Crystal Engineering: Fluorine as a New Steering Group

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For the first time fluorine has been examined as a steering group for crystal engineering. In sharp contrast to the packing and photo behaviour of unsubstituted coumarin, molecules of both 6- and 7-fluorocoumarins are found to attain a packing mode which enables them to undergo [2 + 2] photodimerization in the solid state leading stereospecifically to a mirror symmetric dimer.

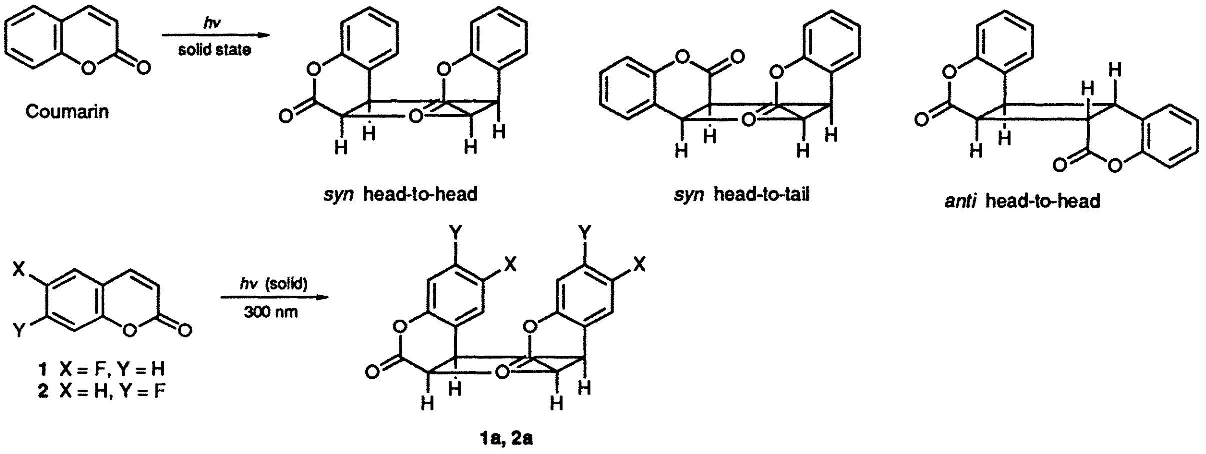
From the pioneering work by Schmidt *et al.*,[1–4] it emerged that the crucial factor that determines the success of a [2 + 2] topochemical photo cycloaddition is a favourable juxtaposition of double bonds of incipient reactive molecules with the centre-to-centre distance of the double bonds being less than *ca.* 4.2 Å; (the β packing mode). Ever since this discovery the most challenging problem in the area is that of 'Crystal Engineering' which aims at pre-organising the molecules of interest into a packing mode favourable for photodimerization.[5] Efforts in this direction led to the identification of steering groups such as chloro,[6–9] bromo[10] and sulfur.[11] We present here the first report on the use of fluoro-substitution to bring about a packing mode favourable for stereospecific photodimerization.

Coumarin which was earlier reported[12] to be photostable in the crystalline state has in fact been found to react,[13] though in a non-topochemical fashion, yielding three photodimers differing in stereochemistry; *syn* head-to-head, *syn* head-to-tail and *anti* head-to-head (Scheme 1). However, chloro[7] and bromo[10] groups have already been shown to be able to steer molecules of coumarin to the β-packing mode. It was considered to be worth examining the steering capability of other halogen atoms *i.e.* fluorine and iodine. The results pertaining to the photo behaviour in relation to the nature of crystal packing of fluoro-substituted coumarins are discussed in this paper.

Experimental

Both 6-fluorocoumarin **1** and 7-fluorocoumarin **2** were synthesized and purified by a procedure similar to the one reported.[8] Powdered samples of these compounds were irradiated in a Rayonet photochemical reactor (λ = 300 nm) at room temperature. The progress of the reaction was monitored by ^{1}H NMR spectroscopy and thin layer chromatography (TLC). After an irradiation period of *ca.* 40 h, each of these (**1** and **2**) gave, in total contrast to the photobehaviour of unsubstituted coumarin, a single stereospecific mirror symmetric dimer (**1a** and **2a** respectively) in quantitative yield (*ca.* 100% as measured from ^{1}H NMR spectra) (Scheme 1). The dimers **1a** and **2a** were both purified by column chromatography and characterised as *syn* head-to-head by comparison of their spectral properties with those of similar coumarin dimers.[14,15]

