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Hydrogen-bonded chains in 3,5-bis(4-fluorophenyl)-1-phenyl-1*H*-pyrazole and complex hydrogen-bonded sheets in (5*RS*,6*SR*)-6-(4-fluorobenzoyl)-5-(4-fluorophenyl)-2-(4-hydroxyphenyl)-5,6-dihydro-4*H*-1,3,4-oxadiazine *N*,*N*-dimethylformamide monosolvate

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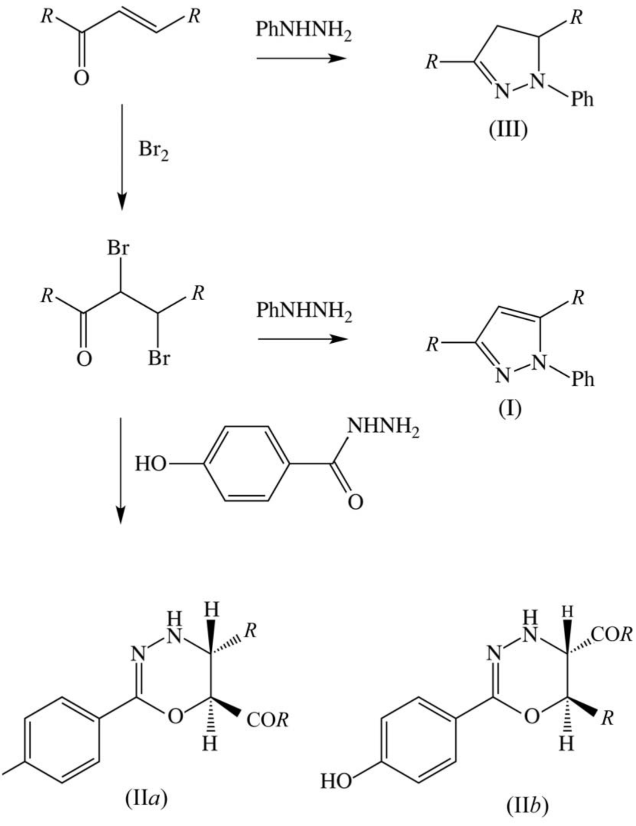
Two different heterocycles, a pyrazole and an oxadiazine, are formed by the reactions of a common precursor, (2*RS*,3*SR*)-2,3-dibromo-1,3-bis(4-fluorophenyl)propan-1-one, with different simple hydrazines. In 3,5-bis(4-fluorophenyl)-1-phenyl-1*H*-pyrazole, $C_{21}H_{14}F_2N_2$, (I), formed using phenylhydrazine, there is some aromatic-type delocalization in the pyrazole ring, and the molecules are linked into simple chains by a single C—H$\cdots\pi$(arene) hydrogen bond. The reaction with 4-hydroxybenzohydrazide gives (5*RS*,6*SR*)-6-(4-fluorobenzoyl)-5-(4-fluorophenyl)-2-(4-hydroxyphenyl)-5,6-dihydro-4*H*-1,3,4-oxadiazine, which was crystallized from *N*,*N*-dimethylformamide to give the monosolvate, $C_{22}H_{16}F_2N_2O_3\cdot C_3H_7NO$, (II), in which the solvent molecule is disordered over two sets of atomic sites having occupancies of 0.557 (10) and 0.443 (10). The oxadiazine molecules in (II) are linked by a combination of N—H$\cdots$N and C—H$\cdots$O hydrogen bonds to form complex sheets, having the hydrogen bonds in the central layer and with the solvent molecules attached at the outer faces by O—H$\cdots$O hydrogen bonds.

Keywords: crystal structure; hydrogen bonding; biological activity; pyrazoles; oxadiazines.

1. Introduction

Pyrazole derivatives occupy an important position in the design and synthesis of novel biologically active agents, as they display a wide range of biological activities, such as antitumour, antibacterial, antifungal, antiviral, antiparasitic, antitubercular and insecticidal properties (Hes *et al.*, 1978; Grosscurt *et al.*, 1979; Amir *et al.*, 2008). Some of these compounds also display anti-oxidant, anti-inflammatory and analgesic properties (Amir & Kumar, 2005; Sarojini *et al.*, 2010). Oxadiazines are also associated with a variety of biological activities, including antibacterial, cardiovascular, plant-growth regulating, insecticidal, acaricidal, anticonvulsive, miticidal and nematocidal activities (Kornet, 1996; Khan *et al.*, 2002).



(II) = (II*a*)·DMF
R = 4-FC$_6$H$_4$

It is thus of interest to explore new routes to these heterocyclic systems, and here we report the synthesis and structural characteristics of examples of both heterocyclic systems, a pyrazole and an oxadiazine, respectively, derived from the reactions of a common precursor, 2,3-dibromo-1,3-bis(4-fluorophenyl)propan-1-one, with different simple hydrazines. The dibromo precursor was itself prepared by addition of molecular bromine to 1,3-bis(4-fluorophenyl)prop-2-en-1-one, where it is formed as a racemic mixture of the (2*R*,3*S*) and (2*S*,3*R*) diastereoisomers, as shown by the deposited atomic coordinates (Jasinski *et al.*, 2010*b*), although the stereochemistry was not mentioned in the original structure report. This dibromopropanone reacts with phenylhydrazine to form 3,5-bis(4-fluorophenyl)-1-phenyl-1*H*-pyrazole, (I), in a cyclization reaction mediated by an excess of base which involves the elimination of one molecule of water and two molecules of hydrogen bromide. However, with 4-hydroxybenzohydrazide, the oxadiazine derivative (5*RS*,6*SR*)-

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6-(4-fluorobenzoyl)-5-(4-fluorophenyl)-2-(4-hydroxyphenyl)-5,6-dihydro-4*H*-1,3,4-oxadiazine is formed, which on crystallization from *N*,*N*-dimethylformamide (DMF) forms a stoichiometric monosolvate, (II). The synthesis of a reduced analogue of (I), namely 3,5-bis(4-fluorophenyl)-1-phenyl-4,5-dihydro-1*H*-pyrazole, (III) (see Scheme), prepared by a cycloaddition reaction between 1,3-bis(4-fluorophenyl)prop-2-en-1-one and phenylhydrazine, has recently been described (Jasinski *et al.*, 2010*a*). The purposes of the present study are: (i) the confirmation of the molecular constitutions of (I) and (II), in particular both the regiochemistry of the formation of the oxadiazine component (II*a*) as opposed to the alternative isomeric form (II*b*) (see Scheme); (ii) the stereochemistry of this component; (iii) the exploration of the supramolecular assembly in both (I) and (II); (iv) the comparison of (I) with its reduced analogue, (III).

2. Experimental

2.1. Synthesis and crystallization

For the synthesis of (I), a mixture of (2*RS*,3*SR*)-2,3-dibromo-1,3-bis(4-fluorophenyl)propan-1-one (4.04 g, 0.01 mol), phenylhydrazine (1.08 g, 0.01 mol) and triethylamine (3 ml) in ethanol (20 ml) was heated under reflux for 6 h. The reaction mixture was then cooled to ambient temperature and poured into ice-cold water. The resulting precipitate was collected by filtration and purified by recrystallization from ethanol, at ambient temperature and in the presence of air (yield 71%, m.p. 341–343 K). IR (KBr, ν, cm^{-1}): 3061 (Ar–H), 1597 (C=N), 1219 (C—F); ^{1}H NMR (DMSO-d_6): δ 7.16 (*s*, 1H, pyrazole-H), 7.21–7.94 (*m*, 13H, Ar–H); LCMS: *m*/*z* 333.1 (M^+ + 1). Analysis found: C 75.8, H 4.2, N 8.4%; $C_{21}H_{14}F_2N_2$ requires: C 75.9, H 4.2, N 8.4%.

For the synthesis of (II), a mixture of (2*RS*,3*SR*)-2,3-dibromo-1,3-bis(4-fluorophenyl)propan-1-one (4.04 g, 0.01 mol), 4-hydroxybenzohydrazide (1.52 g, 0.01 mol) and triethylamine (3 ml) in ethanol (15 ml) was heated under reflux for 8 h. The reaction mixture was then cooled to ambient temperature and poured into ice-cold water. The resulting solid was collected by filtration, dried and recrystallized from ethanol to give the solvent-free form (II*a*) (yield 64%, m.p. 484–487 K). IR (KBr, ν, cm^{-1}): 3267 (OH), 3074, 2937 (CH_2), 1658 (C=O), 1593 (C=N), 1215 (C—F); ^{1}H NMR (DMSO-d_6): δ 4.33 (*d*, 1H, CH), 6.15 (*d*, 1H, CH), 6.90 (*s*, 1H, NH), 6.72–8.03 (*m*, 12H, Ar–H), 9.64 (*s*, 1H, Ar–OH); LCMS: *m*/*z* 394.8 (M^+ + 1). Analysis found: C 67.7, H 4.0, N 7.1%; $C_{22}H_{16}F_2N_2O_3$ requires: C 67.0, H 4.1, N 7.1%. Crystals suitable for single-crystal X-ray diffraction were grown by slow evaporation, at ambient temperature and in the presence of air, of a solution in DMF, yielding the monosolvate (II).

