

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

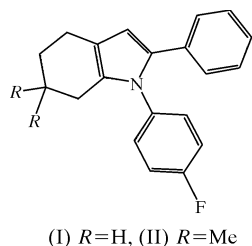
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The crystal structures of 1-(4-fluorophenyl)-2-phenyl-4,5,6,7-tetrahydro-1*H*-indole, C₂₀H₁₈FN, and 1-(4-fluorophenyl)-6,6-dimethyl-2-phenyl-4,5,6,7-tetrahydro-1*H*-indole, C₂₂H₂₂FN, have been determined in order to study the role of ‘organic fluorine’ 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.

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; Cg1 and Cg2 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

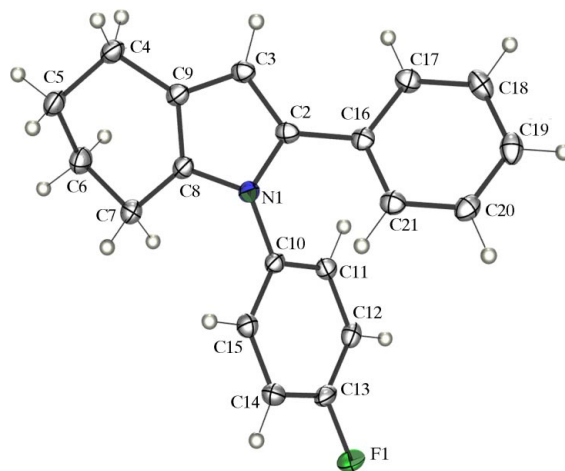


Figure 1
A view of (I), with displacement ellipsoids shown at the 50% probability level.

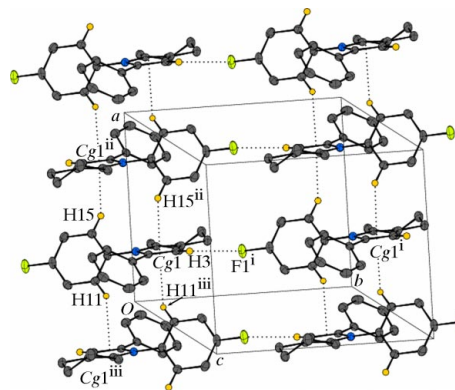


Figure 2
A packing diagram of (I), showing sheets of molecules in the *ab* plane linked *via* C—H··· π and C—H···F interactions. [Symmetry codes: (i) $x, 1 + y, z$; (ii) $1 - x, -y, -z$; (iii) $-x, -y, -z$.] Corresponding geometric details are given in Table 2.

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··· π 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···F interaction, along with two independent C—H··· π interactions (Table 4). These C—H··· π interactions *via* atoms H11 and H15 form a sheet motif in the *bc* plane, resulting in molecular dimers (Fig. 5; Cg3 and Cg4 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···F interaction through methyl atom H22A (Fig. 5), generating a

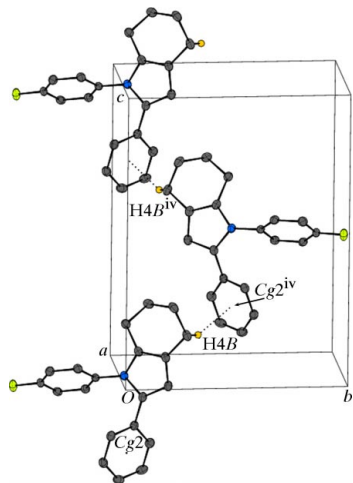


Figure 3
A molecular chain in (I), generated *via* C—H··· π interactions along the *c* axis. [Symmetry code: (iv) $x, \frac{1}{2} - y, \frac{1}{2} + z$.]

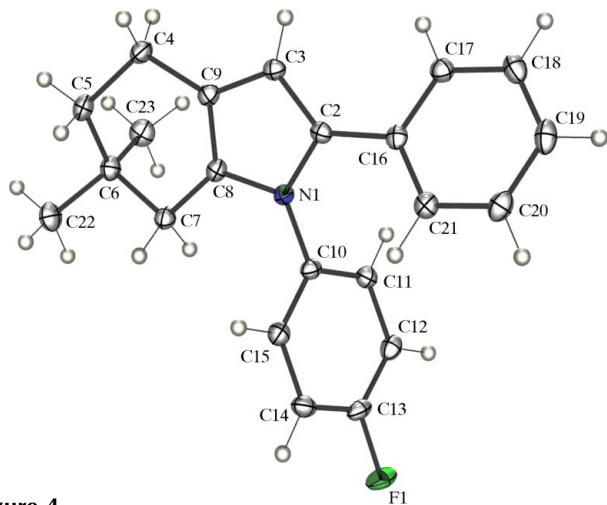


Figure 4
A view of (II), with displacement ellipsoids shown at the 50% probability level.

