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Crystal engineering *via* C—H···F and C—H···π interactions in two substituted indoles

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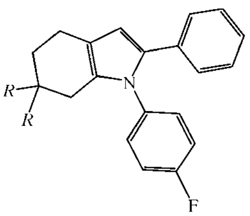
The crystal structures of 1-(4-fluorophenyl)-2-phenyl-4,5,6,7-tetrahydro-1*H*-indole, $C_{20}H_{18}FN$, and 1-(4-fluorophenyl)-6,6-dimethyl-2-phenyl-4,5,6,7-tetrahydro-1*H*-indole, $C_{22}H_{22}FN$, have been determined in order to study the role of 'organic fluorine' in crystal engineering. These molecules pack in the crystal structure *via* different types of molecular motifs utilizing weak C—H···F and C—H···π interactions.

Comment

Crystal engineering *via* manipulation of hydrogen bonding has attracted much interest recently (Aakeröy, 1997; Guru Row, 1999; Desiraju, 2000, 2002; Hunter *et al.*, 2001). Weak C—H···π (Nishio *et al.*, 1995; Umezawa *et al.*, 1999; Takahashi *et al.*, 2000), π-stacking (Hunter, 1993, 1994) and C—H···O (Desiraju & Steiner, 1999; Steiner, 2002) interactions have been found to generate different crystal-engineering motifs. Organohalogen compounds have also been found to generate motifs *via* C—H···*X*, *X*···*X* and C—*X*···π interactions (Thalladi *et al.*, 1998). It has been shown that fluorine does not readily accept hydrogen bonds and hence behaves differently from chlorine and bromine (Shimoni & Glusker, 1994; Howard *et al.*, 1996; Dunitz & Taylor, 1997; Desiraju & Parthasarathi, 1989). We have shown that a significant number of compounds pack *via* weak interactions involving organic fluorine only (Prasanna & Row, 2000*a*,*b*,*c*, 2001; Choudhury *et al.*, 2002; Choudhury & Guru Row, 2004) and generate different packing motifs *via* F···F, C—H···F and C—F···π interactions.



(I) *R*=H, (II) *R*=Me

A structural study of 1-(4-fluorophenyl)-2-phenyl-4,5,6,7-tetrahydro-1*H*-indole, (I), and 1-(4-fluorophenyl)-6,6-dimethyl-2-phenyl-4,5,6,7-tetrahydro-1*H*-indole, (II), was undertaken because, in these compounds, the interactions predominantly involve 'organic fluorine' and there are no other strong directional interactions involving H atoms.

A view of (I), with the atom-labeling scheme, is shown in Fig. 1. In the tetrahydroindole ring, atoms C5 and C6 deviate from the C4/C9/C8/C7 plane by 0.310 (2) and −0.456 (2) Å, respectively. The two phenyl rings (C10–C15 and C16–C21) subtend an angle of 126.41 (4)° between their planes. Selected torsion angles are given in Table 1. The molecules pack *via* a C—H···F interaction, along with three independent C—H···π interactions (Table 2). Two independent C—H···π interactions *via* atoms H11 and H15 form a chain of molecular dimers in the crystallographic *a* direction (Fig. 2; *Cg*1 and *Cg*2 are the centers of gravity of the N1/C2/C3/C9/C8 and C16–C21 rings, respectively). These dimers are connected to similar neighboring chains of molecular dimers *via* one C—H···F

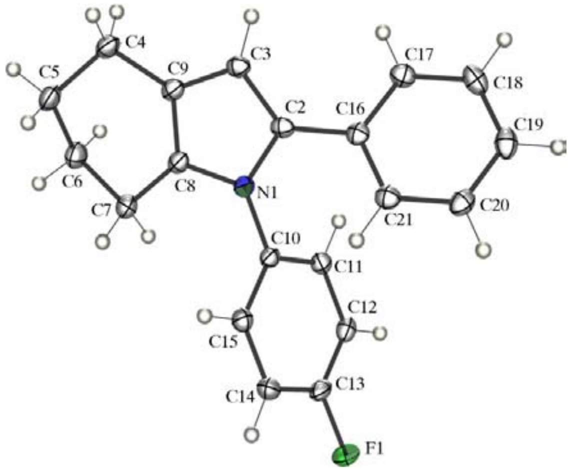


Figure 1
A view of (I), with displacement ellipsoids shown at the 50% probability level.

