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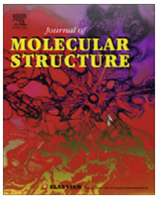

C–H···F, C–H···O interactions in the crystal structure of 2-(2-nitrophenyl)-3-pentafluorophenyl-oxirane and 2-pentafluorophenyl-3-phenyl-1-(*p*-tosyl)-aziridine

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ABSTRACT

Existence and nature of C–H···F, C–H···O interactions in 2-(2-nitrophenyl)-3-pentafluorophenyl-oxirane (**1**) and 2-pentafluorophenyl-3-phenyl-1-(*p*-tosyl)-aziridine (**2**) are discussed. In compound **1** with a linear molecule, C–H···F, C–H···O hydrogen bonds assemble adjacent molecules into the two-dimensional layers, F···F, O···F interactions connect adjacent layers into three-dimensional supramolecular networks. Owing to the inductive effect of nitro group, the C–H acidity of nitrophenyl increases and the numbers of C–H···F, C–H···O hydrogen bonds also increase, C–H···F, C–H···O interactions become stronger and more important. 1D ribbons of compound **2** are stabilized by C–H···F, C–H···O intermolecular interactions. Nonplanar tritopic molecule would demand the formation of a π···π packing interactions between benzene rings and pentafluorobenzene rings in **2**.

1. Introduction

Intermolecular interactions play an important role in the formation of stable and structurally well-defined supramolecular structures [1–4]. Halogen atoms are typically located at the periphery of organic molecules and are thus ideally positioned to be involved in intermolecular interactions [5] and halogen atoms are much larger and polarizable than hydrogen atoms; thus halogen bonds are more sensitive to steric hindrance than hydrogen bonds [6]. Some results of studies prove it is possible to carefully tune the strength of the halogen bond in a given halocarbon by modifying the substituents on the carbon skeleton [7,8]. With the exception of halogen bonds, the C–H group is known to be a hydrogen-bond donor as well as weak but directional C–H···F, C–H···O intermolecular interactions are serve as tools in engineering molecular assemblies [9–12]. Organic fluorine and its role as a hydrogen-bond acceptor are of recent interest [13,14]. We have previously reported that the self-assemblies of melamine with aromatic carboxylic acids, 1,5-naphthalenedisulfonic acid were assisted by an interplay of strong N–H···O and N–H···N hydrogen bonds interactions and the geometry of the molecules [15,16]. Here, organic molecules equipped with fluorine atoms and oxygen atoms, which have linear and nonplanar tritopic geometries, respectively, 2-(2-nitrophenyl)-3-pentafluorophenyl-oxirane (**1**) and 2-pentafluorophenyl-3-phenyl-1-(*p*-tosyl)-aziridine (**2**) have been synthesized, with the intent of finding reproducible assembly strategies.

2. Experimental section

2.1. Synthesis

In the a dry Schrock tube, tetrahydrothiophene (44 mg, 0.5 mmol) for **1**, triphenylarsenic (31 mg, 0.1 mmol) for **2**, aromatic aldehyde (75.5 mg, 0.5 mmol) for **1**, imino (129.5 mg, 0.5 mmol) for **2**, $Rh_2(OAc)_4$ (4 mg, 10 mmol), anhydrous THF (2 ml) were added in turn under N_2 atmosphere. Then pentafluorophenyldiazomethane (156 mg, 0.75 mmol) in THF solution was added dropwise with injection pump over 2 h. After addition, the reaction mixture was stirred and refluxed for another 2 h at room temperature. After filtered and concentrated under reduced pressure using a rotary evaporator, the solvent was evaporated and the residue was purified by column chromatography. The crude crystals thus obtained were recrystallized.