X-Ray Structural Analysis and Refinement.—Crystals of **1** and **2** were obtained from acetone and ethanol–chloroform (1 : 1) mixture respectively by the slow evaporation method, and single crystal X-ray diffraction studies of each were undertaken. Accurate cell dimensions and intensity data were obtained from an Enraf-Nonius CAD-4 diffractometer using monochromated Cu-Kα (λ = 1.5418 Å) radiation. The measurement conditions and structural details are listed in Table 1. The data were corrected for Lorentz and polarization factors but not for absorption. Structures of both **1** and **2** were solved using SHELXS 86[16] and full-matrix least-squares refinement in blocks were carried out using SHELX 76.[17] The refinement of **2** was straightforward. In case of **1**, the $|E|^2$ statistics showed hypercentric distribution and also the bond lengths (see Table 2), particularly of C(2)=O(2) and C(6)–F(1), were unusual. This is indicative of disorder. Hence refinement in the centric space group $P\bar{1}$ was initiated. With the number of molecules in the unit cell being one, it was required to treat the molecule as disordered with the crystallographic centre of inversion coinciding with the centre of the C(9)–C(10) bond. However, the *R*-factor did not converge below 11.8% in the space group $P\bar{1}$. And, with a more significant observation, that the powdered



Scheme 1

Table 1 Crystal data for compounds 1 and 2

Compound	1	2
Mol. formula	$C_9H_5O_2F$	$C_9H_5O_2F$
M_r	164.14	164.14
Space group	$P1$	$P2_1$
Z	1	2
a/Å	3.744(2)	3.917(4)
b/Å	6.562(2)	5.928(1)
c/Å	7.801(5)	15.437(4)
α/°	102.76(3)	90.00
β/°	99.68(4)	90.98(4)
γ/°	102.53(3)	90.00
V/Å^3	177.7(2)	358.4(4)
D_m/Mg m^{-3}	1.54	1.53
D_x/Mg m^{-3}	1.534	1.521
μ/cm^{-1}	10.41	10.32
F(000)	84.0	168.0
Crystal size/mm	0.4 × 0.2 × 0.08	0.25 × 0.25 × 0.1
θ limit/°	60.0	60.0
Mode of data collection	$\omega/2\theta$	$\omega/2\theta$
No. of intensity controls	3	3
No. of unique reflections	604	584
No. of observed reflections	384 $[\lvert F_o\rvert > 3\sigma(F_o)]$	487 $[\lvert F_o\rvert > 4\sigma(F_o)]$
No. of variables	129	129
Final R^a	0.068	0.062
Weighted R (Rw^b)	0.066	0.071
Weighting function (w)	$1.9303/(\sigma^2\lvert F_o\rvert + 0.002\,651\lvert F_o\rvert^2)$	$2.5361/(\sigma^2\lvert F_o\rvert + 0.001\,739\lvert F_o\rvert^2)$
Residual electron density $\Delta\rho$/Å^{-3}	±0.28	±0.22

[a] $R = \Sigma(\lvert F_o\rvert - \lvert F_c\rvert)/\Sigma\lvert F_o\rvert$. [b] $Rw = \Sigma\{w^{\frac{1}{2}}(\lvert F_o\rvert - \lvert F_c\rvert)\}/\Sigma(w^{\frac{1}{2}}\lvert F_o\rvert)$

Table 2 Selected bond lengths

Atoms	Distance/Å	Atoms	Distance/Å
Compound **1**		Compound **2**	
O(1)–C(2)	1.309(10)	O(1)–C(2)	1.406(8)
O(1)–C(9)	1.423(8)	O(1)–C(9)	1.369(9)
O(2)–C(2)	1.285(8)	O(2)–C(2)	1.204(10)
C(2)–C(3)	1.469(12)	C(2)–C(3)	1.426(11)
C(3)–C(4)	1.324(10)	C(3)–C(4)	1.338(11)
C(4)–C(10)	1.465(11)	C(4)–C(10)	1.425(9)
C(5)–C(6)	1.425(11)	C(5)–C(6)	1.368(9)
C(5)–C(10)	1.368(7)	C(5)–C(10)	1.409(10)
C(6)–C(7)	1.314(12)	C(6)–C(7)	1.349(11)
C(6)–F(1)	1.291(8)	C(7)–C(8)	1.377(11)
C(7)–C(8)	1.394(9)	C(7)–F(1)	1.363(7)
C(8)–C(9)	1.340(11)	C(8)–C(9)	1.379(9)
C(9)–C(10)	1.394(11)	C(9)–C(10)	1.407(10)

