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Fully and partially fluorinated flavone derivatives

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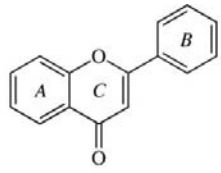
In the crystal structures of the fully and partially fluorinated flavone derivatives 5,6,7,8-tetrafluoro-2-(2,3,4,5,6-pentafluorophenyl)-4*H*-1-benzopyran-4-one, $C_{15}HF_9O_2$, (I), and 5,6,7,8-tetrafluoro-2-phenyl-4*H*-1-benzopyran-4-one, $C_{15}H_6F_4O_2$, (II), the pentafluorophenyl group and the pyranone moiety in (I) are twisted due to repulsion of the F substituents, and a $CO(\delta^-)\cdots\pi(\delta^+)$ intermolecular interaction is observed between the carbonyl O atom and the pentafluorophenyl group. In (II), on the other hand, the phenyl group and the pyranone moiety are almost coplanar, and arene–perfluoroarene interactions are observed in the head-to-tail intermolecular columnar stacking between the phenyl group and the tetrafluorophenylene moiety.

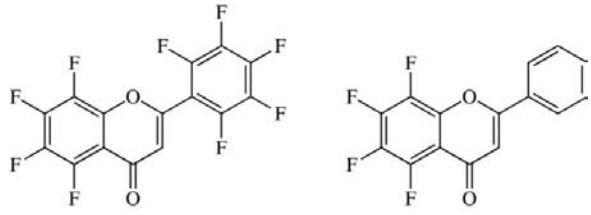
Comment

Flavone derivatives are one of the very important yellow pigments in natural plants. In particular, related compounds with the flavone framework have been widely investigated as unique biologically active reagents (Havsteen, 1983; Das & Rosazza, 2006). More than 100 flavone derivatives and nine naphthoflavone derivatives were found in a search of the Cambridge Structural Database (CSD, Version 5.30 of November 2008; Allen, 2002) and the crystal structure of flavone was determined by Waller *et al.* (2003). However, only two kinds of fluorinated flavone derivatives have been reported to date, namely 3-[1-(2,2-dimethylhydrazinylidene)-ethyl]-6,7-difluoro-2-phenyl-4*H*-1-benzopyran-4-one (Vales *et al.*, 2001) and 3-(4-fluorophenyl)-1*H*-naphtho[2,1-*b*]pyran-1-one (Neuman *et al.*, 1989). We report here the first perfluorinated derivatives of the flavone framework, synthesized in order to understand the influence of fluorination effects on molecular structure and crystal packing, *viz.* 5,6,7,8-tetrafluoro-2-(2,3,4,5,6-pentafluorophenyl)-4*H*-1-benzopyran-4-one, (I), and 5,6,7,8-tetrafluoro-2-phenyl-4*H*-1-benzopyran-4-one, (II).

Fully fluorinated aromatic compounds show an interaction with anionic species (Quiñonero *et al.*, 2002) and/or aromatic hydrocarbons (Patrick & Prosser, 1960; Williams, 1993; Hori *et al.*, 2009), based on reversal of the charge orientation of the quadrupole moments compared with aromatic compounds. Accordingly, compounds (I), (II) and the nonfluorinated flavone (Waller *et al.*, 2003) show completely different arrangements in these molecular packings. For example, three kinds of electrostatic interactions, *viz.* dipole–π, arene–perfluoroarene and π–π interactions, are predominantly observed in (I), (II) and flavone, respectively.



Flavone



The molecular structures of (I) and (II) are shown in Fig. 1. The structure of (II) exhibits full-molecule disorder, with site-occupancy ratios of 0.938 (2) and 0.062 (2), respectively, for components *A* and *B*; only the major component, *A*, is shown here. In Fig. 2, the relationship between the disordered