2.2. Refinement

Crystal data, data collection and structure refinement details are summarized in Table 1. All H atoms were located in difference maps and then treated as riding atoms. C-bound H atoms were treated as riding in geometrically idealized positions, with C—H = 0.95 (aromatic and pyrazole), 0.98 (CH_3) or 1.00 Å (aliphatic C—H), and with $U_{iso}(H) = kU_{eq}(C)$, where

Table 1
Experimental details.

	(I)	(II)
Crystal data		
Chemical formula	$C_{21}H_{14}F_2N_2$	$C_{22}H_{16}F_2N_2O_3 \cdot C_3H_7NO$
M_r	332.34	467.46
Crystal system, space group	Monoclinic, *C*2/*c*	Monoclinic, *P*2$_1$/*c*
Temperature (K)	123	173
a, *b*, *c* (Å)	31.729 (2), 10.4118 (7), 10.1697 (6)	17.5182 (7), 7.4306 (3), 17.5595 (7)
β (°)	97.700 (7)	101.252 (4)
V (Å^3)	3329.3 (4)	2241.80 (16)
Z	8	4
Radiation type	Cu *K*α	Cu *K*α
μ (mm^{-1})	0.78	0.89
Crystal size (mm)	0.53 × 0.18 × 0.06	0.30 × 0.20 × 0.10
Data collection		
Diffractometer	Agilent Xcalibur Eos Gemini diffractometer	Agilent Xcalibur Gemini diffractometer with a Ruby detector
Absorption correction	Multi-scan (*SADABS*; Sheldrick, 2003)	Multi-scan (*CrysAlis RED*; Agilent, 2012)
T_{min}, T_{max}	0.634, 0.954	0.681, 0.915
No. of measured, independent and observed [$I > 2\sigma(I)$] reflections	5609, 3034, 2550	20862, 4492, 4029
R_{int}	0.043	0.042
$(\sin \theta/\lambda)_{max}$ (Å^{-1})	0.601	0.622
Refinement		
$R[F^2 > 2\sigma(F^2)]$, $wR(F^2)$, *S*	0.066, 0.174, 1.05	0.048, 0.147, 1.12
No. of reflections	3034	4492
No. of parameters	226	328
No. of restraints	0	8
H-atom treatment	H-atom parameters constrained	H-atom parameters constrained
$\Delta\rho_{max}$, $\Delta\rho_{min}$ (e Å^{-3})	0.45, −0.28	0.28, −0.22

Computer programs: *CrysAlis PRO* (Agilent, 2012), *CrysAlis RED* (Agilent, 2012), *SHELXS97* (Sheldrick, 2008), *SHELXL2014* (Sheldrick, 2014) and *PLATON* (Spek, 2009).

k = 1.5 for the methyl groups, which were permitted to rotate but not to tilt, and 1.2 for all other C-bound H atoms. The N- or O-bound H atoms in (II) were permitted to ride at the positions located in difference maps, with $U_{\rm iso}$(H) = 1.2$U_{\rm eq}$(N) or 1.5$U_{\rm eq}$(O), giving N—H and O—H distances of 0.91 and 0.92 Å, respectively. It was apparent that the DMF component in (II) was disordered over two sets of atomic sites with similar occupancies. The bond distances and the one-angle non-bonded distances in the minor orientation were constrained to be identical to the corresponding distances in the major orientation, subject to uncertainties of 0.01 and 0.005 Å, respectively, and the anisotropic displacement parameters of pairs of atoms occupying the same approximate volume of physical space were constrained to be equal. Under these conditions, free refinement of the site occupancies gave values of 0.552 (9) and 0.438 (9), respectively; accordingly, these occupancies were thereafter constrained to sum to unity, giving final values of 0.557 (10) and 0.443 (10).

3. Results and discussion

In (I) (Fig. 1), the bond distances in the pyrazole ring (Table 2) provide evidence for some aromatic-type delocalization. Thus, the distances N1—C5 and N2—C3 differ by only *ca* 0.03 Å, even though these bonds are formally single and double, respectively. Similarly, the distances C3—C4 and C4—C5 differ by only *ca* 0.03 Å, although again these are formally single and double bonds, respectively. The molecular conformation of (I) can be specified in terms of three torsion angles (Table 2) defining the orientations of the three aryl rings relative to the central pyrazole ring. The dihedral angles between the planes of the pyrazole ring and those of the three aryl rings containing atoms C11, C31 and C51 are 55.88 (9), 23.69 (9) and 52.08 (9)°, respectively. The molecules of (I) therefore exhibit no internal symmetry and they are thus conformationally chiral, although the centrosymmetric space group accommodates equal numbers of the two conformational enantiomers.

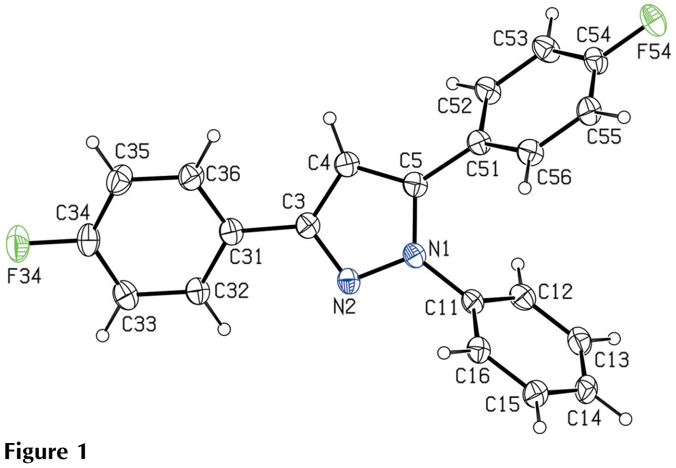

Figure 1
The molecular structure of (I), showing the atom-labelling scheme. Displacement ellipsoids are drawn at the 30% probability level.

Table 2
Selected geometric parameters (Å, °) for (I).

N1—N2	1.361 (2)	C4—C5	1.371 (2)
N2—C3	1.334 (2)	C5—N1	1.365 (2)
C3—C4	1.401 (2)		
N2—N1—C11—C12	124.34 (16)	C4—C5—C51—C52	−52.3 (2)
N2—C3—C31—C32	−24.1 (2)		

Table 3
Selected geometric parameters (Å, °) for (II).

O1—C2	1.3602 (16)	N4—C5	1.4648 (17)
C2—N3	1.2718 (19)	C5—C6	1.540 (2)
N3—N4	1.4084 (16)	C6—O1	1.4318 (16)
O1—C2—C21—C22	4.7 (2)	C5—C6—C67—C61	−84.54 (16)
N4—C5—C51—C52	−44.16 (18)	C6—C67—C61—C62	−20.1 (2)
C5—C6—C67—O67	89.51 (16)		

Compound (II) crystallizes as a monosolvate with DMF (Fig. 2), in which the DMF component is disordered over two sets of atomic sites having similar but non-identical occupancies, *viz.* 0.557 (10) and 0.443 (10), respectively (see *Refinement*, §2.2). There are two stereogenic centres in the oxadiazine component at atoms C5 and C6. The reference molecule was selected as one having the *R* configuration at atom C5 and, on this basis, the configuration at atom C6 is *S*. The centrosymmetric space group confirms that the oxadiazine component is present as a racemic mixture of the (5*R*,6*S*) and (5*S*,6*R*) diastereoisomers, as expected from the (2*RS*,3*SR*) stereochemistry of the dibromopropanone precursor. The ring-puckering parameters (Cremer & Pople, 1975), calculated for the atom sequence O1–C2–N3–N4–C5–C6, are Q = 0.5044 (15) Å, θ = 53.24 (16)° and φ = 238.0 (2)°. For an idealized envelope conformation, the ring-puckering angles (Boeyens, 1978) are θ = 54.7° and $\varphi = (k \times 60)°$, where k represents an integer. The oxadiazine ring thus has an envelope conformation and the ring is folded across the line N4···C6. The distances within the oxadiazine ring (Table 3) are fully consistent with its oxidation level, with a clear distinction between the single and double C—N bonds, *viz.* N4—C5 and C2—N3, respectively. The molecules are thus

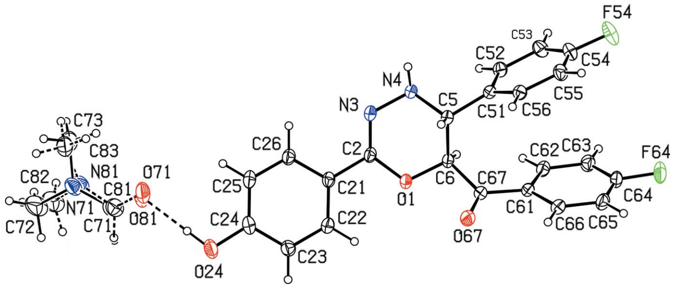

Figure 2
The independent molecular components of (II), showing the (5*R*,6*S*) diastereoisomer of the oxadiazine component, the atom-labelling scheme and the O—H···O hydrogen bond (dashed line) to the major orientation of the DMF component. The occupancies of the two DMF orientations are 0.557 (10) and 0.443 (10). Displacement ellipsoids are drawn at the 30% probability level.

conformationally chiral, as well as configurationally chiral. The isolated yield of this component indicates that the isomeric form shown in (II*a*) is, at the least, the dominant product, as opposed to (II*b*), although the formation of a small proportion of this alternative isomer cannot be ruled out.