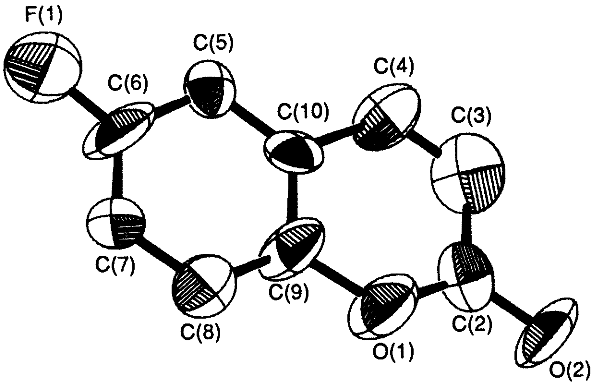


Fig. 1

specimen of **1** exhibits second harmonic generation (SHG) (Nd:YAG, λ = 1064 nm), it became clear that the space group of **1** could not be centric. Hence the refinement in a centric space group was given up in favour of refinement in the space group $P1$. However, it is to be noted that the deviation in the bond lengths of **1** from the accepted values must be due to a partial and disproportionate orientational disorder (F *versus* O) as observed in the crystal structure of, for example, 4-chlorobenzonitrile (Cl *versus* CN).[18] All other details such as the final R values, residual electron densities *etc.* are provided in Table 1. As the crystals were not of a very good quality, the number of reflections with $\lvert F_o\rvert \geqslant 3\sigma(F_o)$ was limited (Table 1) with the result that the accuracy in bond lengths, angles *etc.* is not high. Anisotropic thermal parameters of non-hydrogen atoms, atomic coordinates, and bond lengths and angles involving hydrogen atoms have been deposited at the Cambridge Crystallographic Data Centre (CCDC).*

Results and Discussion

The perspective views[19] with atomic numbering of the molecules **1** and **2** are shown in Figs. 1 and 2 respectively. The bond lengths of both structures are listed in Table 2 and bond angles in Table 3. The stereo packing arrangements[20] of molecules **1** and **2** are presented in Figs. 3 and 4 respectively.

It is clear from the packing diagrams of **1** and **2** (Figs. 3 and 4) that the translationally related partners in the crystal lattice produce the dimer with a mirror symmetry which confirms the conclusion drawn from the spectral data. For a [2 + 2] photodimerization reaction to occur in the solid state the overlap of π orbitals of the reactive partners should be favourable. The relevant geometrical parameters in this connection (see Fig. 5) are (i) θ_1, the rotation of one of the double bonds with respect to the other, (ii) θ_2, the angle of parallelogram formed by the atoms of the reactive double bonds, (iii) θ_3, the dihedral angle between the plane passing through the double bonds and that through one of the double bonds and the atoms connected to it, and (iv) d, the centre-to-centre distance of the double bonds. These parameters should ideally be 0, 90, 90° and *ca.* 4 Å respectively. Corresponding values of the above parameters obtained from the crystal

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* For details of the deposition scheme see 'Instructions for Authors', *J. Chem. Soc., Perkin Trans. 2*, 1993, issue 1.