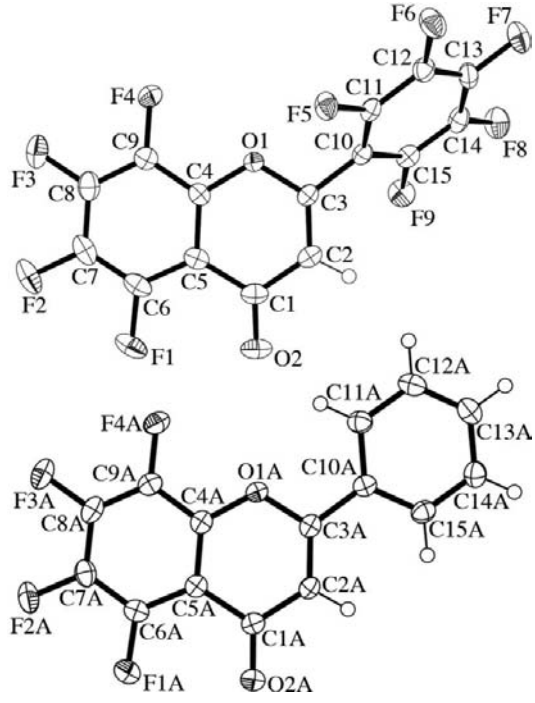


Figure 1
The molecular structure of (I) (top) and that of component *A* of (II) (bottom), both at 100 K, showing the atom-labelling schemes. Displacement ellipsoids are drawn at the 50% probability level and H atoms are shown as small spheres of arbitrary radii.

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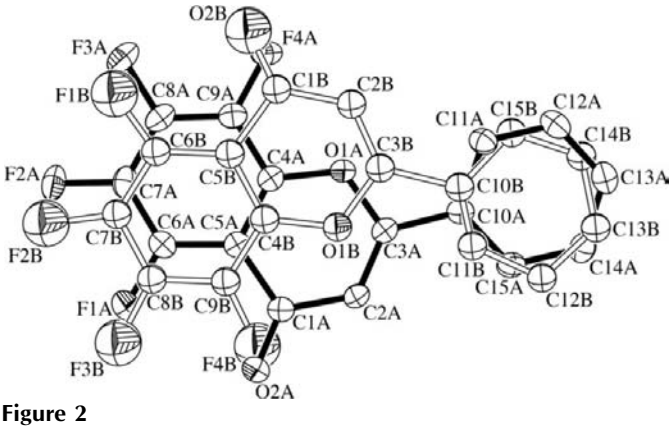

Figure 2
The major *A* (solid lines) and minor *B* (open lines) components of (II); the occupancy of component *B* is 6.2 (2)%. Displacement ellipsoids are drawn at the 50% probability level.

components *A* and *B* is shown. The minor *B* component is related to the major *A* component by an approximate twofold rotation about the molecular length. This sort of disorder is often found in planar molecules with weak intermolecular contacts (Ferguson *et al.*, 1999). Hereinafter, we only discuss the major component, *i.e. A*. The hydrogen-bond geometries of (I) and component *A* of (II) are summarized in Tables 1 and 2, respectively. Selected bond lengths and angles for (I), component *A* of (II) and flavone (two crystallographically independent molecules, denoted flavone-1 and flavone-2) are given in Table 3.

In the molecular structure of (I), the benzopyranone ring system (rings *A* and *C*) is planar and the r.m.s. deviation of atoms C1–C9/O1 is 0.018 Å. The pentafluorophenyl group and the pyranone moiety are highly twisted with respect to each other and the dihedral angle between the planes of the two rings defined by atoms C10–C15 (ring *B*) and C1–C3/O1/C4/C5 (ring *C*) is 52.78 (4)° (Fig. 1). On the other hand, in component *A* of (II), the phenyl group and the pyranone moiety are almost coplanar and the dihedral angle between the planes of the two rings defined by rings *B* and *C* is 7.88 (8)°, the benzopyranone ring system also being planar (the r.m.s. deviation of the ten atoms is 0.015 Å). The difference in twist angles can be explained by the steric repulsion introduced by the F-substituent at atom C15 in (I). The carbonyl double bonds in (I) and component *A* of (II) are slightly but significantly more localized than those in nonfluorinated flavone (Table 3). The C1—C5—C6 angles in the fluorinated compounds, *viz.* (I) and component *A* of (II), are larger than those of nonfluorinated flavone. This is considered to be due to basic steric effects and electrostatic repulsion between atoms O2 and F1. Due to the influence of the F-substitution at F1, the C2—C1—C5 and C3—O1—C4 angles of the two fluorinated compounds are smaller than those of the nonfluorinated flavone (Table 3). The r.m.s. deviations of the structural overlay (Macrae *et al.*, 2006) of the 12 atoms in the benzopyranone ring system (C1–C10/O1/O2) in (I), (II) and flavone are small, *e.g.* 0.04 Å between (I) and flavone-1 and (I) and flavone-2, and 0.03 Å between (II) and flavone-1, (II) and flavone-2, and (I) and (II).

