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2,4-Difluorobenzaldehyde benzoylhydrazone and 2,4-dichlorobenzaldehyde benzoylhydrazone are isostructural at 120 K with Z' = 2: complex sheets built from N—H···O, C—H···O and C—H···π(arene) hydrogen bonds

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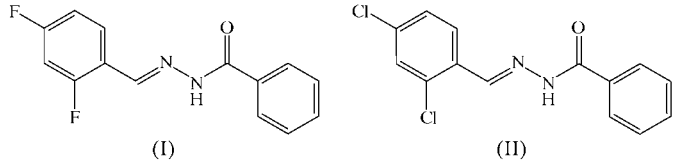
At 120 K, 2,4-difluorobenzaldehyde benzoylhydrazone, $C_{14}H_{10}F_2N_2O$, (I), and 2,4-dichlorobenzaldehyde benzoylhydrazone, $C_{14}H_{10}Cl_2N_2O$, (II), are isomorphous and isostructural in $P2_1/n$ with Z' = 2. In each structure, eight independent hydrogen bonds, *viz*. two of N—H···O type, five of C—H···O type and one of C—H···π(arene) type, link the molecules into complex sheets, within which two independent one-dimensional substructures can be identified.

Comment

As part of our continuing studies of the supermolecular structures of imines and hydrazones, we now report the structures of the title compounds, (I) and (II) (Figs. 1 and 2, respectively). The title compounds were initially prepared as part of a programme to test and compare the bactericidal activities of aroyl and pyridinoyl benzenecarbaldehyde hydrazones, ArCH═NNHCOPh and ArCH═NNHCO-C_5H_5N. The pyridinoyl compounds possessed such activities, but the benzoyl derivatives were found not to be active. While the influence of the pyridine N atom is clear, structural differences may also be of importance.

Compounds (I) and (II) both crystallize with Z' = 2 in space group $P2_1/n$. The unit-cell dimensions and atomic coordinates indicate that the two compounds are isomorphous and isostructural. The structure of compound (II) has been reported very recently using diffraction data collected at 294 (2) K (Jing *et al.*, 2005), and it is clear that no phase change occurs between 294 and 120 K. Although the N—H···O and C—H···O hydrogen bonds were identified in the structure of (II), a description of the supramolecular structure was not given.



In each compound, the molecules deviate only slightly from being fully planar, as shown by the values of the five torsion angles defining the conformation of each independent molecule (Table 1). In compound (I), none of these torsion angles deviates from 180° by more than 10° and the deviations indicate clearly that the two molecules selected to form the asymmetric unit of (I) are, in fact, approximately enantiomorphous. A careful search for possible additional crystallographic symmetry, however, revealed none. The precision of the structure determination for compound (II) is rather less good than that for compound (I), but the same conclusions apply. The bond lengths and angles present no unexpected values.

In each of (I) and (II), the molecules are linked into complex sheets by a total of eight independent hydrogen bonds (Tables 2 and 3), and the formation of the sheet is readily analysed in terms of two independent one-dimensional substructures. We discuss in detail here only the supramolecular structure of compound (I). Within the selected asymmetric unit (Fig. 1), the two molecules are linked by three hydrogen bonds, all utilizing atom O47 as the acceptor, and with atoms C17, N21 and C26 as the donors. In an entirely