Table 3 Selected bond angles

Atoms	Angle/°	Atoms	Angle/°
Compound **1**		Compound **2**	
C(2)–O(1)–C(9)	126.1(6)	C(2)–O(1)–C(9)	121.4(5)
O(1)–C(2)–O(2)	121.6(6)	O(1)–C(2)–O(2)	115.1(6)
O(2)–C(2)–C(3)	120.7(6)	O(2)–C(2)–C(3)	127.3(6)
O(1)–C(2)–C(3)	117.5(6)	O(1)–C(2)–C(3)	117.6(6)
C(2)–C(3)–C(4)	120.0(8)	C(2)–C(3)–C(4)	120.9(6)
C(3)–C(4)–C(10)	120.9(7)	C(3)–C(4)–C(10)	121.8(7)
C(6)–C(5)–C(10)	115.3(6)	C(6)–C(5)–C(10)	121.4(6)
C(5)–C(6)–F(1)	112.6(7)	C(5)–C(6)–C(7)	117.8(6)
C(5)–C(6)–C(7)	122.8(7)	C(6)–C(7)–F(1)	120.5(7)
C(7)–C(6)–F(1)	124.4(8)	C(6)–C(7)–C(8)	125.0(6)
C(6)–C(7)–C(8)	120.8(7)	C(8)–C(7)–F(1)	114.6(7)
C(7)–C(8)–C(9)	118.6(7)	C(7)–C(8)–C(9)	116.9(7)
O(1)–C(9)–C(8)	123.2(7)	O(1)–C(9)–C(8)	118.0(7)
C(8)–C(9)–C(10)	121.0(7)	C(8)–C(9)–C(10)	121.3(6)
O(1)–C(9)–C(10)	115.8(6)	O(1)–C(9)–C(10)	120.8(6)
C(5)–C(10)–C(9)	121.5(6)	C(5)–C(10)–C(9)	117.6(6)
C(4)–C(10)–C(9)	119.5(6)	C(4)–C(10)–C(9)	117.5(6)
C(4)–C(10)–C(5)	119.0(6)	C(4)–C(10)–C(5)	124.9(6)

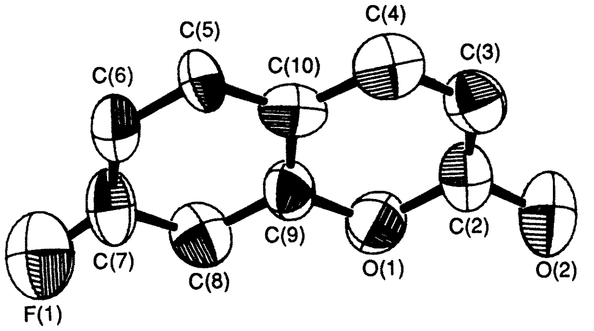

Fig. 2

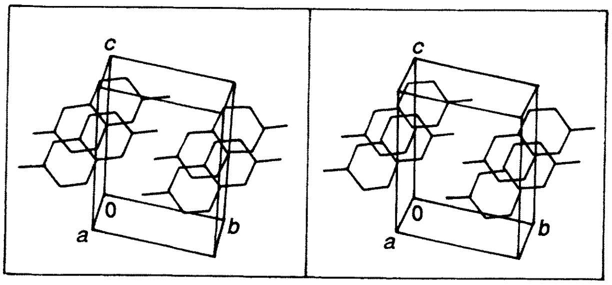

Fig. 3

structures are; 0, 88.6, 66.3° and 3.74 Å for **1** and 0, 122.3, 87.6° and 3.92 Å for **2**. Deviations from the ideal values of these parameters have also been observed in many other cases of topochemical dimerization reactions[5] showing that the dictum regarding the ideal overlap of π orbitals is no longer strictly operational. Although it is clear from the observations reported in this paper so far that fluorine substitution is what is responsible for the steering of molecules of coumarin to the β-packing mode, the nature of the intermolecular interaction that brings about the observed packing remains to be discovered. The fluorine atom is much smaller than any other halogen atom. Its van der Waals radius[21] (1.47 Å) is considerably smaller than that of Cl (1.75), Br (1.85), I (1.98 Å) and rather close to that of the hydrogen atom (1.2 Å). Thus, from the similarity of the atomic sizes of fluorine and hydrogen, one would not anticipate any radical difference in the packing of fluorocoumarin molecules from that of the unsubstituted coumarin molecules. But the fact that fluorine does steer the molecules of coumarin to the β-packing mode (as seen from the crystal structures of **1** and **2**) prompted us to undertake an analysis of the Cambridge Structural Database.[22]