The molecules of (I) are linked by a single C—H···π(arene) hydrogen bond (Table 4). Molecules related by the *c*-glide plane at $y = \frac{1}{2}$ are linked into a chain running parallel to the [001] direction (Fig. 3). Four chains pass through each unit cell but there are no direction-specific interactions between adjacent chains. Despite the presence of three independent aryl rings, no aromatic π–π stacking interactions are present in the crystal structure of (I).

The supramolecular assembly of (II) is considerably more complex than that in (I). The independent molecular components are linked by O—H···O hydrogen bonds (Table 5 and Fig. 2), but the DMF component is not involved in any other direction-specific intermolecular interactions, and its role may be principally that of occupying otherwise void spaces within the structure defined by the oxadiazine component. A combination of N—H···N and C—H···O hydrogen bonds (Table 5) links the oxadiazine molecules into complex sheets, from which the DMF molecules are simply pendent, and the formation of the sheet structure is readily analysed in terms of two simple substructures (Ferguson *et al.*, 1998*a*,*b*; Gregson *et al.*, 2000).

In the simpler of the two substructures, two inversion-related oxadiazine molecules are linked by symmetry-related N—H···N hydrogen bonds to form a cyclic centrosymmetric dimer characterized by an $R_2^2(6)$ (Bernstein *et al.*, 1995) motif (Fig. 4). The reference dimer is centred at $(\frac{1}{2}, \frac{1}{2}, \frac{1}{2})$ and this finite zero-dimensional substructure can be regarded as a key building block in the sheet formation. In the second substructure, which is one-dimensional, oxadiazine molecules which are related by the 2_1 screw axis along $(\frac{1}{2}, y, \frac{1}{4})$ are linked by two independent C—H···O hydrogen bonds to form a $C(5)C(7)[R_2^1(6)]$ chain of rings running parallel to the [010] direction (Fig. 5). The combination of these two substructures has the effect of directly linking the reference $R_2^2(6)$ dimer centred at $(\frac{1}{2}, \frac{1}{2}, \frac{1}{2})$ to the four symmetry-related dimers centred at $(\frac{1}{2}, 0, 0)$, $(\frac{1}{2}, 1, 0)$, $(\frac{1}{2}, 0, 1)$ and $(\frac{1}{2}, 1, 1)$, so leading to the formation of a sheet lying parallel to (100) (Fig. 6). Just one sheet of this type passes through each unit cell and the DMF components are pendent from it, on the outer faces of the sheet, while the hydrogen bonds linking the oxadiazine components lie in the central portion of the sheet (Fig. 7).

Table 4
Hydrogen-bond geometry (Å, °) for (I).

*Cg*1 represents the centroid of the C11–C16 ring.

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
C55—H55···*Cg*1^{i}	0.95	2.68	3.5674 (10)	155

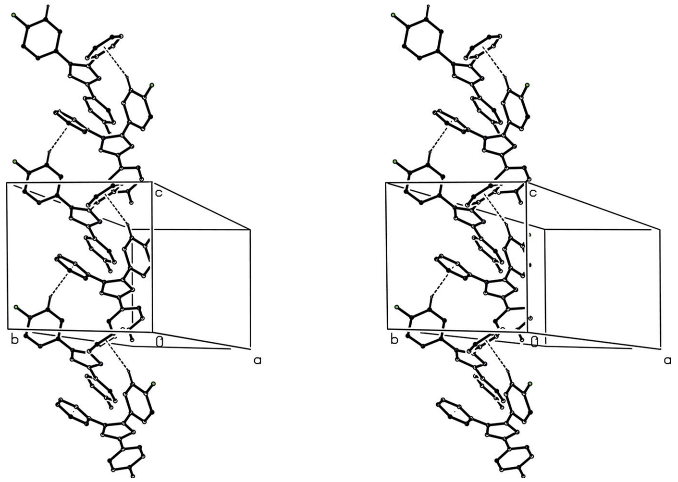

Figure 3
A stereoview of part of the crystal structure of (I), showing the formation of a chain parallel to [001] built from C—H···π(arene) hydrogen bonds (dashed lines). For the sake of clarity, H atoms not involved in the motif shown have been omitted.

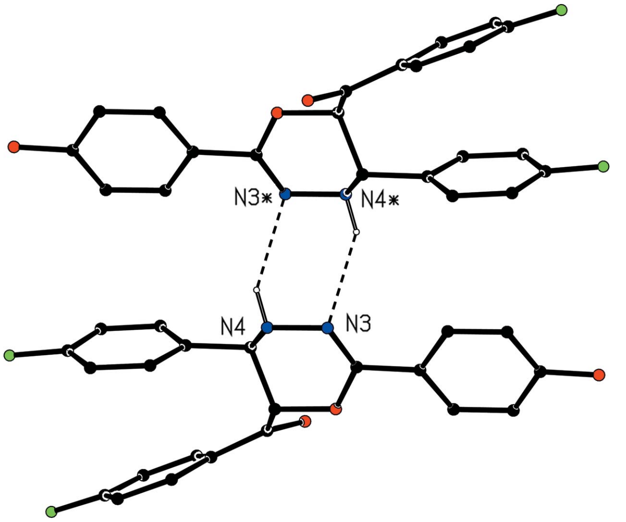

Figure 4
Part of the crystal structure of (II), showing the formation of a cyclic centrosymmetric $R_2^2(6)$ dimer. Hydrogen bonds are shown as dashed lines. For the sake of clarity, the unit-cell outline, the DMF components and H atoms not involved in the motif shown have been omitted. Atoms marked with an asterisk (*) are at the symmetry position $(-x + 1, -y + 1, -z + 1)$.

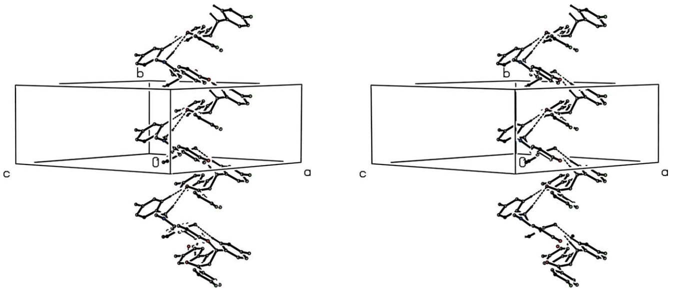

Figure 5
A stereoview of part of the crystal structure of (II), showing the formation of a $C(5)C(7)[R_2^1(6)]$ chain of rings running parallel to the [010] direction and built from C—H···O hydrogen bonds, shown as dashed lines. For the sake of clarity, the DMF components and H atoms not involved in the motif shown have been omitted.

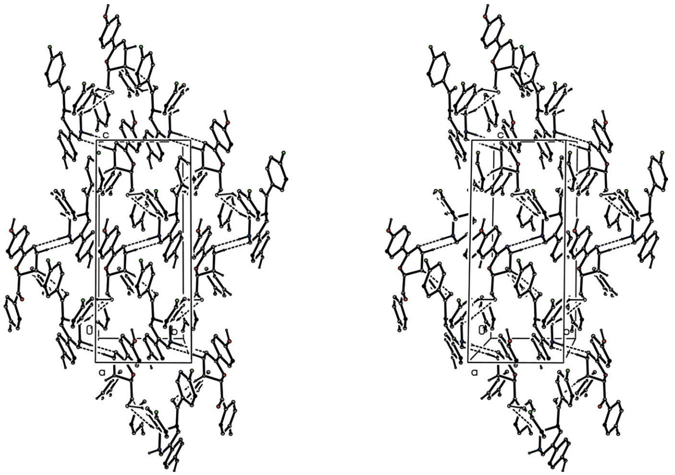

Figure 6
A stereoview of part of the crystal structure of (II), showing the formation of a hydrogen-bonded sheet parallel to (100). Hydrogen bonds are shown as dashed lines. For the sake of clarity, the DMF components and H atoms not involved in the motifs shown have been omitted.

Table 5
Hydrogen-bond geometry (Å, °) for (II).