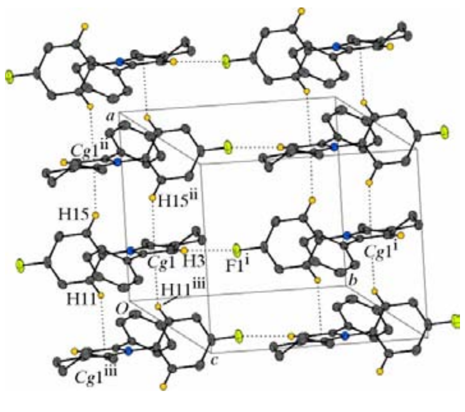


Figure 2
A packing diagram of (I), showing sheets of molecules in the *ab* plane linked *via* C—H···π and C—H···F interactions. [Symmetry codes: (i) *x*, 1 + *y*, *z*; (ii) 1 − *x*, −*y*, −*z*; (iii) −*x*, −*y*, −*z*.] Corresponding geometric details are given in Table 2.

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interaction through atom H3, generating a sheet of molecules, as shown in Fig. 2, by a combination of inversion and translation operations. A further C—H$\cdots\pi$ interaction generates a chain of molecules *via* a glide operation along the *c* axis (Fig. 3); this interaction links the sheets and gives rise to a three-dimensional network.

Fig. 4 depicts (II) with the atom-labeling scheme. In the tetrahydroindole ring, atoms C5 and C6 deviate from the C4/C9/C8/C7 plane by 0.340 (2) and −0.420 (2) Å, respectively. The two phenyl rings (C10–C15 and C16–C21) subtend an angle of 115.38 (4)° between their planes. Selected torsion angles are given in Table 3. The molecules pack *via* a C—H$\cdots$F interaction, along with two independent C—H$\cdots\pi$ interactions (Table 4). These C—H$\cdots\pi$ interactions *via* atoms H11 and H15 form a sheet motif in the *bc* plane, resulting in molecular dimers (Fig. 5; *Cg*3 and *Cg*4 are the centers of gravity of the N1/C2/C3/C9/C8 and C16–C21 rings, respectively). These dimers are linked *via* a unique C—H$\cdots$F interaction through methyl atom H22*A* (Fig. 5), generating a sheet structure; there are only van der Waals interactions between the sheets.

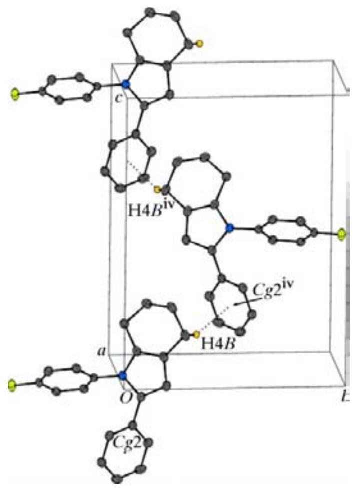

Figure 3
A molecular chain in (I), generated *via* C—H$\cdots\pi$ interactions along the *c* axis. [Symmetry code: (iv) $x, \frac{1}{2} - y, \frac{1}{2} + z$.]

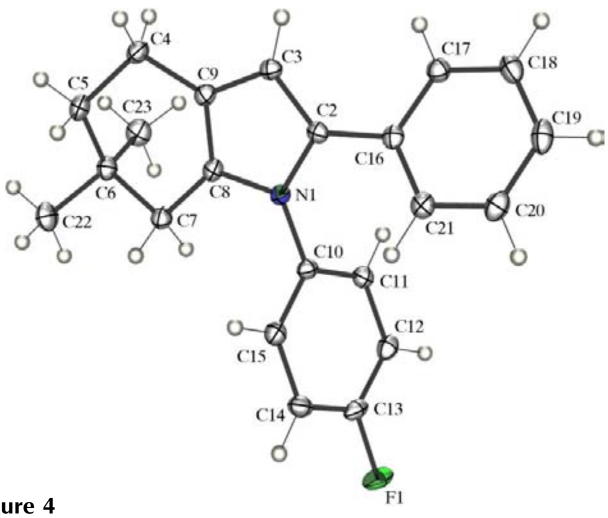

Figure 4
A view of (II), with displacement ellipsoids shown at the 50% probability level.