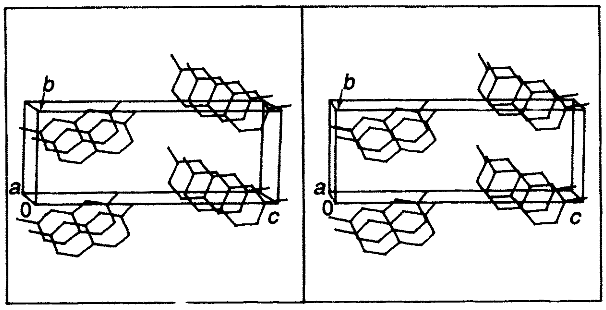

Fig. 4

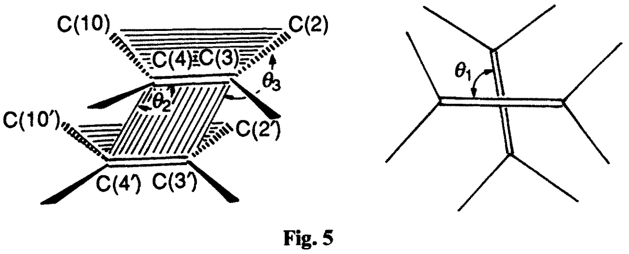

Fig. 5

The Data Base (1989, version 3.4, 71 630 entries) was used to retrieve the reference codes (REFCODES) of the crystal structures of fluoro-substituted organic compounds. Only diffractometer data-based structures were considered. Structures containing (*a*) disorder in the lattice, (*b*) halogen atoms other than fluorine, (*c*) metal atoms and (*d*) ions, were omitted from the list. This resulted in 397 entries. Intermolecular F ··· F contacts shorter than 2.94 Å were computed for all the structures in the above list using the program GSTAT89. In all, there were 154 short contacts (*i.e.* < 2.94 Å). It is noteworthy that distances as short as, for example, 2.62 and 2.68 Å were encountered in (1*S*,2*S*,α-*S*)-1-α-carboxyethyl-3,3-bis(trifluoromethyl)diaziridine and pentafluorobenzoic acid respectively. One of the very interesting and extremely relevant cases that was encountered in our analysis of the REFCODES is the following; 2-*H*, 2'-*H*-octafluorobiphenyl[23] adopts a *cis* conformation (instead of *trans* which one would normally expect, based on steric reasons), with the F(6) ··· F(6') interatomic distance being 2.81 Å, significantly shorter than twice the van der Waals radius of the fluorine atom.

In view of the above observations it was surprising to note that in the crystal structures of both **1** and **2** there are no intermolecular F ··· F contacts shorter than 2.94 Å between the translationally related molecules (*i.e.* the stacking pairs). The role of the fluoro group in inducing β-packing of the coumarin molecule is, however, beyond doubt and this prompted us to probe a little further. The analysis of the Database for cases of planar aromatic compounds revealed that whereas benzoic acid, benzonitrile, benzamide and 1,4-diphenylene molecules pack with their shortest axis longer than *ca.* 5 Å, the corresponding fluoro-substituted molecules, namely, *ortho*-, *meta*- and *para*-fluorobenzoic acid, *p*-fluorobenzonitrile, *p*-fluorobenzamide and perfluoro-1,4-diphenylene, in their respective crystal lattices are β-packed wth one of the crystallographic axes as short as *ca.* 4 Å. These observations are strongly indicative of the ability of fluorine to steer the planar aromatic molecules to the β-packing mode. It is significant to note that in the crystal structures of all the above mentioned β-packed fluoroaromatic molecules there are no short F ··· F contacts involving the translation related pairs. It may be mentioned at this stage that a similar Database analysis[7] revealed that in all of the chloroaromatic structures with β-packing packing mode (with no exception) there was not a

Table 4 Calculated lattice energies

Compound	van der Waals contribution/ kJ mol^{-1}	Coulombic contribution/ kJ mol^{-1}	Total
6-Fluorocoumarin	−64.06	−4.43	−68.49
7-Fluorocoumarin	−63.34	−4.27	−67.61
6-Flourocoumarin (F replaced by H)	−61.59	−2.84	−64.43
7-Fluorocoumarin (F replaced by H)	−60.67	−1.67	−62.34
Coumarin	−65.65	−3.22	−68.87
Coumarin (H-6 replaced by F)	−67.70	−3.05	−70.75
Coumarin (H-7 replaced by F)	−68.37	−2.22	−70.59

single short intermolecular Cl···Cl contact between the translation related molecules. In the light of this, the absence of short F···F contacts involving the translation related pairs in the crystal structures of **1** and **2** is not incomprehensible. The main reason for this appears to be that, in a planar molecular system like fluorocoumarin, a very high π–π repulsion would result if the translation-related molecules were to stack within a distance of 2.94 Å.