2.1.1. Compound **1**

Colorless crystal. m.p. 82–84 °C. Anal. Calcd for $C_{14}H_6F_5NO_3$: C; 50.76, H; 1.81, N; 4.23%. Found: C; 50.70, H; 1.83, N; 4.25%. IR (KBr) cm^{-1}: 3107, 1657, 1611, 1577, 1521, 1501, 1348, 1332, 1122. ^1H NMR ($CDCl_3$, 300 MHz) δ ^1H NMR (in $CDCl_3$) δ: 8.23 (m, 1H, Ar–H), 7.72 (m, 2H, Ar–H), 7.55 (d, $J = 1.8$ Hz, Ar–H), 5.15 (d,

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J = 1.8 Hz, CH), 3.98 (s, 1H, CH). ^{19}F NMR (in $CDCl_3$) δ-144.2 (m, 2F), −152.3 (t, *J* = 21.2 Hz, 1F), −161.2 (m, 2F).

2.1.2. Compound **2**

Colorless crystal. m.p. 139–141 °C. Anal. Calcd for $C_{21}H_{14}F_5NO_2S$: C; 57.40, H; 3.18, N; 3.19%. Found: C; 57.40, H; 3.17, N; 3.18%. IR (KBr) 1930, 1658, 1596, 1525, 1500, 1458, 1335, 1324 cm^{-1}. ^{1}H NMR (in $CDCl_3$) δ7.95 (d, J^2 = 8.1 Hz, 2H, Ar–H), 7.30 (m, 7H, Ar–H), 4.71 (d, *J* = 3.9 Hz, 1H, CH), 3.79 (d, *J* = 4.2 Hz, 1H, CH), 2.42 (s, 3H, Ar–CH_3). ^{19}F NMR (in $CDCl_3$) δ-137.4 (d, *J* = 17.5 Hz, 2F), −151.5 (t, *J* = 20.6 Hz, 1F), −161.4 (m, 2F).

2.2. Structural characterizations

Diffraction intensities for **1** and **2** were collected at 293 K on a Bruker Smart Apex CCD diffractometer with graphite-monochromated Mo Kα radiation (λ = 0.71073 Å). Absorption corrections were applied using SADABS [17]. The structures were solved by direct methods and refined with full-matrix least-squares technique using SHELXS-97 and SHELXL-97 programs, respectively [18]. The organic hydrogen atoms were generated geometrically (C–H 0.96 Å). Crystal data as well as details of data collection and refinement for the compounds **1** and **2** are summarized in Table 1. A summary of hydrogen bonding interactions observed in **1** and **2** is provided in Table 2.

Table 1
Crystal data and structure refinement for compounds **1** and **2**.

Compound	1	2
Empirical formula	$C_{14}H_6F_5NO_3$	$C_{21}H_{14}F_5NO_2S$
Formula weight	331.20	439.39
Temperature (K)	293(2)	293(2)
Wavelength (Å)	0.71073	0.71073
Crystal color	Colorless	Colorless
Crystal size (mm)	0.32 × 0.23 × 18	0.42 × 0.22 × 0.09
Crystal system	Monoclinic	Triclinic
Space group	$P2_1/n$	$P\bar{1}$
a (Å)	7.298(1)	7.747(2)
b (Å)	12.616(2)	9.419(2)
c (Å)	13.957(2)	14.952(3)
α (°)	90.00	74.701(5)
β (°)	95.331(3)	76.265(5)
γ (°)	90.00	66.196(4)
Volume (Å^3)	1279.4(4)	952.2(4)
Dc (Mg/m^3)	1.719	1.533
Z	4	2
No. of data/params	2938/233	4166/280
μ (mm^{-1})	0.169	0.236
Range for data collection	2.18° < θ < 28.28°	4.81° < θ < 38.93°
h range	−9 to 9	−8 to 10
k range	−15 to 16	−11 to 12
l range	−18 to 13	−19 to 17
Reflns collected	7535	5749
Reflns unique	2938	4166
Observed reflns	1318	1661
R_{int}	0.0917	0.0690
R_1[a]	0.0452	0.0718
Completeness (to θ = 26°)	99.8%	97.9%
wR_2[b]	0.0886	0.1523
F(000)	664	448
Goodness-of-fit	1.057	1.090
$\Delta\rho_{max}/\Delta\rho_{min}$ (eÅ^{-3})	0.19/−0.20	0.36/−0.38

[a] $R_1 = \sum||F_0| - |F_C||/\sum|F_0|$.

