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-1H-indole, $\text{C}_{20}\text{H}_{18}\text{FN}$, and 1-(4-fluorophenyl)-6,6-dimethyl-2-phenyl-4,5,6,7-tetrahydro-1H-indole, $\text{C}_{22}\text{H}_{22}\text{FN}$, 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, 2000a,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-1H-indole, (I), and 1-(4-fluorophenyl)-6,6-dimethyl-2-phenyl-4,5,6,7-tetrahydro-1H-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 $-0.456 (2) \AA$, 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 interaction.

![Figure 1](image1.png)

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

![Figure 2](image2.png)

**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 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)**

<table>
<thead>
<tr>
<th>Crystal data</th>
</tr>
</thead>
<tbody>
<tr>
<td>C20H18FN</td>
</tr>
<tr>
<td>Mr = 291.35</td>
</tr>
<tr>
<td>Monoclinic, P21/c</td>
</tr>
<tr>
<td>a = 9.256 (6) Å</td>
</tr>
<tr>
<td>b = 10.939 (7) Å</td>
</tr>
<tr>
<td>c = 15.169 (9) Å</td>
</tr>
<tr>
<td>β = 97.75 (1)°</td>
</tr>
<tr>
<td>V = 1521.9 (17) Å³</td>
</tr>
<tr>
<td>Z = 4</td>
</tr>
<tr>
<td>Dc = 1.272 Mg m⁻³</td>
</tr>
<tr>
<td>Mo Kα radiation</td>
</tr>
<tr>
<td>Cell parameters from 758 reflections</td>
</tr>
<tr>
<td>θ = 23.245°</td>
</tr>
<tr>
<td>μ = 0.088 mm⁻¹</td>
</tr>
<tr>
<td>T = 100.0 (2) K</td>
</tr>
</tbody>
</table>

Rod, colorless

0.60 x 0.20 x 0.20 mm
Data collection

Bruker SMART CCD area-detector
diffractometer

$\varphi$ and $\omega$ scans

Absorption correction: multi-scan
(SADABS; Sheldrick, 1996)

$T_{max} = 0.912, T_{min} = 0.984$

15212 measured reflections

3073 independent reflections

Refinement

Refinement on $F^2$

$R(F^2) = 0.038$

$wR(F^2) = 0.097$

$S = 1.03$

3073 reflections

271 parameters

All H-atom parameters reefined

Table 1

Selected torsion angles (°) for (I).

| C10–N1–C2–C16 | −3.09 (18) |
| C6–C5–C4–C9 | −42.60 (16) |
| C4–C5–C6–C7 | 64.40 (16) |
| C5–C6–C7–C8 | −47.59 (16) |
| C10–N1–C8–C9 | −175.33 (11) |

Symmetry codes: (i) $x, y, z$; (ii) $1 - x, 1 - y, 1 - z$; (iii) $1 - x, -y, -z$; (iv) $x, -\frac{3}{2}, -y, \frac{1}{2}$.

Table 2

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

| Cg1 and Cg2 are the centers of gravity of the N1/C2/C3/C9/C8 and C16–C21 rings, respectively. |

<table>
<thead>
<tr>
<th>$D - H \cdots A$</th>
<th>$D - H$</th>
<th>$H \cdots A$</th>
<th>$D \cdots A$</th>
<th>$D - H \cdots A$</th>
</tr>
</thead>
<tbody>
<tr>
<td>C3–H3—F1'i</td>
<td>2.56 (2)</td>
<td>3.292 (2)</td>
<td>131 (1)</td>
<td></td>
</tr>
<tr>
<td>C15–H15–Cg1ii</td>
<td>2.68 (2)</td>
<td>3.495 (3)</td>
<td>141 (1)</td>
<td></td>
</tr>
<tr>
<td>C11–H11–Cg1ii</td>
<td>2.82 (2)</td>
<td>3.646 (3)</td>
<td>144 (1)</td>
<td></td>
</tr>
<tr>
<td>C4–H4B–Cg2iii</td>
<td>2.82 (2)</td>
<td>3.708 (3)</td>
<td>149 (1)</td>
<td></td>
</tr>
</tbody>
</table>

Symmetry codes: (i) $x, 1 + y, z$; (ii) $1 - x, -y, -z$; (iii) $-x, -y, -z$; (iv) $x, -\frac{1}{2}, -y, \frac{3}{2} + z$.

Table 3

Selected torsion angles (°) for (II).

| C10–N1–C2–C16 | −7.05 (16) |
| C9–C4–C5–C6 | −44.48 (13) |
| C4–C5–C6–C7 | 62.90 (12) |
| C5–C6–C7–C8 | −44.57 (12) |
| C10–N1–C8–C9 | −176.39 (9) |

Table 4

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

Cg3 and Cg4 are the centers of gravity of the N1/C2/C3/C9/C8 and C16–C21 rings, respectively.

<table>
<thead>
<tr>
<th>$D - H \cdots A$</th>
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<th>$H \cdots A$</th>
<th>$D \cdots A$</th>
<th>$D - H \cdots A$</th>
</tr>
</thead>
<tbody>
<tr>
<td>C22–H22A—F1v</td>
<td>0.99 (2)</td>
<td>2.50 (2)</td>
<td>3.422 (2)</td>
<td>154 (1)</td>
</tr>
<tr>
<td>C15–H15–Cg3iv</td>
<td>0.98 (2)</td>
<td>2.73 (2)</td>
<td>3.549 (2)</td>
<td>141 (1)</td>
</tr>
<tr>
<td>C12–H12–Cg4iv</td>
<td>0.98 (2)</td>
<td>2.62 (2)</td>
<td>3.659 (2)</td>
<td>154 (1)</td>
</tr>
</tbody>
</table>

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

Compound (II)

Crystal data

$C_{24}H_{32}F_N$

$M_r = 319.41$

Triclinic, $P\overline{1}$

$\alpha = 9.273 (2)$ Å

$\beta = 10.786 (2)$ Å

$\gamma = 10.936 (2)$ Å

$\alpha = 61.647 (3)^\circ$

$\beta = 65.525 (3)^\circ$

$\gamma = 69.210 (3)^\circ$

$V = 858.9 (3)$ Å$^3$

$Z = 2$

$D_1 = 1.235$ Mg m$^-3$

Data collection

Bruker SMART CCD area-detector
diffractometer

$\varphi$ and $\omega$ scans

Absorption correction: multi-scan
(SADABS; Sheldrick, 1996)

$T_{max} = 0.938, T_{min} = 0.969$

6945 measured reflections

3474 independent reflections

References


