed or variable. In our experience, when the split molecular model is completely defined, it is convenient to start again with isotropic atoms and assigning a population factor for all the models (normally they are only two, with population factor 0.5). The initial restraints must be hard but must not be too dependent on the molecular conformation. The assumption of strong restraints for bond distances and softer for 1–3 distances is probably a good criterion. In our experience the SHELXL function SAME, that automatically defines the similitude between chemically equivalent groups of atoms, is difficult to use because the initial model may be very poorly defined and the use of this instruction may bring to inconsistent results. DFIX or at least SADI routines, specifying all the distances to be collectively refined, is much more useful, especially at the very beginning. Also at this stage the use of a damping factor may greatly help. After any group of least squares cycles, the geometry of the independent models must be controlled. When two atoms are too close to each other, they sometimes need to be exchanged from a part to the other and, in that case, it is convenient to reset their U_{iso} to a expected value. At this stage, if the mean U_{iso} is very different for the different parts it may be convenient to decide if the population factor must be refined. When the refinement of the two parts is geometrically stabilized, the anisotropic refinement can be applied. At this stage, some cautions must be used because the correlations between coordinates and ADPs could be very large and if so we newly start with a damping factor. Similar ADPs for all the atoms of a part have also to be imposed, but if the distance between two atoms in different parts is too short (for example less than half the data resolution), these atoms have to be constrained to the same ADPs. At the last stage of the refinement, the damping factor has to be eliminated and the restraints softened, playing attention that the correlation factors between refined parameters remain sufficiently low. Additionally, the Fourier maps for **3a** can be displayed showing the reduction of the disorder in the three different models (Fig. 8).

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