[b] $wR_2 = \sum\left[w(F_0^2 - F_C^2)^2\right]/\sum\left[w(F_0^2)^2\right]^{1/2}$.

Table 2
Hydrogen bonding parameters in **1** and **2**.

D–H···A	D–H (Å)	H···A (Å)	D···A (Å)	∠D–H···A (°)
1				
C17–H17···O1#1	0.93	2.54	3.427(2)	158.7
C7–H7···F4#1	0.98	2.51	3.170(2)	124.4
2				
C10–H3···O3#2	0.94	2.51	3.289(2)	141.3
C11–H4···F3#3	1.02	2.59	3.608(2)	170.6
C12–H5···F1#4	1.00	2.58	3.290(2)	127.3

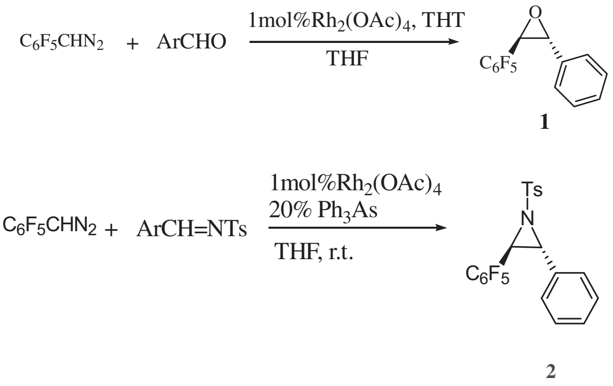
Symm. code: **1**, #1: 1 + *x*,*y*,*z*; **2**, #2: 1/2 + *x*,1/2 − *y*,1/2 + *z*; #3: *x*, −1 + *y*, *z*; #4: −1/2 + *x*, 1/2 − *y*, −1/2 + *z*.

3. Results and discussion

The compounds **1** and **2** were synthesized from pentafluorophenyldiazomethane and aromatic aldehyde for **1**, imino for **2** (Scheme 1). The nature of their self-assembly was investigated using single crystal X-ray diffraction studies. We are interested in examining the difference of C–H···F, C–H···O interactions in **1** and **2**. Consequently, the compounds **1** and **2** were prepared and characterized.

3.1. Crystal structure of 2-(2-nitrophenyl)-3-pentafluorophenyl-oxirane (*1*)

Compound **1** is a linear molecule and the pentafluorobenzene rings are approximately coplanar with the aromatic rings [dihedral angle 5.2°], which promote to form a 2D net (Fig. 1a). Indeed, individual molecules are aligned in vertical rows and in a "head-to-tail" fashion, with adjacent vertical rows running in antiparallel directions as shown in Fig. 2. Fluorine atoms in **1** are extremely activated toward participation in intermolecular interactions, four of the five fluorine atoms are engaged in halogen bonding and weak hydrogen bonds, including examples of two C–H···F hydrogen bonds, one O···F interaction and four F···F halogen bonds. Interestingly, three of five fluorine atoms (F1, F3, F5) of pentafluorophenyl moieties form bifurcated contacts with fluorine atoms (F3, F1, F2) and hydrogen atoms (H4–C11, H5–C12) or oxygen atom (O3) from different molecules, respectively. Thus, this fluorine atoms (F1, F3, F5) function as C–H···F hydrogen bond and halogen bond acceptors (nucleophile, Lewis bases) toward neighboring electrophilic fluorine atoms or oxygen atoms, hydrogen atoms as donors (Lewis acids) as shown in Figs. 2 and 3a. A similar bifurcated hydrogen bonding motif was encountered in a structure of phloroglucinol ester [9]. It is to be noted that the atom F4 in **1** also did not participate in any intermolecular interactions, owing to not match with hydrogen donors in geometry. Careful examination of the intermolecular interactions of compound **1** reveal that C–H groups on the benzene ring of nitrophenyl moiety strong ability to form attractive C–H···F or C–H···O interactions. Three hydrogen atoms of four hydrogen atoms on the benzene ring of nitrophenyl moiety are involved in the formation of intermolecular C–H···O interactions. Owing to the inductive effect of nitro group, which is electron withdrawing, it will