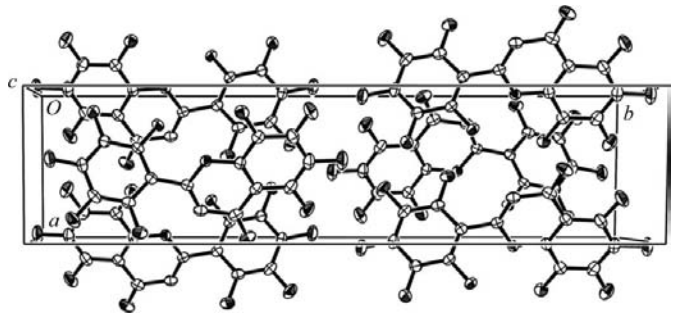

Figure 3
A view of part of the crystal structure of (I), viewed approximately along the *c* axis.

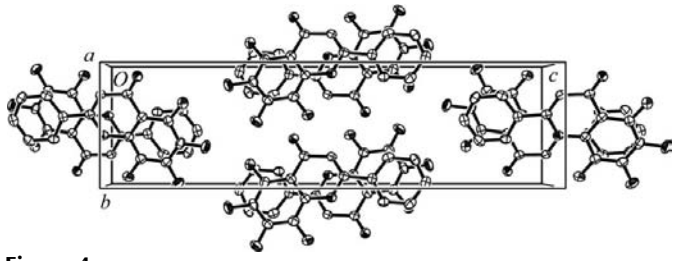

Figure 4
A view of part of the crystal structure of (II), viewed approximately along the *a* axis, showing the intermolecular columnar stacking through arene–perfluoroarene interactions.

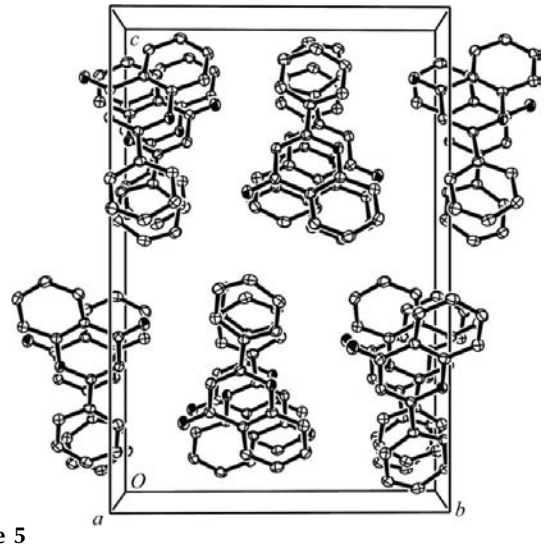

Figure 5
A view of part of the crystal structure of flavone, viewed approximately along the *a* axis, showing the head-to-head stacking through the phenyl groups (Waller *et al.*, 2003).

The crystal packings of (I), (II) and flavone are quite different, as shown in Figs. 3, 4 and 5, respectively. In the crystal structure of (I), no remarkable intermolecular π–π stacking is observed for either the pentafluorophenyl group or the pyranone moiety, while the π planes of the pentafluorophenyl (*B*) and tetrafluorobenzopyranone (*A* and *C*) rings are arranged in an antiparallel manner. Carbonyl atom O2 at (x, y, z) interacts closely with a pentafluorophenyl group at ($x + \frac{1}{2}$, $-y + \frac{1}{2}$, $z - \frac{1}{2}$) and, *vice versa*, the pentafluorophenyl group at (x, y, z) interacts with carbonyl atom O2^{iii} [symmetry code:

(iii) $x-\frac{1}{2}, -y+\frac{1}{2}, z+\frac{1}{2}$]; the O2$\cdots$*CgB*^{iv} distance [symmetry code: (iv) $x+\frac{1}{2}, -y+\frac{1}{2}, z-\frac{1}{2}$] is 2.9228 (15) Å, where *CgB* is the centroid of pentafluorophenyl ring *B*. Thus, the negative charge orientation of the O atom and the positive charge of the centroid of the fluorinated ring interact, which can be classified as a dipole–π interaction. Accordingly, the molecules are in a head-to-tail arrangement diagonally in the *ac* plane. Intermolecular C—F$\cdots\pi$ interactions are also observed, with distances F4$\cdots$*CgB*^{iii}, F6$\cdots$*CgA*^{v} and F9$\cdots$*CgC*^{vi} [symmetry codes: (v) $x-\frac{1}{2}, -y+\frac{1}{2}, z-\frac{1}{2}$; (vi) $x+\frac{1}{2}, -y+\frac{1}{2}, z+\frac{1}{2}$] between the F atoms and the ring centroids of 3.0765 (13), 3.1580 (13), and 3.1332 (13) Å, respectively. Intermolecular interactions induced by fluorination are also observed, which are the weak C2—H2$\cdots$F5^{i} hydrogen bond (Desiraju, 1996; Thalladi *et al.*, 1998) [symmetry code: (i) $x+1, y, z$; Table 1] and the dipole–dipole interaction between C1═O2 and C9^{i}—F4^{i} [the C1$\cdots$F4^{i} and O2$\cdots$C9^{i} short intermolecular distances are 2.973 (2) and 2.916 (2) Å, respectively].