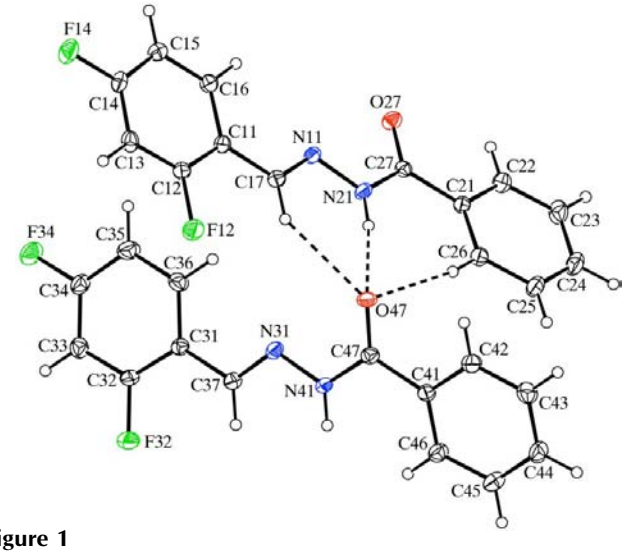


Figure 1
The two independent molecules of compound (I), showing the atom-labelling scheme and the three hydrogen bonds (dashed lines) within the selected asymmetric unit. Displacement ellipsoids are drawn at the 30% probability level.

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similar way, atoms C37, N41 and C46 at (x, y, z) all act as hydrogen-bond donors to atom O27 at $(-\frac{1}{2}+x, \frac{1}{2}-y, -\frac{1}{2}+z)$, hence forming a complex chain of rings running parallel to the [101] direction, as generated by the *n*-glide plane at $y = \frac{1}{4}$ (Fig. 3). This chain contains two independent pairs of edge-fused $R_2^1(6)$ and $R_2^1(7)$ rings (Bernstein *et al.*, 1995), and the corresponding pairs of hydrogen bonds generate three independent chains of $C_2^2(8)$, $C_2^2(10)$ and $C_2^2(12)$ types, where the donors are atoms N21 and N41, C26 and C46, and C17 and C37, respectively.

In the second one-dimensional substructure, the bimolecular aggregates (Fig. 1) are linked by a combination of one C—H···O hydrogen bond and one C—H···π(arene) hydrogen bond. Aryl atom C13 at (x, y, z) acts as donor to atom O27 at $(\frac{1}{2}+x, \frac{1}{2}-y, -\frac{1}{2}+z)$, while atom C23 at (x, y, z) acts as donor to the fluorinated aryl ring C31–C36 at $(-\frac{1}{2}+x, \frac{1}{2}-y, \frac{1}{2}+z)$. The concerted action of these two hydrogen bonds, together with that of the hydrogen bonds within the asymmetric unit, produces a second chain of rings, this time running parallel to the $[10\bar{1}]$ direction, but again generated by the *n*-glide plane at $y = \frac{1}{4}$ (Fig. 4). The combination of these two chains lying along [101] and $[10\bar{1}]$ and inclined to one another by *ca* 70° then generates a very complex sheet lying parallel to (010). Two such sheets, generated by the *n*-glide planes at $y = \frac{1}{4}$ and $y = \frac{3}{4}$, respectively, and related to one another by inversion, pass through each unit cell, but there are no direction-specific interactions between adjacent sheets.

In compound (II), the N—H···O and C—H···O hydrogen bonds (Table 3) play exactly the same role as those in compound (I), but the C—H···π(arene) hydrogen bond in (II) reinforces the [101] chain, rather than the $[10\bar{1}]$ chain as in compound (I).

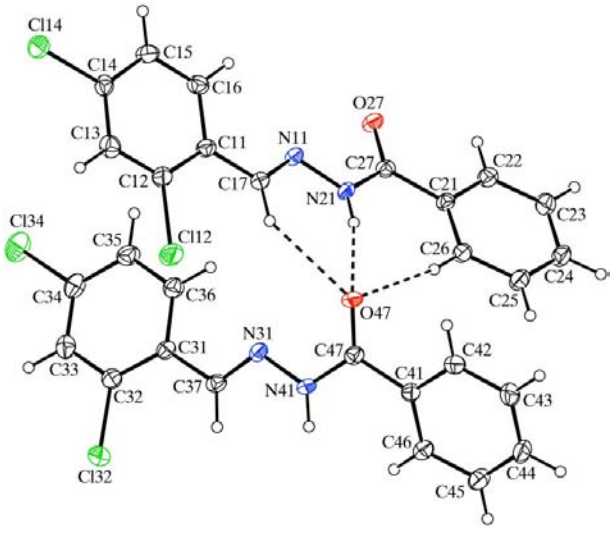

Figure 2
The two independent molecules of compound (II), showing the atom-labelling scheme and the three hydrogen bonds (dashed lines) within the selected asymmetric unit. Displacement ellipsoids are drawn at the 30% probability level.