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
N4—H4···N3^{i}	0.91	2.32	3.1188 (19)	146
O24—H24···O71	0.92	1.75	2.67 (3)	179
O24—H24···O81	0.92	1.78	2.69 (3)	174
C5—H5···O67^{ii}	1.00	2.55	3.4844 (19)	155
C56—H56···O67^{ii}	0.95	2.43	3.3080 (18)	153

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

There are several interesting differences between (I), reported here, and its reduced analogue, (III) (Jasinski *et al.*, 2010*a*). Firstly, (III) crystallizes in the space group $P2_1/c$, whereas (I) crystallizes in $C2/c$. Secondly, the heterocyclic ring in (III) is folded into an envelope conformation across a line corresponding to N1···C4 in (I), while the corresponding ring in (I) is planar. Lastly, the molecules of (III) are linked by two independent C—H···π(arene) hydrogen bonds to form sheets parallel to $(10\overline{2})$, in contrast with the chains formed in (I).

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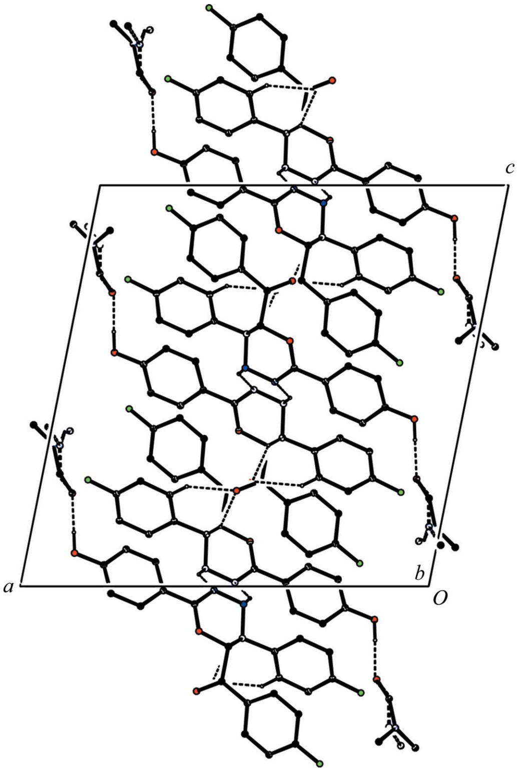

Figure 7
A projection, along [010], of part of the crystal structure of (II), showing a cross-section of the (100) sheet with the hydrogen bonds linking the oxadiazine molecules in the central portion of the sheet and the DMF components on the outer faces of the sheet. Hydrogen bonds are shown as dashed lines. For the sake of clarity, H atoms not involved in hydrogen bonding have been omitted.

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Hydrogen-bonded chains in 3,5-bis(4-fluorophenyl)-1-phenyl-1*H*-pyrazole and complex hydrogen-bonded sheets in (5*RS*,6*SR*)-6-(4-fluorobenzoyl)-5-(4-fluorophenyl)-2-(4-hydroxyphenyl)-5,6-dihydro-4*H*-1,3,4-oxadiazine *N*,*N*-dimethylformamide monosolvate

Seranthimata Samshuddin, Jerry P. Jasinski, James A. Golen, Badiadka Narayana, Hemmige S. Yathirajan and Christopher Glidewell

Computing details

For both compounds, data collection: *CrysAlis PRO* (Agilent, 2012); cell refinement: *CrysAlis PRO* (Agilent, 2012); data reduction: *CrysAlis RED* (Agilent, 2012); program(s) used to solve structure: *SHELXS97* (Sheldrick, 2008); program(s) used to refine structure: *SHELXL2014* (Sheldrick, 2014); molecular graphics: *PLATON* (Spek, 2009); software used to prepare material for publication: *SHELXL2014* (Sheldrick, 2014) and *PLATON* (Spek, 2009).

(I) 3,5-Bis(4-fluorophenyl)-1-phenyl-1*H*-pyrazole

Crystal data

$C_{21}H_{14}F_2N_2$
M_r = 332.34
Monoclinic, $C2/c$
a = 31.729 (2) Å
b = 10.4118 (7) Å
c = 10.1697 (6) Å
β = 97.700 (7)°
V = 3329.3 (4) Å^3
Z = 8

$F(000)$ = 1376
D_x = 1.326 Mg m^{-3}
Cu $K\alpha$ radiation, λ = 1.54178 Å
Cell parameters from 3279 reflections
θ = 4.5–74.0°
μ = 0.78 mm^{-1}
T = 123 K
Needle, colourless
0.53 × 0.18 × 0.06 mm

Data collection

Agilent Xcalibur Eos Gemini diffractometer
Radiation source: Enhance (Cu) X-ray Source
ω scans
Absorption correction: multi-scan (*SADABS*; Sheldrick, 2003)
T_{min} = 0.634, T_{max} = 0.954
5609 measured reflections

3034 independent reflections
2550 reflections with $I > 2\sigma(I)$
R_{int} = 0.043
θ_{max} = 68.0°, θ_{min} = 4.5°
$h = -38\rightarrow38$
$k = -12\rightarrow12$
$l = -12\rightarrow12$

Refinement

Refinement on F^2
Least-squares matrix: full
$R[F^2 > 2\sigma(F^2)]$ = 0.066
$wR(F^2)$ = 0.174

S = 1.05
3034 reflections
226 parameters
0 restraints

Primary atom site location: structure-invariant direct methods
Secondary atom site location: difference Fourier map
Hydrogen site location: inferred from neighbouring sites
H-atom parameters constrained
$w = 1/[\sigma^2(F_o^2) + (0.1381P)^2]$
where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{\max} < 0.001$
$\Delta\rho_{\max} = 0.45$ e Å^{-3}
$\Delta\rho_{\min} = -0.28$ e Å^{-3}

Special details

Geometry. All e.s.d.'s (except the e.s.d. in the dihedral angle between two l.s. planes) are estimated using the full covariance matrix. The cell e.s.d.'s are taken into account individually in the estimation of e.s.d.'s in distances, angles and torsion angles; correlations between e.s.d.'s in cell parameters are only used when they are defined by crystal symmetry. An approximate (isotropic) treatment of cell e.s.d.'s is used for estimating e.s.d.'s involving l.s. planes.

Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (Å²)

	x	*y*	*z*	U_{iso}*/U_{eq}
N1	0.13371 (4)	0.44853 (14)	0.35913 (13)	0.0345 (4)
N2	0.16415 (4)	0.49490 (14)	0.28947 (13)	0.0352 (4)
C3	0.18664 (5)	0.39192 (16)	0.26360 (15)	0.0351 (4)
C4	0.17090 (5)	0.28044 (17)	0.31686 (15)	0.0379 (4)
H4	0.1815	0.1955	0.3117	0.046*
C5	0.13705 (5)	0.31896 (17)	0.37802 (14)	0.0357 (4)
C11	0.10308 (5)	0.53422 (16)	0.40305 (15)	0.0340 (4)
C12	0.05987 (6)	0.51085 (18)	0.36792 (18)	0.0419 (4)
H12	0.0505	0.4397	0.3133	0.050*
C13	0.03068 (6)	0.5933 (2)	0.41411 (19)	0.0460 (5)
H13	0.0011	0.5783	0.3912	0.055*
C14	0.04453 (6)	0.6975 (2)	0.49341 (17)	0.0449 (5)
H14	0.0244	0.7530	0.5254	0.054*
C15	0.08774 (6)	0.72055 (19)	0.52594 (16)	0.0425 (4)
H15	0.0972	0.7927	0.5791	0.051*
C16	0.11720 (5)	0.63877 (17)	0.48114 (15)	0.0370 (4)
H16	0.1468	0.6542	0.5037	0.044*
C31	0.22321 (6)	0.40194 (17)	0.18827 (15)	0.0370 (4)
C32	0.22715 (5)	0.50278 (18)	0.10057 (16)	0.0374 (4)
H32	0.2059	0.5676	0.0882	0.045*
C33	0.26193 (6)	0.50909 (19)	0.03120 (17)	0.0435 (5)
H33	0.2646	0.5774	−0.0290	0.052*
C34	0.29230 (6)	0.4150 (2)	0.05113 (18)	0.0480 (5)
F34	0.32611 (4)	0.42090 (15)	−0.01819 (14)	0.0665 (4)
C35	0.28951 (7)	0.3133 (2)	0.13592 (19)	0.0521 (5)
H35	0.3108	0.2487	0.1472	0.063*
C36	0.25471 (6)	0.3080 (2)	0.20418 (17)	0.0450 (5)
H36	0.2522	0.2386	0.2633	0.054*
C51	0.10909 (5)	0.24330 (17)	0.45337 (15)	0.0361 (4)
C52	0.08954 (6)	0.13365 (18)	0.39643 (16)	0.0431 (4)
H52	0.0941	0.1097	0.3093	0.052*
C53	0.06364 (7)	0.05875 (19)	0.46407 (18)	0.0452 (5)
H53	0.0502	−0.0161	0.4248	0.054*