It was then considered worthwhile to carry out lattice energy calculations to assess the relative contributions of van der Waals and electrostatic energies. The program WMIN developed by Busing[24] was used to calculate lattice energy. The energy is calculated as a pairwise van der Waals attractive and repulsive potential as well as Coulombic term as in eqn. (1). The

$$E = -\sum_{i}^{\text{one cell}} \sum_{j\neq i}^{\text{all cells}} A_i A_j r_{ij}^{-6} + \sum_{i}^{\text{one cell}} \sum_{j\neq i}^{\text{all cells}} D_i D_j r_{ij}^{-12} + 1/k \sum_{i}^{\text{one cell}} \sum_{j\neq i}^{\text{all cells}} q_i q_j r_{ij}^{-1} \tag{1}$$

first and the second terms in the above equation represent the van der Waals attractive and repulsive contributions respectively; r_{ij} is the distance between the i^{th} and j^{th} atoms. The third term represents Coulombic interaction. The charge q on each of the atoms in the molecule is calculated using the program MNDO[25] and the constants used (A and D) are due to Mirsky.[26] A value of 3.0 D was chosen for k, the relative permittivity of the crystalline medium.

Lattice energy computed for different cases are listed in Table 4. The calculated lattice energies for the fluorocoumarins **1** and **2** are −68.5 and −67.6 kJ mol^{-1} respectively. It is interesting to observe that when F is replaced by H in the crystal lattice of **1** and **2** there is a small loss in the lattice stabilization energy. In another situation we find that the lattice energy of the unsubstituted coumarin is −68.9 kJ mol^{-1}. Since its crystal structure[27] is different from that of **1** or **2** no direct comparison can be made but the interesting point observed (see Table 4) is that when H(6) and H(7) of coumarin were separately replaced by F there was an increase, though small, in the lattice energy. These results are indicative of the extra stabilization, albeit small, provided by F in the crystal. Another fact emerging from Table 4 is that the lattice stabilization energy in all of the cases considered comes principally from the van der Waals interaction rather than from Coulombic interaction.

Although there is sufficient evidence in support of the fluoro group as a powerful steering group, the absence of any short F···F contacts in the crystals of **1** and **2** is noteworthy. On the other hand, short intermolecular F···H contacts were observed in both the structures; F(1)···H(3) = 2.45 Å, F(1)···C(3) = 3.46 Å, F(1)···H(3)–C(3) = 164.9° and F(1)···H(8) = 2.53 Å, F(1)···C(8) = 3.50 Å, F(1)···H(8)–C(8) = 154.3° in **1** and F(1)···H(6) = 2.54 Å, F(1)···C(6) = 3.49 Å and F(1)···H(6)–C(6) = 154.5° in **2**. These values indicate the presence of C–H···F hydrogen bonds in the crystals of **1** and **2**. It may be mentioned that, from Database analysis of fluorohydrocarbons Desiraju *et al.*[28] concluded that the strongly dipolar nature of F···H interactions results in a greater number of these interactions as compared to F···F interactions. Besides these, there are also C–H···O hydrogen bonds in the crystal structures of both **1** and **2** [**1**: C(4)···O(2) = 3.48, H(4)···O(2) = 2.44 Å, C(4)–H(4)···O(2) = 162.0°; C(5)···O(1) = 3.48, H(5)···O(1) = 2.47 Å, C(5)–H(5)···O(1) = 163.9°; C(7)···O(2) = 3.44, H(7)···O(2) = 2.47 Å, C(7)–H(7)···O(2) = 163.9°; **2**: C(3)···O(2) = 3.36, H(3)···O(2) = 2.31 Å, C(3)–H(3)···O(2) = 161.6°]. It is relevant to emphasize that the observed C–H···O interactions cannot be the sole factor responsible for the observed β-packing mode in **1** and **2** since such C–H···O interactions are present in the crystal structure of unsubstituted coumarin[27] (which is not β-packed) as well; [C(4)···O(2) = 3.50, H(4)···O(2) = 2.62 Å, C(4)–H(4)···O(2) = 155.9°; C(5)···O(2) = 3.48, H(5)–O(2) = 2.60 Å, C(5)–H(5)···O(2) = 147.5°]. It thus follows from all these observations that while fluorine is undoubtedly the cause for bringing the molecules closer together, the ultimate crystal structure that we observe is a symphony of various interactions such as F···F, F···H, π–π, C–H···O and C–H···F, all of which contribute to the final structure.

Conclusions

The results presented in this paper, albeit based on only two cases, demonstrate convincingly that the fluoro group, especially when substituted on planar aromatic molecules, could be useful as a β-packing promoter. The results derived from the Database analysis of planar fluoroaromatics lend support to the above conclusion.

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