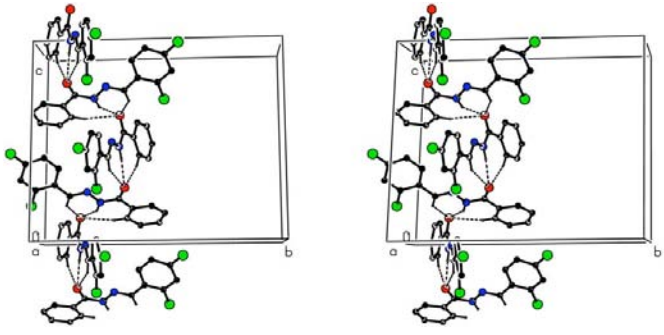

Figure 3
A stereoview of part of the crystal structure of compound (I), showing the formation of a hydrogen-bonded chain of rings along [101]. For the sake of clarity, H atoms not involved in the hydrogen bonds shown have been omitted.

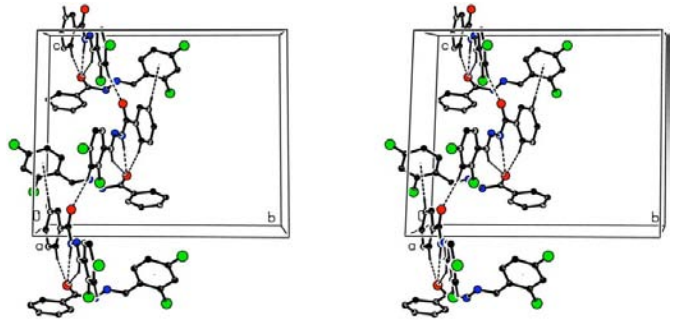

Figure 4
A stereoview of part of the crystal structure of compound (II), showing the formation of a hydrogen-bonded chain of rings along $[10\bar{1}]$. For the sake of clarity, H atoms not involved in the hydrogen bonds shown have been omitted.

Experimental

A solution of benzohydrazide ($PhCONHNH_2$, 5 mmol) and the appropriate substituted benzaldehyde (5 mmol) in tetrahydrofuran (20 ml) was heated under reflux for 15–18 h under an atmosphere of dinitrogen. After the solution had been cooled, the solvent was removed under reduced pressure and the resulting solid was washed successively with propan-2-ol and diethyl ether. Crystals suitable for single-crystal X-ray diffraction were grown by slow evaporation of solutions in methanol–heptane [3:1 *v*/*v* for (I) and 2:1 *v*/*v* for (II)]. Analysis for compound (I): yield 78%, m.p. 461–463 K; MS, *m*/*z* 260, $[M]^+$; ^{1}H NMR (DMSO-d_6): δ 7.23 (1H, *dd*, *J* = 8.2 and 8.5 Hz, H5), 7.39 (1H, *dd*, *J* = 9.4 and 9.2 Hz, H6), 7.55 (2H, *dd*, *J* = 7.2 and 7.5 Hz, H3′ and H5′), 7.62 (1H, *d*, *J* = 7.2 Hz, H4′), 7.94 (2H, *d*, *J* = 7.5 Hz, H2′ and H6′), 8.02 (1H, *dd*, *J* = 8.2 and 15.0 Hz, H3′), 8.67 (1H, *s*, N═C—H), 12.02 (1H, *s*, NH); ^{13}C NMR (DMSO-d_6): δ 104.5 (*t*, *J* = 25.0 Hz, C3), 112.7 (*dd*, *J* = 2.5 and 22.5 Hz, C5), 118.8 (*dd*, *J* = 2.5 and 10.0 Hz, C1), 127.5, 127.7, 128.6, 132.0, 133.2, 139.7 (C═N), 161.0 (*dd*, *J* = 12.4 and 250.9 Hz, C4), 163.2, 163.3 (*dd*, *J* = 12.2 and 248.2 Hz, C2); IR (KBr pellet, ν, cm^{-1}): 3177 (NH), 1654 (CO). Analysis for compound (II): yield 74%, m.p. 462–464 K; MS, *m*/*z* 293, $[M]^+$; ^{1}H NMR