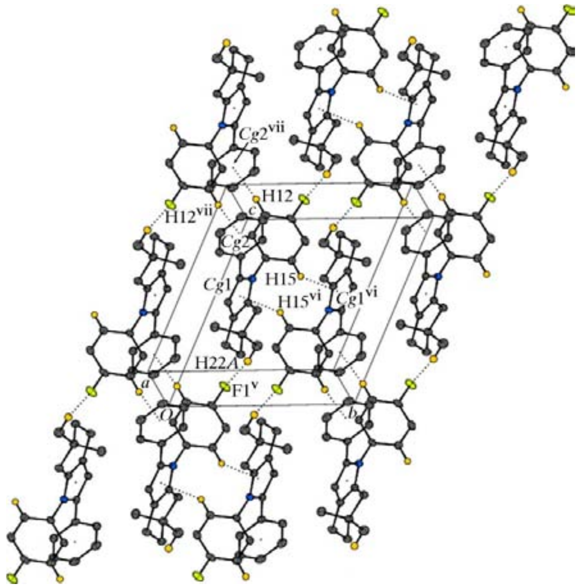

Figure 5
A packing diagram of (II), showing a molecular sheet in the *bc* plane, generated *via* C—H$\cdots\pi$ and C—H$\cdots$F interactions. [Symmetry codes: (v) $x, y, z - 1$; (vi) $1 - x, 1 - y, 1 - z$; (vii) $1 - x, -y, 2 - z$.] Corresponding geometric details are given in Table 4.

In a previous study (Choudhury *et al.*, 2004), we showed that, in the presence of a strong acceptor such as C=O, the C—H$\cdots$O interaction takes priority over C—H$\cdots$F and C—H$\cdots\pi$ interactions. Although C—H$\cdots$F interactions are weaker than C—H$\cdots$O interactions, these appear to play a significant role in the packing of molecules in the crystal structure because of a subtle change in the C—H$\cdots$F and C—H$\cdots\pi$ interactions in the two structures described here. Our current results suggest that, while interactions involving 'organic fluorine' have a significant influence in generating supramolecular assemblies in organic solids, the general use of these interactions for the *a priori* prediction of packing motifs is yet to be harnessed.

Experimental

Compounds (I) and (II) were synthesized according to the procedure reported by Nagarajan *et al.* (1985). The compounds were crystallized from solutions in dichloromethane and hexane (1:3) by slow evaporation at 263 K. Colorless crystals of (I) grew as long rods, whereas crystals of (II) grew as pale-yellow prisms.

Compound (I)

Crystal data

$C_{20}H_{18}FN$
$M_r = 291.35$
Monoclinic, $P2_1/c$
$a = 9.256$ (6) Å
$b = 10.939$ (7) Å
$c = 15.169$ (9) Å
$\beta = 97.75$ (1)°
$V = 1521.9$ (17) Å^3
$Z = 4$

$D_x = 1.272$ Mg m^{-3}
Mo $K\alpha$ radiation
Cell parameters from 758 reflections
$\theta = 2.3$–24.5°
$\mu = 0.08$ mm^{-1}
$T = 100.0$ (2) K
Rod, colorless
0.60 × 0.20 × 0.20 mm

Data collection

Bruker SMART CCD area-detector diffractometer
φ and ω scans
Absorption correction: multi-scan (*SADABS*; Sheldrick, 1996)
$T_{\min} = 0.912$, $T_{\max} = 0.984$
15 212 measured reflections
3073 independent reflections
2619 reflections with $I > 2\sigma(I)$
$R_{\text{int}} = 0.030$
$\theta_{\max} = 26.4°$
$h = -11 \rightarrow 11$
$k = -13 \rightarrow 13$
$l = -18 \rightarrow 18$

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2) = 0.038$
$wR(F^2) = 0.097$
$S = 1.03$
3073 reflections
271 parameters
All H-atom parameters refined
$w = 1/[\sigma^2(F_o^2) + (0.0457P)^2 + 0.5815P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{\max} < 0.001$
$\Delta\rho_{\max} = 0.29$ e Å^{-3}
$\Delta\rho_{\min} = -0.20$ e Å^{-3}

Table 1
Selected torsion angles (°) for (I).

C10—N1—C2—C16	−3.09 (18)	C6—C7—C8—C9	15.50 (18)
C6—C5—C4—C9	−42.60 (16)	C7—C8—C9—C4	3.6 (2)
C4—C5—C6—C7	64.40 (16)	C5—C4—C9—C8	9.98 (17)
C5—C6—C7—C8	−47.59 (16)	C8—N1—C10—C11	113.62 (13)
C10—N1—C8—C9	−175.33 (11)	N1—C2—C16—C17	138.10 (12)

Table 2
Hydrogen-bonding geometry (Å, °) for (I).

*Cg*1 and *Cg*2 are the centers of gravity of the N1/C2/C3/C9/C8 and C16–C21 rings, respectively.