C54	0.05790 (6)	0.09629 (18)	0.59035 (16)	0.0402 (4)
F54	0.03250 (4)	0.02330 (12)	0.65751 (11)	0.0532 (4)
C55	0.07689 (6)	0.20333 (19)	0.65105 (16)	0.0437 (4)
H55	0.0725	0.2258	0.7388	0.052*
C56	0.10252 (6)	0.27784 (18)	0.58130 (16)	0.0415 (4)
H56	0.1157	0.3529	0.6210	0.050*

Atomic displacement parameters (Å^2)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
N1	0.0408 (7)	0.0413 (8)	0.0216 (6)	−0.0010 (6)	0.0055 (5)	0.0031 (5)
N2	0.0392 (7)	0.0447 (8)	0.0220 (6)	−0.0001 (6)	0.0054 (5)	0.0022 (5)
C3	0.0426 (9)	0.0429 (9)	0.0194 (7)	0.0006 (7)	0.0023 (6)	−0.0011 (6)
C4	0.0490 (10)	0.0410 (9)	0.0239 (8)	0.0024 (7)	0.0055 (7)	−0.0001 (6)
C5	0.0462 (9)	0.0407 (9)	0.0200 (7)	−0.0009 (7)	0.0037 (6)	−0.0006 (6)
C11	0.0421 (9)	0.0405 (9)	0.0201 (7)	0.0012 (6)	0.0069 (6)	0.0062 (6)
C12	0.0445 (10)	0.0457 (10)	0.0348 (9)	−0.0029 (7)	0.0030 (7)	0.0062 (7)
C13	0.0383 (9)	0.0566 (11)	0.0440 (10)	0.0010 (8)	0.0089 (7)	0.0130 (9)
C14	0.0493 (10)	0.0578 (11)	0.0305 (8)	0.0125 (8)	0.0157 (7)	0.0105 (8)
C15	0.0545 (10)	0.0494 (10)	0.0244 (8)	0.0049 (8)	0.0089 (7)	0.0000 (7)
C16	0.0414 (9)	0.0472 (9)	0.0225 (8)	0.0010 (7)	0.0042 (6)	0.0023 (7)
C31	0.0435 (9)	0.0464 (9)	0.0208 (7)	−0.0012 (7)	0.0035 (6)	−0.0020 (6)
C32	0.0405 (9)	0.0470 (10)	0.0242 (8)	−0.0009 (7)	0.0027 (6)	0.0003 (6)
C33	0.0483 (10)	0.0559 (11)	0.0264 (8)	−0.0072 (8)	0.0049 (7)	0.0014 (7)
C34	0.0454 (10)	0.0680 (13)	0.0327 (9)	−0.0014 (9)	0.0133 (7)	−0.0058 (8)
F34	0.0576 (7)	0.0897 (10)	0.0585 (8)	0.0045 (7)	0.0301 (6)	0.0034 (7)
C35	0.0549 (11)	0.0621 (12)	0.0411 (10)	0.0130 (9)	0.0127 (8)	−0.0009 (9)
C36	0.0553 (11)	0.0503 (10)	0.0309 (8)	0.0079 (8)	0.0112 (7)	0.0030 (7)
C51	0.0444 (9)	0.0411 (9)	0.0231 (7)	0.0016 (7)	0.0053 (6)	0.0027 (6)
C52	0.0614 (11)	0.0464 (10)	0.0231 (8)	−0.0058 (8)	0.0110 (7)	−0.0024 (7)
C53	0.0599 (11)	0.0453 (10)	0.0307 (8)	−0.0106 (8)	0.0070 (8)	0.0001 (7)
C54	0.0443 (9)	0.0496 (10)	0.0275 (8)	−0.0003 (7)	0.0075 (7)	0.0090 (7)
F54	0.0597 (7)	0.0669 (8)	0.0351 (6)	−0.0119 (5)	0.0142 (5)	0.0100 (5)
C55	0.0565 (11)	0.0540 (11)	0.0223 (7)	0.0019 (8)	0.0115 (7)	−0.0003 (7)
C56	0.0544 (10)	0.0440 (10)	0.0259 (8)	−0.0030 (8)	0.0052 (7)	−0.0034 (7)

Geometric parameters (Å, º)

N1—N2	1.361 (2)	C31—C32	1.394 (3)
N1—C11	1.434 (2)	C32—C33	1.389 (3)
N2—C3	1.334 (2)	C32—H32	0.9500
C3—C4	1.401 (2)	C33—C34	1.370 (3)
C4—C5	1.371 (2)	C33—H33	0.9500
C5—N1	1.365 (2)	C34—F34	1.362 (2)
C3—C31	1.477 (2)	C34—C35	1.376 (3)
C4—H4	0.9500	C35—C36	1.382 (3)
C5—C51	1.476 (2)	C35—H35	0.9500
C11—C16	1.386 (2)	C36—H36	0.9500

C11—C12	1.391 (3)	C51—C52	1.388 (3)
C12—C13	1.390 (3)	C51—C56	1.392 (2)
C12—H12	0.9500	C52—C53	1.381 (3)
C13—C14	1.387 (3)	C52—H52	0.9500
C13—H13	0.9500	C53—C54	1.378 (3)
C14—C15	1.388 (3)	C53—H53	0.9500
C14—H14	0.9500	C54—F54	1.357 (2)
C15—C16	1.386 (2)	C54—C55	1.373 (3)
C15—H15	0.9500	C55—C56	1.386 (3)
C16—H16	0.9500	C55—H55	0.9500
C31—C36	1.392 (3)	C56—H56	0.9500

N2—N1—C5	112.14 (14)	C33—C32—C31	120.40 (17)
N2—N1—C11	119.96 (14)	C33—C32—H32	119.8
C5—N1—C11	127.90 (14)	C31—C32—H32	119.8
C3—N2—N1	104.68 (14)	C34—C33—C32	118.82 (18)
N2—C3—C4	111.22 (15)	C34—C33—H33	120.6
N2—C3—C31	121.59 (16)	C32—C33—H33	120.6
C4—C3—C31	127.20 (16)	F34—C34—C33	118.57 (19)
C5—C4—C3	105.93 (15)	F34—C34—C35	118.73 (18)
C5—C4—H4	127.0	C33—C34—C35	122.69 (17)
C3—C4—H4	127.0	C34—C35—C36	117.93 (19)
N1—C5—C4	106.03 (15)	C34—C35—H35	121.0
N1—C5—C51	124.06 (15)	C36—C35—H35	121.0
C4—C5—C51	129.89 (16)	C35—C36—C31	121.54 (19)
C16—C11—C12	121.09 (16)	C35—C36—H36	119.2
C16—C11—N1	119.11 (15)	C31—C36—H36	119.2
C12—C11—N1	119.79 (16)	C52—C51—C56	119.19 (17)
C13—C12—C11	118.90 (17)	C52—C51—C5	119.26 (15)
C13—C12—H12	120.5	C56—C51—C5	121.54 (16)
C11—C12—H12	120.5	C53—C52—C51	121.27 (16)
C14—C13—C12	120.40 (17)	C53—C52—H52	119.4
C14—C13—H13	119.8	C51—C52—H52	119.4
C12—C13—H13	119.8	C54—C53—C52	117.76 (17)
C13—C14—C15	119.97 (17)	C54—C53—H53	121.1
C13—C14—H14	120.0	C52—C53—H53	121.1
C15—C14—H14	120.0	F54—C54—C55	118.86 (16)
C16—C15—C14	120.25 (18)	F54—C54—C53	118.16 (17)
C16—C15—H15	119.9	C55—C54—C53	122.98 (17)
C14—C15—H15	119.9	C54—C55—C56	118.45 (16)
C15—C16—C11	119.38 (16)	C54—C55—H55	120.8
C15—C16—H16	120.3	C56—C55—H55	120.8
C11—C16—H16	120.3	C55—C56—C51	120.34 (17)
C36—C31—C32	118.63 (16)	C55—C56—H56	119.8
C36—C31—C3	119.45 (16)	C51—C56—H56	119.8
C32—C31—C3	121.93 (16)		

C5—N1—N2—C3	0.51 (16)	N2—C3—C31—C32	−24.1 (2)