Intermolecular π–π interactions are clearly observed in the crystal structures of (II) and flavone, which are highly planar molecules. Both structures show remarkable π–π stacking to give columns of molecules (Figs. 4 and 5). Within the columns, the carbonyl C═O groups are arranged in an interdigitating manner by dipole–dipole repulsion in both structures. However, the structures of (II) and flavone are clearly different in the relative orientation of neighboring molecules within the columns. In (II), phenyl group *B* and tetrafluorophenylene moiety *A* interact closely by head-to-tail arrangement of the molecules, clearly showing an arene–perfluoroarene interaction; the intermolecular distances between the two centroids of the rings, *CgC*$\cdots$*CgC*^{vii} [symmetry code: (vii) $-x+2, -y+1, -z+2$] and *CgA*$\cdots$*CgB*^{viii} [symmetry code: (viii) $-x+1, -y+1, -z+2$], are 3.5015 (11) and 3.5371 (12) Å, respectively. The perpendicular distances from the ring centroids to the adjacent planes are 3.3605 (6) and 3.4481 (6) Å, respectively. In contrast, in the flavone structure, the phenyl groups are overlapped by a head-to-head arrangement of the flavone molecules (Waller *et al.*, 2003), showing π–π stacking; the intermolecular distances *CgC*$\cdots$*CgC*^{ix} [symmetry code: (ix) $x+\frac{1}{2}, -y+\frac{3}{2}, -z+1$] and *CgB*$\cdots$*CgB*^{ix} are 3.7904 (15) and 3.8128 (15) Å, respectively; the perpendicular distances from the ring centroids to the adjacent planes are 3.4176 (7) and 3.4707 (7) Å, respectively. Thus, the phenyl group preferentially interacts with the tetrafluorophenylene moiety through an arene–perfluoroarene interaction, as opposed to interacting with another phenyl group through a π–π interaction. In addition, the weak intermolecular C12*A*—H12*A*$\cdots$F2*A*^{ii} hydrogen bond [symmetry code: (ii) $x-\frac{1}{2}, -y+\frac{3}{2}, z-\frac{1}{2}$] is observed in (II), as shown in Table 2. Intermolecular C—F$\cdots\pi$ interactions are also observed in (II), *viz.* C6*A*—F1*A*$\cdots$*CgB*^{vii}, with F1*A*$\cdots$*CgB*^{vii} = 3.3769 (16) Å and C6*A*—F1*A*$\cdots$*CgB*^{vii} = 86.32 (9)°.

Experimental

The two title fluorinated flavone derivatives were obtained from the elimination process of the corresponding dibenzoylmethanide derivatives. Crystals of (I) and (II) were obtained in poor yield from the synthetic processes involving bis(pentafluorobenzoyl)methane and benzoyl(pentafluorobenzoyl)methane, respectively (Uhlemann *et al.*, 1972; Hori *et al.*, 2009). The compounds were crystallized by slow evaporation from an MeOH solution to give crystals suitable for X-ray crystallography.

Compound (I)

Crystal data

$C_{15}HF_9O_2$
M_r = 384.16
Monoclinic, $P2_1/n$
a = 6.2221 (7) Å
b = 25.234 (3) Å
c = 8.4624 (9) Å
β = 95.355 (1)°
V = 1322.8 (2) Å^3
Z = 4
Mo $K\alpha$ radiation
μ = 0.21 mm^{-1}
T = 100 K
0.30 × 0.20 × 0.06 mm

Data collection

Bruker APEXII CCD area-detector diffractometer
Absorption correction: empirical (using intensity measurements) (*SADABS*; Sheldrick, 1996)
T_{min} = 0.939, T_{max} = 0.987
14615 measured reflections
2998 independent reflections
2433 reflections with $I > 2\sigma(I)$
R_{int} = 0.026