Scheme 1. Synthesis of the compounds (**1–2**).

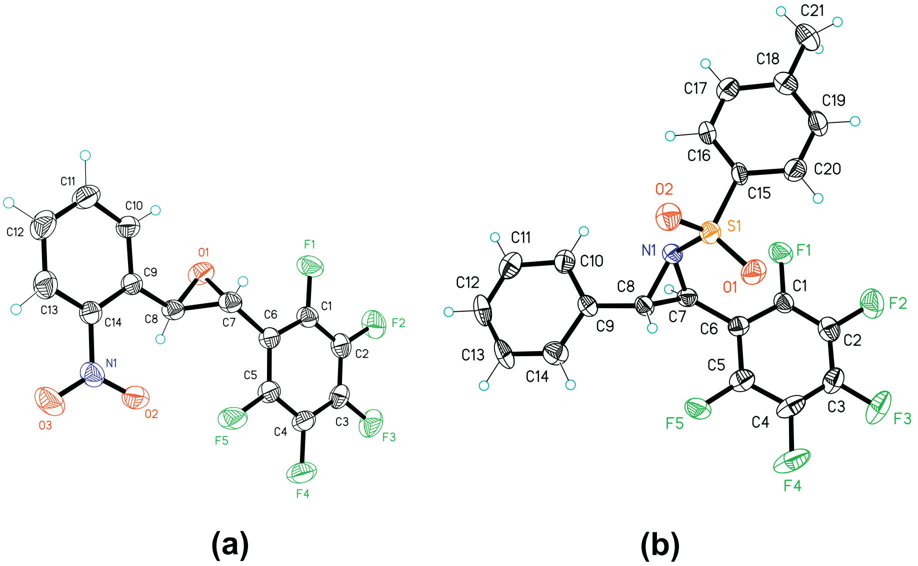


Fig. 1. (a) ORTEP of **1** drawn with 30% ellipsoidal probability. (b) ORTEP of **2** drawn with 30% ellipsoidal probability.

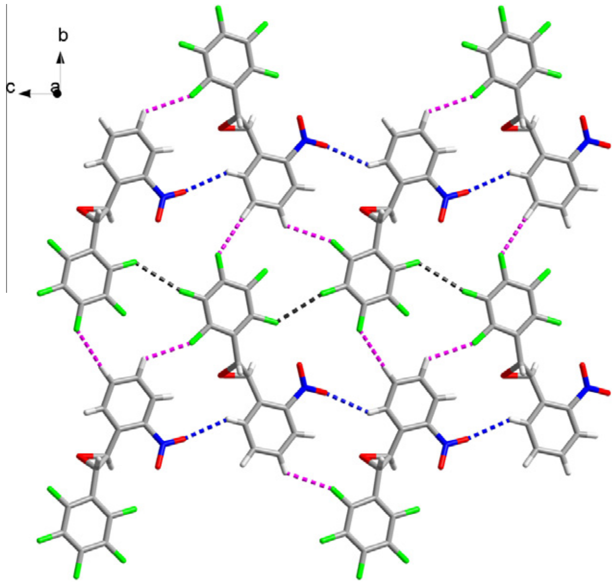


Fig. 2. 2D sheet exhibiting C–H···F, C–H···O hydrogen bonding and F···F interactions in the structure of **1.**