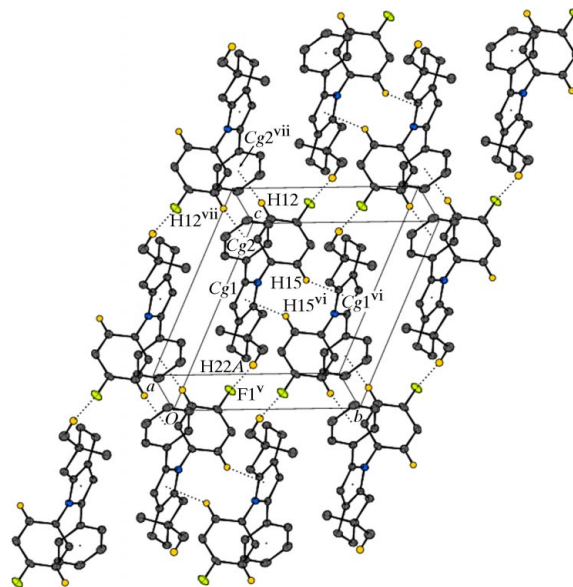


Figure 5
A packing diagram of (II), showing a molecular sheet in the *bc* plane, generated *via* C—H··· π and C—H···F interactions. [Symmetry codes: (v) $x, y, z - 1$; (vi) $1 - x, 1 - y, 1 - z$; (vii) $1 - x, -y, 2 - z$.] Corresponding geometric details are given in Table 4.

sheet structure; there are only van der Waals interactions between the sheets.

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···O interaction takes priority over C—H···F and C—H··· π interactions. Although C—H···F interactions are weaker than C—H···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···F and C—H··· π 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

C₂₀H₁₈FN
M_r = 291.35
 Monoclinic, *P*₂₁/*c*
a = 9.256 (6) Å
b = 10.939 (7) Å
c = 15.169 (9) Å
 β = 97.75 (1)°
V = 1521.9 (17) Å³
Z = 4

D_x = 1.272 Mg m⁻³
 Mo *K* α radiation
 Cell parameters from 758 reflections
 θ = 2.3–24.5°
 μ = 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

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 $P = (F_o^2 + 2F_c^2)/3$
 $(\Delta/\sigma)_{\max} < 0.001$
 $\Delta\rho_{\max} = 0.29 \text{ e } \text{\AA}^{-3}$
 $\Delta\rho_{\min} = -0.20 \text{ e } \text{\AA}^{-3}$

Table 1

Selected torsion angles ($^\circ$) 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 (\AA , $^\circ$) for (I).

Cg1 and Cg2 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 ⁱ	0.98 (2)	2.56 (2)	3.292 (2)	131 (1)
C15–H15 \cdots Cg1 ⁱⁱ	0.98 (2)	2.68 (2)	3.495 (3)	141 (1)
C11–H11 \cdots Cg1 ⁱⁱⁱ	0.97 (2)	2.82 (2)	3.646 (3)	144 (1)
C4–H4B \cdots Cg2 ^{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, $P\bar{1}$
 $a = 9.273$ (2) \AA
 $b = 10.786$ (2) \AA
 $c = 10.936$ (2) \AA
 $\alpha = 61.647$ (3) $^\circ$
 $\beta = 65.525$ (3) $^\circ$
 $\gamma = 69.210$ (3) $^\circ$
 $V = 858.9$ (3) \AA^3
 $Z = 2$
 $D_x = 1.235$ Mg m^{-3}

Mo $K\alpha$ radiation
Cell parameters from 945 reflections
 $\theta = 2.4\text{--}24.4^\circ$
 $\mu = 0.08 \text{ mm}^{-1}$
 $T = 100.0 \text{ K}$
Prism, pale yellow
 $0.55 \times 0.50 \times 0.40 \text{ mm}$

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

Table 3

Selected torsion angles ($^\circ$) 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 (\AA , $^\circ$) for (II).

Cg3 and Cg4 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–H22A \cdots F1 ^v	0.99 (2)	2.50 (2)	3.422 (2)	154 (1)
C15–H15 \cdots Cg3 ^{vi}	0.98 (2)	2.73 (2)	3.549 (2)	141 (1)
C12–H12 \cdots Cg4 ^{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 $P = (F_o^2 + 2F_c^2)/3$
 $(\Delta/\sigma)_{\max} = 0.001$
 $\Delta\rho_{\max} = 0.30 \text{ e } \text{\AA}^{-3}$
 $\Delta\rho_{\min} = -0.26 \text{ e } \text{\AA}^{-3}$

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

For both compounds, data collection: SMART (Bruker, 2004); cell refinement: SMART; data reduction: SAINT (Bruker, 2004); program(s) used to solve structure: SIR92 (Altomare *et al.*, 1993); program(s) used to refine structure: SHELXL97 (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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