C11—N1—N2—C3	−179.46 (13)	C4—C3—C31—C32	156.25 (16)
N1—N2—C3—C4	−0.32 (17)	C36—C31—C32—C33	−0.2 (2)
N1—N2—C3—C31	179.94 (13)	C3—C31—C32—C33	−179.90 (15)
N2—C3—C4—C5	0.02 (18)	C31—C32—C33—C34	−0.4 (3)
C31—C3—C4—C5	179.75 (14)	C32—C33—C34—F34	179.32 (16)
N2—N1—C5—C4	−0.50 (17)	C32—C33—C34—C35	0.9 (3)
C11—N1—C5—C4	179.46 (14)	F34—C34—C35—C36	−179.20 (18)
N2—N1—C5—C51	178.20 (13)	C33—C34—C35—C36	−0.8 (3)
C11—N1—C5—C51	−1.8 (2)	C34—C35—C36—C31	0.1 (3)
C3—C4—C5—N1	0.28 (16)	C32—C31—C36—C35	0.4 (3)
C3—C4—C5—C51	−178.32 (15)	C3—C31—C36—C35	−179.97 (17)
N2—N1—C11—C16	−56.22 (19)	N1—C5—C51—C52	129.37 (18)
C5—N1—C11—C16	123.82 (17)	C4—C5—C51—C52	−52.3 (2)
N2—N1—C11—C12	124.34 (16)	N1—C5—C51—C56	−51.9 (2)
C5—N1—C11—C12	−55.6 (2)	C4—C5—C51—C56	126.44 (19)
C16—C11—C12—C13	−0.9 (3)	C56—C51—C52—C53	0.2 (3)
N1—C11—C12—C13	178.49 (15)	C5—C51—C52—C53	178.97 (17)
C11—C12—C13—C14	0.3 (3)	C51—C52—C53—C54	−0.1 (3)
C12—C13—C14—C15	0.7 (3)	C52—C53—C54—F54	179.98 (17)
C13—C14—C15—C16	−1.0 (3)	C52—C53—C54—C55	−0.4 (3)
C14—C15—C16—C11	0.3 (3)	F54—C54—C55—C56	−179.52 (16)
C12—C11—C16—C15	0.6 (2)	C53—C54—C55—C56	0.9 (3)
N1—C11—C16—C15	−178.80 (14)	C54—C55—C56—C51	−0.8 (3)
N2—C3—C31—C36	156.29 (16)	C52—C51—C56—C55	0.2 (3)
C4—C3—C31—C36	−23.4 (2)	C5—C51—C56—C55	−178.47 (16)

Hydrogen-bond geometry (Å, º)

Cg1 represents the centroid of the C11–C16 ring.

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
C55—H55···*Cg*1^{i}	0.95	2.68	3.5674 (10)	155

Symmetry code: (i) *x*, −*y*+1, *z*+1/2.

(II) (5*RS*,6*SR*)-6-(4-Fluorobenzoyl)-5-(4-fluorophenyl)-2-(4-hydroxyphenyl)-5,6-dihydro-4*H*-1,3,4-oxadiazine *N*,*N*-dimethylformamide monosolvate

Crystal data

$C_{22}H_{16}F_2N_2O_3\cdot C_3H_7NO$
$M_r = 467.46$
Monoclinic, $P2_1/c$
$a = 17.5182\ (7)$ Å
$b = 7.4306\ (3)$ Å
$c = 17.5595\ (7)$ Å
$\beta = 101.252\ (4)°$
$V = 2241.80\ (16)$ Å^3
$Z = 4$

$F(000) = 976$
$D_x = 1.385$ Mg m^{-3}
Cu $K\alpha$ radiation, $\lambda = 1.54178$ Å
Cell parameters from 4487 reflections
$\theta = 5.1–73.5°$
$\mu = 0.89$ mm^{-1}
$T = 173$ K
Block, colourless
0.30 × 0.20 × 0.10 mm

Data collection

Agilent Xcalibur Gemini
diffractometer with Ruby detector
Radiation source: Enhance (Cu) X-ray Source
ω scans
Absorption correction: multi-scan
(*CrysAlis RED*; Agilent, 2012)
$T_{\min} = 0.681$, $T_{\max} = 0.915$
20862 measured reflections

4492 independent reflections
4029 reflections with $I > 2\sigma(I)$
$R_{\text{int}} = 0.042$
$\theta_{\max} = 73.5°$, $\theta_{\min} = 5.1°$
$h = -21 \rightarrow 21$
$k = -9 \rightarrow 9$
$l = -21 \rightarrow 20$

Refinement

Refinement on F^2
Least-squares matrix: full
$R[F^2 > 2\sigma(F^2)] = 0.048$
$wR(F^2) = 0.147$
$S = 1.12$
4492 reflections
328 parameters
8 restraints
Primary atom site location: structure-invariant
direct methods
Secondary atom site location: difference Fourier
map

Hydrogen site location: inferred from
neighbouring sites
H-atom parameters constrained
$w = 1/[\sigma^2(F_o^2) + (0.0828P)^2 + 0.4962P]$
where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{\max} < 0.001$
$\Delta\rho_{\max} = 0.28$ e Å^{-3}
$\Delta\rho_{\min} = -0.22$ e Å^{-3}
Extinction correction: *SHELXL2014* (Sheldrick,
2014), $Fc^* = kFc[1+0.001xFc^2\lambda^3/\sin(2\theta)]^{-1/4}$
Extinction coefficient: 0.0045 (5)

Special details

Geometry. All e.s.d.'s (except the e.s.d. in the dihedral angle between two l.s. planes) are estimated using the full covariance matrix. The cell e.s.d.'s are taken into account individually in the estimation of e.s.d.'s in distances, angles and torsion angles; correlations between e.s.d.'s in cell parameters are only used when they are defined by crystal symmetry. An approximate (isotropic) treatment of cell e.s.d.'s is used for estimating e.s.d.'s involving l.s. planes.

Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (Å^2)

	x	y	z	U_{iso}*/U_{eq}	Occ. (<1)
O1	0.54057 (6)	0.09857 (15)	0.38825 (6)	0.0393 (3)	
C2	0.56472 (8)	0.18855 (19)	0.45613 (7)	0.0312 (3)	
N3	0.52360 (7)	0.29026 (18)	0.49027 (7)	0.0355 (3)	
N4	0.44462 (7)	0.31235 (18)	0.45558 (7)	0.0349 (3)	
H4	0.4317	0.4237	0.4702	0.042*	
C5	0.43087 (8)	0.3059 (2)	0.37062 (8)	0.0304 (3)	
H5	0.4614	0.4033	0.3511	0.036*	
C6	0.46110 (8)	0.1210 (2)	0.35015 (8)	0.0317 (3)	
H6	0.4283	0.0227	0.3657	0.038*	
C21	0.64783 (8)	0.15928 (19)	0.48957 (8)	0.0312 (3)	
C22	0.69582 (9)	0.0605 (2)	0.45070 (8)	0.0347 (3)	
H22	0.6746	0.0074	0.4020	0.042*	
C23	0.77445 (9)	0.0384 (2)	0.48228 (9)	0.0385 (4)	
H23	0.8065	−0.0300	0.4553	0.046*	
C24	0.80613 (9)	0.1164 (2)	0.55345 (9)	0.0385 (4)	
C25	0.75867 (9)	0.2159 (2)	0.59270 (9)	0.0386 (4)	
H25	0.7801	0.2699	0.6412	0.046*	
C26	0.68056 (9)	0.2364 (2)	0.56129 (8)	0.0357 (3)	

H26	0.6485	0.3037	0.5887	0.043*	
O24	0.88326 (7)	0.08818 (18)	0.58294 (7)	0.0498 (3)	
H24	0.8950	0.1192	0.6346	0.075*	
C51	0.34530 (8)	0.33191 (19)	0.33759 (8)	0.0301 (3)	
C52	0.28957 (9)	0.2422 (2)	0.36982 (8)	0.0345 (3)	
H52	0.3053	0.1717	0.4153	0.041*	
C53	0.21092 (9)	0.2545 (2)	0.33622 (10)	0.0416 (4)	
H53	0.1726	0.1950	0.3585	0.050*	
C54	0.19040 (9)	0.3556 (2)	0.26975 (10)	0.0421 (4)	
F54	0.11395 (6)	0.36116 (18)	0.23453 (7)	0.0637 (4)	
C55	0.24334 (9)	0.4505 (2)	0.23741 (9)	0.0391 (4)	
H55	0.2269	0.5222	0.1924	0.047*	
C56	0.32151 (8)	0.4392 (2)	0.27214 (8)	0.0338 (3)	
H56	0.3591	0.5050	0.2511	0.041*	
C67	0.46022 (8)	0.1118 (2)	0.26265 (8)	0.0334 (3)	
O67	0.51715 (6)	0.16080 (18)	0.23857 (6)	0.0459 (3)	
C61	0.38685 (8)	0.0600 (2)	0.20898 (8)	0.0315 (3)	
C62	0.32639 (9)	−0.0316 (2)	0.23270 (8)	0.0358 (3)	
H62	0.3330	−0.0742	0.2846	0.043*	
C63	0.25645 (9)	−0.0616 (2)	0.18153 (9)	0.0405 (4)	
H63	0.2149	−0.1236	0.1976	0.049*	
C64	0.24931 (9)	0.0011 (2)	0.10688 (9)	0.0401 (4)	
F64	0.18020 (6)	−0.02128 (17)	0.05734 (6)	0.0591 (3)	
C65	0.30860 (10)	0.0869 (2)	0.08015 (8)	0.0411 (4)	
H65	0.3021	0.1247	0.0276	0.049*	
C66	0.37782 (9)	0.1169 (2)	0.13173 (8)	0.0366 (3)	
H66	0.4195	0.1764	0.1147	0.044*	
N71	0.9875 (6)	0.1371 (15)	0.8529 (7)	0.052 (2)	0.557 (10)
C71	0.958 (4)	0.086 (5)	0.7803 (9)	0.0530 (18)	0.557 (10)
H71	0.9828	−0.0221	0.7554	0.064*	0.5574
O71	0.918 (3)	0.183 (5)	0.7321 (12)	0.0602 (19)	0.557 (10)
C72	1.0460 (5)	0.0279 (13)	0.9027 (4)	0.087 (2)	0.557 (10)
H72A	1.0704	−0.0535	0.8706	0.131*	0.557 (10)
H72B	1.0212	−0.0428	0.9382	0.131*	0.557 (10)
H72C	1.0857	0.1065	0.9327	0.131*	0.557 (10)
C73	0.9538 (14)	0.289 (2)	0.8875 (13)	0.056 (2)	0.557 (10)
H73A	0.9175	0.3534	0.8470	0.084*	0.557 (10)
H73B	0.9955	0.3711	0.9115	0.084*	0.557 (10)
H73C	0.9259	0.2452	0.9270	0.084*	0.557 (10)
N81	0.9715 (9)	0.1101 (19)	0.8507 (9)	0.052 (2)	0.443 (10)
C81	0.956 (5)	0.100 (7)	0.7733 (12)	0.0530 (18)	0.443 (10)
H81	0.9828	−0.0020	0.7554	0.064*	0.4426
O81	0.914 (4)	0.204 (7)	0.7313 (15)	0.0602 (19)	0.443 (10)
C82	1.0095 (6)	−0.0389 (17)	0.8974 (5)	0.087 (2)	0.443 (10)
H82A	0.9737	−0.0904	0.9280	0.131*	0.443 (10)
H82B	1.0563	0.0050	0.9323	0.131*	0.443 (10)
H82C	1.0240	−0.1316	0.8631	0.131*	0.443 (10)
C83	0.9660 (18)	0.283 (2)	0.8891 (17)	0.056 (2)	0.443 (10)