decrease the electronic density on the benzene ring, which means that benzene ring of nitrophenyl moiety has the more acidic protons to form C–H···F or C–H···O hydrogen bonds. In two-dimensional sheets of **1**, the adjacent molecules are connected via C–H···O and C–H···F interactions in a "head-to-tail" fashion, with pentafluorobenzene ring of one molecule and adjacent pentafluorobenzene ring of another molecule in following row are held by a pair of type F···F halogen bonds involving F2 and F5 atoms. Notable, F···F instance ($d_{F\cdots F}$ = 2.844 Å) is shorter than those of 1,2,3,5-tetrafluorobenzene ($d_{F\cdots F}$ = 2.923, $d_{F\cdots F}$ = 2.987 Å) [19]. Two type C–H···F intermolecular interactions are formed between each phenyl moiety and adjacent two pentafluorobenzene moieties from different rows as shown in Fig. 2. The 2D sheet extends in the *bc* plane. In **1**, nitro oxygen atom O2 and the oxygen atom O1 on triatomic cycle skeleton did not participate in any contacts due to space steric effects. Results of studies of Gautam R. Desiraju and co-workers in 10 fluorobenzenes showed that fluorine would form C–H···F interactions rather than F···F contacts [20]. However, it should be noted that in this study, F···F and O···F halogen bonding interactions seemingly play a central role in stabilizing the crystal structure of **1**. The F···F halogen bond ($d_{F1\cdots F3}$ = 2.925 Å) from different layers serves to connect adjacent 2D sheet as shown in Fig. 3a., which are further stacked into 3D structures by O···F and F···F interactions (Fig. 3b). The F···F and O···F interactions to connect adjacent 2D sheet ($d_{F\cdots F}$ = 2.925 Å, $d_{O\cdots F}$ = 2.964 Å) are similar and longer than those to connect adjacent molecules in same layers ($d_{F\cdots F}$ = 2.844 Å).

3.2. Crystal structure of 2-pentafluorophenyl-3-phenyl-1-(p-tosyl)-aziridine (2)

Compound **2** exhibits nonplanar tritopic molecule compared to linear compound **1** owing to the introduction of the tosyl moiety on the triatomic cycle skeletons (Fig. 1b), pentafluorobenzene rings

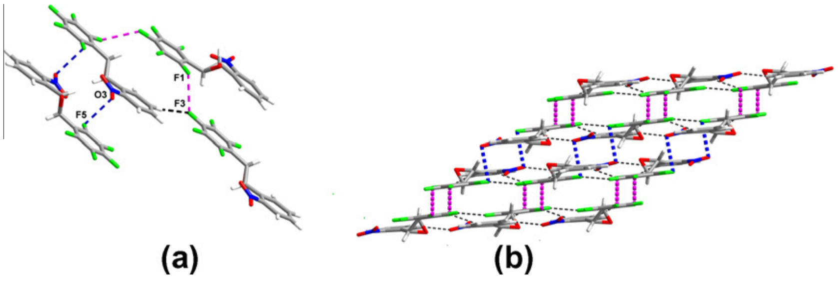


Fig. 3. (a) Adjacent layers are connected via F···F and O···F interactions to form 3D structures in **1**. (b) Packing in **1.**