D—H$\cdots A$	D—H	H$\cdots A$	$D\cdots A$	D—H$\cdots A$
C3—H3$\cdots$F1$^{\text{i}}$	0.98 (2)	2.56 (2)	3.292 (2)	131 (1)
C15—H15$\cdots$*Cg*1$^{\text{ii}}$	0.98 (2)	2.68 (2)	3.495 (3)	141 (1)
C11—H11$\cdots$*Cg*1$^{\text{iii}}$	0.97 (2)	2.82 (2)	3.646 (3)	144 (1)
C4—H4*B*$\cdots$*Cg*2$^{\text{iv}}$	1.00 (2)	2.82 (2)	3.708 (3)	149 (1)

Symmetry codes: (i) $x, 1 + y, z$; (ii) $1 - x, -y, -z$; (iii) $-x, -y, -z$; (iv) $x, \frac{1}{2} - y, \frac{1}{2} + z$.

Compound (II)

Crystal data

$C_{22}H_{22}FN$
$M_r = 319.41$
Triclinic, $P\overline{1}$
$a = 9.273$ (2) Å
$b = 10.786$ (2) Å
$c = 10.936$ (2) Å
$\alpha = 61.647$ (3)°
$\beta = 65.525$ (3)°
$\gamma = 69.210$ (3)°
$V = 858.9$ (3) Å^3
$Z = 2$
$D_x = 1.235$ Mg m^{-3}
Mo $K\alpha$ radiation
Cell parameters from 945 reflections
$\theta = 2.4$–24.4°
$\mu = 0.08$ mm^{-1}
$T = 100.0$ K
Prism, pale yellow
0.55 × 0.50 × 0.40 mm

Data collection

Bruker SMART CCD area-detector diffractometer
φ and ω scans
Absorption correction: multi-scan (*SADABS*; Sheldrick, 1996)
$T_{\min} = 0.938$, $T_{\max} = 0.969$
6945 measured reflections
3474 independent reflections
3193 reflections with $I > 2\sigma(I)$
$R_{\text{int}} = 0.011$
$\theta_{\max} = 26.4°$
$h = -11 \rightarrow 11$
$k = -13 \rightarrow 13$
$l = -13 \rightarrow 13$

Table 3
Selected torsion angles (°) for (II).

C10—N1—C2—C16	−7.05 (16)	C6—C7—C8—C9	14.42 (15)
C9—C4—C5—C6	−44.48 (13)	C7—C8—C9—C4	3.16 (17)
C4—C5—C6—C7	62.90 (12)	C8—N1—C10—C11	113.35 (12)
C5—C6—C7—C8	−44.57 (12)	N1—C2—C16—C17	150.29 (10)
C10—N1—C8—C9	−176.39 (9)		

Table 4
Hydrogen-bonding geometry (Å, °) for (II).

*Cg*3 and *Cg*4 are the centers of gravity of the N1/C2/C3/C9/C8 and C16–C21 rings, respectively.

D—H$\cdots A$	D—H	H$\cdots A$	$D\cdots A$	D—H$\cdots A$
C22—H22*A*$\cdots$F1$^{\text{v}}$	0.99 (2)	2.50 (2)	3.422 (2)	154 (1)
C15—H15$\cdots$*Cg*3$^{\text{vi}}$	0.98 (2)	2.73 (2)	3.549 (2)	141 (1)
C12—H12$\cdots$*Cg*4$^{\text{vii}}$	0.98 (2)	2.62 (2)	3.659 (2)	154 (1)

Symmetry codes: (v) $x, y, z - 1$; (vi) $1 - x, 1 - y, 1 - z$; (vii) $1 - x, -y, 2 - z$.

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.038$
$wR(F^2) = 0.097$
$S = 1.05$
3474 reflections
305 parameters
All H-atom parameters refined
$w = 1/[\sigma^2(F_o^2) + (0.0503P)^2 + 0.2958P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{\max} = 0.001$
$\Delta\rho_{\max} = 0.30$ e Å^{-3}
$\Delta\rho_{\min} = -0.26$ e Å^{-3}

All H atoms were located from difference Fourier maps and were refined isotropically [C—H = 0.960 (16)–1.031 (16) Å for (I) and 0.956 (14)–1.032 (12) Å for (II)].

For both compounds, data collection: *SMART* (Bruker, 2004); cell refinement: *SMART*; data reduction: *SAINT* (Bruker, 2004); program(s) used to solve structure: *SIR*92 (Altomare *et al.*, 1993); program(s) used to refine structure: *SHELXL*97 (Sheldrick, 1997); molecular graphics: *ORTEP*-3 *for Windows* (Farrugia, 1997), *POV-Ray* (The POV-Ray Team, 2004) and *CAMERON* (Watkin *et al.*, 1993); software used to prepare material for publication: *PLATON* (Spek, 2003).

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: FG1756). Services for accessing these data are described at the back of the journal.

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