(DMSO-d_6): δ 7.55 (1H, *d*, *J* = 8.5 Hz, H5), 7.56 (2H, *J* = 7.5 Hz, H3′ and H5′), 7.62 (1H, *d*, *J* = 7.5 Hz, H4′), 7.74 (1H, *s*, H3), 7.95 (2H, *d*, *J* = 7.5 Hz, H2′ and H6′), 8.04 (1H, *d*, *J* = 8.5 Hz, H6), 8.83 (1H, *s*, N=C−H), 12.16 (1H, *s*, NH); ^{13}C NMR (DMSO-d_6): δ 127.5, 128.1, 128.6, 129.4, 130.8, 132.1, 133.0, 133.9, 135.1, 142.5, 166.4; IR (KBr pellet, ν, cm^{-1}): 3086 (NH), 1680 (CO).

Compound (I)

Crystal data

$C_{14}H_{10}F_2N_2O$
M_r = 260.24
Monoclinic, $P2_1/n$
a = 10.1310 (3) Å
b = 17.2172 (6) Å
c = 14.4288 (5) Å
β = 103.957 (2)°
V = 2442.48 (14) Å^3
Z = 8
D_x = 1.415 Mg m^{-3}
Mo $K\alpha$ radiation
Cell parameters from 5577 reflections
θ = 3.0–27.5°
μ = 0.11 mm^{-1}
T = 120 (2) K
Lath, colourless
0.36 × 0.11 × 0.03 mm

Data collection

Bruker–Nonius KappaCCD area-detector diffractometer
φ and ω scans
Absorption correction: multi-scan (*SADABS*; Sheldrick, 2003)
T_{min} = 0.973, T_{max} = 0.997
26932 measured reflections
5577 independent reflections
3589 reflections with $I > 2\sigma(I)$
R_{int} = 0.080
θ_{max} = 27.5°
$h = -13 \rightarrow 13$
$k = -21 \rightarrow 22$
$l = -18 \rightarrow 18$

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)]$ = 0.053
$wR(F^2)$ = 0.130
S = 1.04
5577 reflections
343 parameters
H-atom parameters constrained
$w = 1/[\sigma^2(F_o^2) + (0.0499P)^2 + 0.8675P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} < 0.001$
$\Delta\rho_{max}$ = 0.20 e Å^{-3}
$\Delta\rho_{min}$ = −0.29 e Å^{-3}

Table 1
Selected torsion angles (°) for compounds (I) and (II).

Parameter	(I)		(II)	
	x = 1, y = 2	x = 3, y = 4	x = 1, y = 2	x = 3, y = 4
C*x*1—C*x*7—N*x*1—N*y*1	177.66 (16)	−177.09 (17)	175.3 (3)	−174.9 (3)
C*x*7—N*x*1—N*y*1—C*y*7	−177.33 (17)	179.69 (19)	−179.4 (3)	177.3 (3)
N*x*1—N*y*1—N*y*7—C*y*1	172.31 (16)	−173.40 (17)	170.4 (3)	−168.8 (3)
C*x*2—C*x*1—C*x*7—N*x*1	176.80 (19)	−171.9 (2)	168.6 (4)	−166.3 (3)
C*y*2—C*y*1—C*y*7—N*y*1	177.65 (17)	−175.2 (2)	−176.6 (3)	−167.0 (3)

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

*Cg*1 is the centroid of the C31–C36 ring.