are not coplanar with the aromatic rings. The angle between the mean planes of the benzene ring and the pentafluorobenzene ring is 22.1° with the angle between the mean planes of the benzene ring and methylbenzene ring being 13.5°, and the angle between the mean planes of pentafluorobenzene ring and methylbenzene ring is 10.7°. The packing of the molecules in the crystalline lattice of **2** with nonplanar tritopic molecule is not made most compact (ρ_{calc} of **2** = 1.533 g cm^{-3}, ρ_{calc} of **1** = 1.719 g cm^{-3}) compared to **1** of linear molecule. Owing to the introduction of the bulky tosyl moiety, it is so incompatible with geometry shape in **2** that fluorine atoms bonding patterns in **2** reveal significant differences as compared to those in **1**. Only one (F4) of five fluorine atoms in **2** participates in C–H···F hydrogen bond, other four fluorine atoms did not participates in any intermolecular interactions due to not match with hydrogen bonding donors in process of molecular self-assembly. Fluorine atoms in **2** are extremely deactivated toward participation in intermolecular interactions. It is to be noted that only one (O1) of two oxygen atoms of tosyl moiety engages in C–H···O hydrogen bond, while another oxygen atoms of tosyl moiety did not participate in any intermolecular interactions similar to those of nitro group in **1**, as well as the nitrogen atom on triatomic cycle skeleton did not exhibit any intermolecular interaction similar to the oxygen atom on triatomic cycle skeleton in **1**.

Compound **2** crystallizes as 1D ribbon structures seemingly by various C–H···F and C–H···O hydrogen bonds and the network assemblies found in **2** and **1** differ significantly, not just in their overall topology but also by the presence of significant F···F and O···F close contacts in **1** and the complete absence of such interactions in **2**. Meanwhile, the adjacent molecules are held through a well-defined C–H···F hydrogen bonds and C–H···O hydrogen bonds to form undulate ribbons running *a* axis as shown in Fig. 4. The introduction of the tosyl moiety increases the angle (22.1°) between the mean planes of the benzene ring and the pentafluorobenzene ring compared to those (dihedral angle 5.2°) of **1**, resulting to an additional π···π stacking interactions between aromatic rings and pentafluorobenzene rings (Fig. 5).

A comparison of **2** with compound **1** indicates the importance difference in intermolecular interaction of C–H group on the benzene ring, only one hydrogen atom of four hydrogen atoms on the benzene ring of tosyl moiety is involved in the formation of intermolecular interaction (C–H···O hydrogen bond). It may apparently be attributed to the fact that the inductive effect of methyl group is electron donating and the methyl group of tosyl moiety enhances the electronic density on the benzene ring, making hydrogen atoms on benzene ring of tosyl moiety a weaker acid than those of nitrophenyl moiety in **1**. In addition to, the structure of **2** demonstrates that the C–H group on benzene ring of tosyl moiety prefers to form C–H···O interactions rather than C–H···F interactions. The C–H···O hydrogen bonds are considered to arise from the interactions between a soft donor (C–H) and a soft acceptor (O) while the F atom in the C–F group is a hard acceptor, and this could be one of the reasons why it does not form very effective C–H···F hydrogen bonds [20].

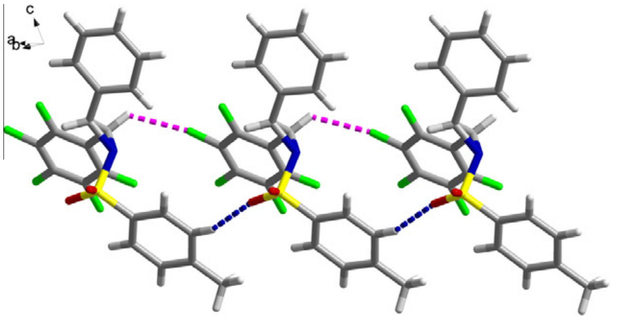


Fig. 4. Ribbon motif maintained by C–H···O and C–H···F hydrogen bonds in **2**.

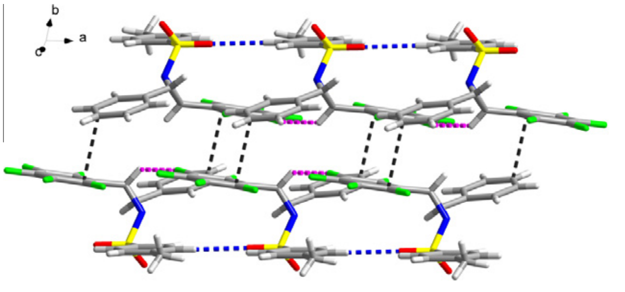


Fig. 5. Aromatic π···π interactions between benzene rings and pentafluorobenzene ring in **2**.