H83A	1.0183	0.3255	0.9121	0.084*	0.443 (10)
H83B	0.9356	0.2680	0.9300	0.084*	0.443 (10)
H83C	0.9403	0.3708	0.8510	0.084*	0.443 (10)

Atomic displacement parameters (Å^2)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
O1	0.0341 (5)	0.0448 (6)	0.0332 (5)	0.0097 (4)	−0.0076 (4)	−0.0118 (4)
C2	0.0346 (7)	0.0327 (7)	0.0233 (6)	0.0008 (5)	−0.0017 (5)	0.0001 (5)
N3	0.0333 (6)	0.0434 (7)	0.0263 (5)	0.0033 (5)	−0.0026 (5)	−0.0034 (5)
N4	0.0319 (6)	0.0451 (7)	0.0256 (6)	0.0054 (5)	0.0004 (5)	−0.0057 (5)
C5	0.0294 (7)	0.0347 (8)	0.0253 (6)	0.0013 (5)	0.0011 (5)	−0.0009 (5)
C6	0.0301 (7)	0.0356 (8)	0.0260 (6)	0.0030 (5)	−0.0028 (5)	−0.0038 (5)
C21	0.0338 (7)	0.0297 (7)	0.0272 (6)	0.0006 (5)	−0.0013 (5)	0.0031 (5)
C22	0.0359 (7)	0.0392 (8)	0.0269 (6)	−0.0012 (6)	0.0010 (5)	−0.0002 (5)
C23	0.0342 (7)	0.0448 (9)	0.0355 (7)	0.0022 (6)	0.0045 (6)	0.0027 (6)
C24	0.0302 (7)	0.0442 (9)	0.0376 (8)	−0.0041 (6)	−0.0024 (6)	0.0074 (6)
C25	0.0396 (8)	0.0388 (8)	0.0322 (7)	−0.0029 (6)	−0.0061 (6)	0.0001 (6)
C26	0.0390 (8)	0.0347 (8)	0.0296 (7)	0.0027 (6)	−0.0024 (6)	−0.0010 (5)
O24	0.0307 (6)	0.0654 (8)	0.0483 (7)	−0.0011 (5)	−0.0043 (5)	0.0012 (6)
C51	0.0304 (7)	0.0319 (7)	0.0266 (6)	0.0029 (5)	0.0024 (5)	−0.0037 (5)
C52	0.0350 (7)	0.0360 (8)	0.0312 (7)	0.0028 (6)	0.0035 (5)	0.0022 (6)
C53	0.0330 (8)	0.0452 (9)	0.0471 (8)	−0.0005 (6)	0.0088 (6)	0.0064 (7)
C54	0.0292 (7)	0.0460 (9)	0.0476 (9)	0.0045 (6)	−0.0008 (6)	0.0046 (7)
F54	0.0300 (5)	0.0774 (8)	0.0769 (8)	0.0016 (5)	−0.0066 (5)	0.0232 (6)
C55	0.0372 (8)	0.0427 (9)	0.0350 (7)	0.0065 (6)	0.0011 (6)	0.0068 (6)
C56	0.0336 (7)	0.0380 (8)	0.0293 (6)	0.0020 (6)	0.0046 (5)	0.0013 (6)
C67	0.0312 (7)	0.0387 (8)	0.0289 (7)	0.0044 (5)	0.0024 (5)	−0.0062 (5)
O67	0.0331 (6)	0.0672 (8)	0.0376 (6)	−0.0033 (5)	0.0072 (4)	−0.0105 (5)
C61	0.0321 (7)	0.0334 (7)	0.0271 (6)	0.0046 (5)	0.0014 (5)	−0.0055 (5)
C62	0.0391 (8)	0.0380 (8)	0.0280 (7)	−0.0004 (6)	0.0011 (6)	−0.0014 (6)
C63	0.0373 (8)	0.0434 (9)	0.0388 (8)	−0.0056 (6)	0.0026 (6)	−0.0046 (6)
C64	0.0365 (8)	0.0433 (9)	0.0346 (7)	0.0027 (6)	−0.0078 (6)	−0.0074 (6)
F64	0.0430 (6)	0.0774 (8)	0.0470 (6)	−0.0055 (5)	−0.0152 (5)	−0.0055 (5)
C65	0.0475 (9)	0.0463 (9)	0.0262 (7)	0.0045 (7)	−0.0011 (6)	−0.0011 (6)
C66	0.0390 (8)	0.0411 (8)	0.0295 (7)	0.0009 (6)	0.0059 (6)	−0.0030 (6)
N71	0.040 (4)	0.075 (3)	0.0429 (10)	0.015 (3)	0.009 (2)	0.0147 (18)
C71	0.048 (2)	0.065 (5)	0.046 (2)	0.007 (3)	0.011 (4)	0.010 (3)
O71	0.048 (4)	0.072 (7)	0.0509 (8)	0.005 (4)	−0.0125 (10)	0.000 (2)
C72	0.085 (4)	0.120 (6)	0.0572 (17)	0.054 (4)	0.014 (3)	0.030 (3)
C73	0.046 (6)	0.0682 (16)	0.0497 (12)	−0.0044 (16)	0.001 (3)	0.0016 (12)
N81	0.040 (4)	0.075 (3)	0.0429 (10)	0.015 (3)	0.009 (2)	0.0147 (18)
C81	0.048 (2)	0.065 (5)	0.046 (2)	0.007 (3)	0.011 (4)	0.010 (3)
O81	0.048 (4)	0.072 (7)	0.0509 (8)	0.005 (4)	−0.0125 (10)	0.000 (2)
C82	0.085 (4)	0.120 (6)	0.0572 (17)	0.054 (4)	0.014 (3)	0.030 (3)
C83	0.046 (6)	0.0682 (16)	0.0497 (12)	−0.0044 (16)	0.001 (3)	0.0016 (12)

Geometric parameters (Å, º)