Refinement

$R[F^2 > 2\sigma(F^2)]$ = 0.035
$wR(F^2)$ = 0.094
S = 1.05
2998 reflections
235 parameters
H-atom parameters constrained
$\Delta\rho_{max}$ = 0.31 e Å^{-3}
$\Delta\rho_{min}$ = −0.20 e Å^{-3}

Compound (II)

Crystal data

$C_{15}H_6F_4O_2$
M_r = 294.20
Monoclinic, $P2_1/n$
a = 7.5400 (11) Å
b = 6.4742 (10) Å
c = 23.920 (4) Å
β = 94.635 (2)°
V = 1163.9 (3) Å^3
Z = 4
Mo $K\alpha$ radiation
μ = 0.15 mm^{-1}
T = 100 K
0.30 × 0.20 × 0.10 mm

Data collection

Bruker APEXII CCD area-detector diffractometer
Absorption correction: empirical (using intensity measurements) (*SADABS*; Sheldrick, 1996)
T_{min} = 0.955, T_{max} = 0.985
6192 measured reflections
2654 independent reflections
1979 reflections with $I > 2\sigma(I)$
R_{int} = 0.021

Refinement

$R[F^2 > 2\sigma(F^2)]$ = 0.040
$wR(F^2)$ = 0.094
S = 1.03
2654 reflections
238 parameters
57 restraints
H-atom parameters constrained
$\Delta\rho_{max}$ = 0.25 e Å^{-3}
$\Delta\rho_{min}$ = −0.16 e Å^{-3}

For the disordered structure of (II), after refinement of the major component with unit occupancy, it was noted in a difference map in the molecular plane that there were a large number of small maxima in the 0.2–0.7 e Å^{-3} range, which could be seen to be a minor component of (II) related to the major component by an approximate twofold rotation about the molecular length. The various minor peaks were labelled *B* atoms in exact correspondance with the major

Table 1
Hydrogen-bond geometry (Å, °) for (I).

D—H···A	D—H	H···A	D···A	D—H···A
C2—H2···F5^{i}	0.95	2.42	3.3126 (19)	157

Symmetry code: (i) $x+1, y, z$.

Table 2
Hydrogen-bond geometry (Å, °) for (II).

D—H···A	D—H	H···A	D···A	D—H···A
C12A—H12A···F2A^{ii}	0.95	2.48	3.198 (2)	132

Symmetry code: (ii) $x-\frac{1}{2}, -y+\frac{3}{2}, z-\frac{1}{2}$.

Table 3
Selected bond distances (Å) and angles (°) for (I), component A of (II), and flavone.

	(I)	Component A of (II)	Flavone-1†	Flavone-2†
C1—O2	1.220 (2)	1.224 (2)	1.235 (2)	1.232 (2)
C1—C2	1.452 (2)	1.445 (2)	1.445 (2)	1.448 (2)
C2—C3	1.339 (2)	1.342 (2)	1.353 (2)	1.354 (2)
C5—C1	1.478 (2)	1.478 (2)	1.476 (2)	1.475 (2)
C1—C5—C6	124.03 (15)	124.13 (16)	122.29 (16)	121.82 (16)
C2—C1—C5	113.86 (14)	114.13 (16)	114.69 (15)	114.18 (15)
C3—O1—C4	118.08 (12)	119.06 (13)	119.26 (13)	119.10 (13)

† Two crystallographically independent molecules, denoted flavone-1 and flavone-2, are observed at 150 K (Waller *et al.*, 2003).

A component. Refinement then continued with the major and minor occupancies refined as linked free variables, with similarity restraints (SAME command in *SHELXL97*; Sheldrick, 2008) employed to force the geometry of the minor component to conform with that of the major component. Atoms of the minor *B* component were refined isotropically, with one global U_{iso} value for the ring atoms and another U_{iso} value for the exocyclic atoms. In both (I) and (II), all H atoms were placed in geometrically idealized positions and refined as riding, with aromatic C—H = 0.95 Å and with $U_{iso}(H) = 1.2U_{eq}(C)$.

For both compounds, data collection: *APEX2* (Bruker, 2006); cell refinement: *SAINT* (Bruker, 2006); data reduction: *SAINT*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 2008); program(s) used to refine structure: *SHELXL97* (Sheldrick, 2008); molecular graphics: *SHELXTL* (Sheldrick, 2008); software used to prepare material for publication: *SHELXTL*.

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: FG3163). Services for accessing these data are described at the back of the journal.

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