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
N21—H21···O47	0.88	2.02	2.889 (2)	170
N41—H41···O27^{i}	0.88	2.12	2.916 (2)	150
C13—H13···O27^{ii}	0.95	2.37	3.286 (3)	162
C17—H17···O47	0.95	2.47	3.277 (2)	143
C26—H26···O47	0.95	2.41	3.340 (3)	167
C37—H37···O27^{i}	0.95	2.50	3.251 (2)	136
C46—H46···O27^{i}	0.95	2.47	3.402 (2)	165
C23—H23···*Cg*1^{iii}	0.95	2.91	3.859 (3)	174

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

Compound (II)

Crystal data

$C_{14}H_{10}Cl_2N_2O$
M_r = 293.14
Monoclinic, $P2_1/n$
a = 10.5093 (5) Å
b = 17.6499 (9) Å
c = 14.7982 (5) Å
β = 104.732 (2)°
V = 2654.7 (2) Å^3
Z = 8
D_x = 1.467 Mg m^{-3}
Mo $K\alpha$ radiation
Cell parameters from 6060 reflections
θ = 3.0–27.5°
μ = 0.48 mm^{-1}
T = 120 (2) K
Needle, colourless
0.12 × 0.03 × 0.03 mm

Data collection

Bruker Nonius KappaCCD area-detector diffractometer
φ and ω scans
Absorption correction: multi-scan (*SADABS*; Sheldrick, 2003)
T_{min} = 0.964, T_{max} = 0.986
38980 measured reflections
6060 independent reflections
3687 reflections with $I > 2\sigma(I)$
R_{int} = 0.102
θ_{max} = 27.5°
$h = -13 \rightarrow 13$
$k = -22 \rightarrow 22$
$l = -19 \rightarrow 19$

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)]$ = 0.061
$wR(F^2)$ = 0.155
S = 1.04
6060 reflections
343 parameters
H-atom parameters constrained
$w = 1/[\sigma^2(F_o^2) + (0.0527P)^2 + 3.4899P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max}$ = 0.001
$\Delta\rho_{max}$ = 0.53 e Å^{-3}
$\Delta\rho_{min}$ = −0.70 e Å^{-3}

Table 3
Hydrogen-bond geometry (Å, °) for (II).

*Cg*2 is the centroid of the C41–C46 ring.

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
N21—H21···O47	0.88	2.10	2.969 (3)	168
N41—H41···O27^{i}	0.88	2.20	2.989 (4)	150
C13—H13···O27^{ii}	0.95	2.47	3.425 (4)	179
C17—H17···O47	0.95	2.49	3.311 (4)	145
C26—H26···O47	0.95	2.41	3.354 (4)	171
C37—H37···O27^{i}	0.95	2.59	3.300 (4)	131
C46—H46···O27^{i}	0.95	2.44	3.381 (4)	170
C35—H35···*Cg*2^{iii}	0.95	2.88	3.480 (5)	122

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

For both compounds, the space group $P2_1/n$ was uniquely assigned from the systematic absences. All H atoms were located in difference maps and subsequently treated as riding atoms, with distances C—H = 0.95 Å and N—H = 0.88 Å, and with U_{iso}(H) = 1.2U_{eq}(C,N).

For both compounds, data collection: *COLLECT* (Nonius, 1999); cell refinement: *DENZO* (Otwinowski & Minor, 1997) and *COLLECT*; data reduction: *DENZO* and *COLLECT*; program(s) used to solve structure: *OSCAIL* (McArdle, 2003) and *SHELXS97* (Sheldrick, 1997); program(s) used to refine structure: *OSCAIL* and *SHELXL97* (Sheldrick, 1997); molecular graphics: *PLATON* (Spek, 2003); software used to prepare material for publication: *SHELXL97* and *PRPKAPPA* (Ferguson, 1999).

The X-ray data were collected at the EPSRC X-ray Crystallographic Service, University of Southampton; the authors thank the staff of the Service for all their help and advice. JLW thanks CNPq and FAPERJ for financial support.

Supplementary data for this paper are available from the IUCr electronic archives (Reference: SK1895). Services for accessing these data are described at the back of the journal.

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