O1—C2	1.3602 (16)	C67—O67	1.2127 (19)
C2—N3	1.2718 (19)	C67—C61	1.4886 (18)
C2—C21	1.4759 (18)	C61—C62	1.389 (2)
N3—N4	1.4084 (16)	C61—C66	1.400 (2)
N4—C5	1.4648 (17)	C62—C63	1.389 (2)
N4—H4	0.9077	C62—H62	0.9500
C5—C51	1.5104 (18)	C63—C64	1.374 (2)
C5—C6	1.540 (2)	C63—H63	0.9500
C6—O1	1.4318 (16)	C64—F64	1.3561 (17)
C5—H5	1.0000	C64—C65	1.377 (3)
C6—C67	1.5350 (18)	C65—C66	1.383 (2)
C6—H6	1.0000	C65—H65	0.9500
C21—C22	1.391 (2)	C66—H66	0.9500
C21—C26	1.4004 (19)	N71—C71	1.335 (13)
C22—C23	1.391 (2)	N71—C72	1.456 (5)
C22—H22	0.9500	N71—C73	1.460 (7)
C23—C24	1.391 (2)	C71—O71	1.218 (5)
C23—H23	0.9500	C71—H71	1.0524
C24—O24	1.3655 (18)	C72—H72A	0.9800
C24—C25	1.392 (2)	C72—H72B	0.9800
C25—C26	1.380 (2)	C72—H72C	0.9800
C25—H25	0.9500	C73—H73A	0.9800
C26—H26	0.9500	C73—H73B	0.9800
O24—H24	0.9198	C73—H73C	0.9800
C51—C52	1.390 (2)	N81—C81	1.336 (14)
C51—C56	1.394 (2)	N81—C82	1.459 (6)
C52—C53	1.392 (2)	N81—C83	1.462 (8)
C52—H52	0.9500	C81—O81	1.217 (7)
C53—C54	1.375 (2)	C81—H81	0.9771
C53—H53	0.9500	C82—H82A	0.9800
C54—F54	1.3619 (17)	C82—H82B	0.9800
C54—C55	1.373 (2)	C82—H82C	0.9800
C55—C56	1.389 (2)	C83—H83A	0.9800
C55—H55	0.9500	C83—H83B	0.9800
C56—H56	0.9500	C83—H83C	0.9800
C2—O1—C6	117.38 (11)	O67—C67—C61	121.62 (13)
N3—C2—O1	126.67 (13)	O67—C67—C6	119.16 (13)
N3—C2—C21	120.37 (12)	C61—C67—C6	118.95 (12)
O1—C2—C21	112.96 (12)	C62—C61—C66	119.33 (13)
C2—N3—N4	117.66 (11)	C62—C61—C67	123.46 (13)
N3—N4—C5	112.91 (11)	C66—C61—C67	117.11 (13)
N3—N4—H4	105.1	C63—C62—C61	120.84 (14)
C5—N4—H4	108.5	C63—C62—H62	119.6
N4—C5—C51	109.92 (11)	C61—C62—H62	119.6
N4—C5—C6	105.74 (11)	C64—C63—C62	117.86 (15)

C51—C5—C6	112.66 (11)	C64—C63—H63	121.1
N4—C5—H5	109.5	C62—C63—H63	121.1
C51—C5—H5	109.5	F64—C64—C63	118.30 (15)
C6—C5—H5	109.5	F64—C64—C65	118.46 (14)
O1—C6—C67	106.34 (11)	C63—C64—C65	123.24 (14)
O1—C6—C5	110.02 (11)	C64—C65—C66	118.34 (14)
C67—C6—C5	109.69 (12)	C64—C65—H65	120.8
O1—C6—H6	110.2	C66—C65—H65	120.8
C67—C6—H6	110.2	C65—C66—C61	120.33 (15)
C5—C6—H6	110.2	C65—C66—H66	119.8
C22—C21—C26	118.46 (13)	C61—C66—H66	119.8
C22—C21—C2	121.76 (12)	C71—N71—C72	120.9 (5)
C26—C21—C2	119.76 (13)	C71—N71—C73	120.1 (10)
C23—C22—C21	120.86 (13)	C72—N71—C73	118.4 (4)
C23—C22—H22	119.6	O71—C71—N71	124.2 (14)
C21—C22—H22	119.6	O71—C71—H71	112.9
C22—C23—C24	119.97 (15)	N71—C71—H71	119.8
C22—C23—H23	120.0	N71—C72—H72A	109.5
C24—C23—H23	120.0	N71—C72—H72B	109.5
O24—C24—C23	117.93 (15)	H72A—C72—H72B	109.5
O24—C24—C25	122.44 (14)	N71—C72—H72C	109.5
C23—C24—C25	119.61 (14)	H72A—C72—H72C	109.5
C26—C25—C24	120.14 (14)	H72B—C72—H72C	109.5
C26—C25—H25	119.9	N71—C73—H73A	109.5
C24—C25—H25	119.9	N71—C73—H73B	109.5
C25—C26—C21	120.95 (14)	H73A—C73—H73B	109.5
C25—C26—H26	119.5	N71—C73—H73C	109.5
C21—C26—H26	119.5	H73A—C73—H73C	109.5
C24—O24—H24	110.5	H73B—C73—H73C	109.5
C52—C51—C56	119.27 (13)	C81—N81—C82	120.6 (5)
C52—C51—C5	120.36 (12)	C81—N81—C83	119.9 (12)
C56—C51—C5	120.30 (13)	C82—N81—C83	118.2 (4)
C51—C52—C53	120.78 (13)	O81—C81—N81	124.1 (16)
C51—C52—H52	119.6	O81—C81—H81	125.0
C53—C52—H52	119.6	N81—C81—H81	110.9
C54—C53—C52	117.94 (14)	N81—C82—H82A	109.5
C54—C53—H53	121.0	N81—C82—H82B	109.5
C52—C53—H53	121.0	H82A—C82—H82B	109.5
F54—C54—C55	118.70 (14)	N81—C82—H82C	109.5
F54—C54—C53	118.22 (15)	H82A—C82—H82C	109.5
C55—C54—C53	123.08 (14)	H82B—C82—H82C	109.5
C54—C55—C56	118.34 (14)	N81—C83—H83A	109.5
C54—C55—H55	120.8	N81—C83—H83B	109.5
C56—C55—H55	120.8	H83A—C83—H83B	109.5
C55—C56—C51	120.50 (14)	N81—C83—H83C	109.5
C55—C56—H56	119.8	H83A—C83—H83C	109.5
C51—C56—H56	119.8	H83B—C83—H83C	109.5

C6—O1—C2—N3	0.8 (2)	C5—C51—C52—C53	−175.08 (14)
C6—O1—C2—C21	−178.72 (12)	C51—C52—C53—C54	1.0 (2)
O1—C2—N3—N4	0.7 (2)	C52—C53—C54—F54	176.92 (15)
C21—C2—N3—N4	−179.81 (12)	C52—C53—C54—C55	−3.0 (3)
C2—N3—N4—C5	−32.99 (19)	F54—C54—C55—C56	−177.81 (15)
N3—N4—C5—C51	−179.56 (12)	C53—C54—C55—C56	2.1 (3)
N3—N4—C5—C6	58.58 (15)	C54—C55—C56—C51	0.8 (2)
C2—O1—C6—C67	146.49 (13)	C52—C51—C56—C55	−2.7 (2)
C2—O1—C6—C5	27.77 (17)	C5—C51—C56—C55	174.17 (13)
N4—C5—C6—O1	−55.17 (14)	O1—C6—C67—O67	−29.42 (19)
C51—C5—C6—O1	−175.24 (11)	C5—C6—C67—O67	89.51 (16)
N4—C5—C6—C67	−171.80 (11)	O1—C6—C67—C61	156.53 (12)
C51—C5—C6—C67	68.12 (15)	C5—C6—C67—C61	−84.54 (16)
N3—C2—C21—C22	−174.85 (14)	O67—C67—C61—C62	166.04 (15)
O1—C2—C21—C22	4.7 (2)	C6—C67—C61—C62	−20.1 (2)
N3—C2—C21—C26	3.3 (2)	O67—C67—C61—C66	−17.7 (2)
O1—C2—C21—C26	−177.09 (13)	C6—C67—C61—C66	156.23 (14)
C26—C21—C22—C23	0.1 (2)	C66—C61—C62—C63	−2.2 (2)
C2—C21—C22—C23	178.30 (13)	C67—C61—C62—C63	173.97 (14)
C21—C22—C23—C24	−0.3 (2)	C61—C62—C63—C64	0.4 (2)
C22—C23—C24—O24	178.72 (14)	C62—C63—C64—F64	−177.43 (14)
C22—C23—C24—C25	0.1 (2)	C62—C63—C64—C65	2.0 (3)
O24—C24—C25—C26	−178.23 (14)	F64—C64—C65—C66	177.10 (14)
C23—C24—C25—C26	0.3 (2)	C63—C64—C65—C66	−2.3 (3)
C24—C25—C26—C21	−0.5 (2)	C64—C65—C66—C61	0.3 (2)
C22—C21—C26—C25	0.3 (2)	C62—C61—C66—C65	1.9 (2)
C2—C21—C26—C25	−177.91 (14)	C67—C61—C66—C65	−174.55 (14)
N4—C5—C51—C52	−44.16 (18)	C72—N71—C71—O71	−168 (6)
C6—C5—C51—C52	73.48 (16)	C73—N71—C71—O71	21 (9)
N4—C5—C51—C56	138.98 (14)	C82—N81—C81—O81	167 (7)
C6—C5—C51—C56	−103.38 (15)	C83—N81—C81—O81	−26 (11)
C56—C51—C52—C53	1.8 (2)		

Hydrogen-bond geometry (Å, º)

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
N4—H4···N3^{i}	0.91	2.32	3.1188 (19)	146
O24—H24···O71	0.92	1.75	2.67 (3)	179
O24—H24···O81	0.92	1.78	2.69 (3)	174
C5—H5···O67^{ii}	1.00	2.55	3.4844 (19)	155
C56—H56···O67^{ii}	0.95	2.43	3.3080 (18)	153

Symmetry codes: (i) $-x+1, -y+1, -z+1$; (ii) $-x+1, y+1/2, -z+1/2$.