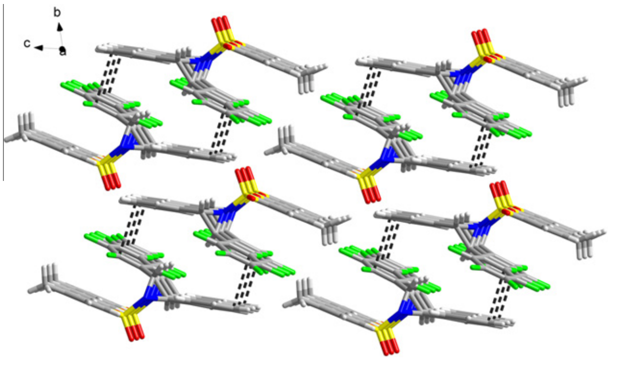


Fig. 6. Extended packing in **2** showing.

It is to be noted that C–H···F hydrogen bonding interactions found in **1** and **2** differ significantly, the hydrogen atoms of benzene rings in **1** serve to hydrogen boning donors. In contrast, hydrogen boning donors in **2** are the hydrogen atoms of aziridine ring. The distance and geometry of C–H···O hydrogen bond ($d_{H\cdots O}$ = 2.54 Å, C–H···O = 158.7°) presents in the structure is similar to those of **1** ($d_{H\cdots O}$ = 2.51 Å, C–H···O = 141.3°), but both contacts fall within the range of attractive interactions. Similar distances and angles were found in the structure of 3-iodotriaroylbenzenes ($d_{H\cdots O}$ = 2.46 Å, C–H···O = 160.3°), and 3-bromoacetophenone ($d_{H\cdots O}$ = 2.42 Å, C–H···O = 133.8, 167.7°) [9]. The association of two such ribbons via π···π interactions is illustrated in Fig. 5 in which pentafluorobenzene donors have been tilted toward the benzene ring acceptors. The distance of centroid to centroid is 4.365 Å, but the shortest contact distance of pentafluorobenzene ring and benzene ring is 3.307 Å involving C1 on pentafluorobenzene ring and C12 on benzene ring. A view of the extended packing observed in **2** is shown in Fig. 6 to illustrate the aromatic π···π interactions between double ribbons in parallel rows. Examination of the extend network present in **2** reveals no significant halogen bonding.

4. Conclusions

The acidity of C–H groups on the benzene ring and geometric shape of molecule are essential in controlling the final supramolecular architecture. Owing to the inductive effect of nitro group, stronger acidity of C–H groups on the benzene ring, more C–H groups participate in intermolecular interactions in **1**. Linear molecule **1** forms 2D networks while nonplanar tritopic molecule **2** self-assembles into one dimension ribbons. In **1**, four of the five fluorine atoms are engaged in intermolecular interactions while only one of five fluorine atoms in **2** participates in intermolecular contact. Fluorine atoms in **1** and **2** are found to be two distinct types of bonding patterns are prominently featured in this work. In contrast, the linear molecule **1** gives rise to 3D network structures in which F···F and O···F interacts seemingly play a central role, while in **2**, C–H···O and C–H···F hydrogen interactions assemble the molecules into 1D ribbons. There are π···π interactions between benzene rings and pentafluorobenzene rings, which are found to consolidate adjacent ribbons. C–H···O and C–H···F interactions are important and appear to control the packing motifs in both compounds.

Supplementary material

Copies of X-ray crystallographic files in CIF format for the structure determination may be obtained free of charge from The Director, CCDC, 12 Union Road, Cambridge, CB2 IEZ, UK (Fax: +44 1223 336033; e-mail: deposit@ccdc.cam.ac.uk).

Acknowledgments

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