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Monoclinic and orthorhombic forms of (*RS*)-(*E*)-4-[2-(4-chlorobenzylidene)hydrazinyl]-6,11-dimethyl-6,11-dihydro-5*H*-benzo[*b*]pyrimido[5,4-*f*]azepine: synthesis, concomitant polymorphism and supramolecular assembly mediated by C—H $\cdots$ N, C—H $\cdots\pi$ (arene) and C—Cl $\cdots\pi$ (arene) interactions

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The title compound, C₂₁H₂₀ClN₅, has been synthesized in two steps from (*RS*)-4-chloro-6,11-dimethyl-6,11-dihydro-5*H*-benzo[*b*]pyrimido[5,4-*f*]azepine and characterized by ¹H and ¹³C NMR spectroscopy and by high-resolution mass spectrometry. Crystallization from hexane–ethyl acetate yields approximately equal quantities of a monoclinic polymorph in the space group *Cc*, (I), and an orthorhombic polymorph in the space group *Pna*2₁, (II). The molecules in polymorphs (I) and (II) show small differences in their molecular conformations, particularly in the shape of the azepine ring and the orientation of the chlorophenyl substituent. The molecules in polymorph (I) are linked by C—H $\cdots$ N and C—H $\cdots\pi$ (arene) hydrogen bonds to form sheets, which are linked into a three-dimensional framework structure by C—Cl $\cdots\pi$ (arene) interactions. There are no C—Cl $\cdots\pi$ (arene) interactions between the molecules in polymorph (II) and the supramolecular assembly takes the form of sheets built from C—H $\cdots$ N and C—H $\cdots\pi$ (arene) hydrogen bonds. Comparisons are made with some related structures.

1. Introduction

Pyrimidines and fused pyrimidines, particularly those compounds containing a pyrimidine unit fused to another heterocyclic ring, constitute a privileged class of structural motifs which are of great interest in the design and discovery of novel compounds exhibiting a wide range of biological and medicinal activities (Costantino & Barlocco, 2006; Gillespie *et al.*, 2008; Kumar *et al.*, 2009; Guetzoyan *et al.*, 2010; Le Corre *et al.*, 2010; Baraldi *et al.*, 2012; DeNinno *et al.*, 2012; Giles *et al.*, 2012; Awadallah *et al.*, 2013; Gangjee *et al.*, 2013). In addition, hydrazones, the condensation products of either hydrazine or an arylhydrazine with carbonyl compounds, also represent valuable intermediates which have been extensively used in medicinal chemistry as building blocks for novel compounds having significant pharmacological properties, including anticancer (Islam *et al.*, 2017), antifungal and antioxidant (Kauthale *et al.*, 2017), antimycobacterial (Angelova *et al.*, 2017), insecticidal (Yang *et al.*, 2016) and leishmanicidal and trypanocidal (Coa *et al.*, 2015) activities, as well as action against the hepatitis C virus (Şenkardes *et al.*, 2016).

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On this basis, compounds which contain both a pyrimidine fused to another heterocycle and a hydrazone functionality represent attractive synthetic targets, both in their own right as bioactive species and as building blocks for the elaboration of more complex bioactive molecules; indeed, it has been shown

recently that compounds of this type exhibit sphingosine kinase 1 inhibitory activity (Vettorazzi *et al.*, 2017). As part of a continuing study of the rational use of substituted 3-allyl-2,4-dichloropyrimidines as appropriate precursors for the construction of novel fused pyrimidine systems, we have recently described a simple and efficient two-step synthetic route to obtain polysubstituted 4-chloro-6,11-dihydro-5H-benzo[b]pyrimido[5,4-f]azepines starting from these simple precursors (Acosta-Quintero *et al.*, 2015). We report here the synthesis, characterization and structure of (*RS*)-(*E*)-4-[2-(4-chlorobenzylidene)hydrazinyl]-6,11-dimethyl-6,11-dihydro-5H-benzo[b]pyrimido[5,4-f]azepine, which was prepared starting from (*RS*)-4-chloro-6,11-dimethyl-6,11-dihydro-5H-benzo[b]pyrimido[5,4-f]azepine.

2. Experimental

2.1. Synthesis and crystallization

For the synthesis of polymorphs (I) and (II), hydrazine monohydrate (150.2 mg, 0.15 ml, 3.0 mmol) was added to a

stirred solution of (*RS*)-4-chloro-6,11-dimethyl-6,11-dihydro-5H-benzo[b]pyrimido[5,4-f]azepine [(A); Acosta-Quintero *et al.*, 2015] (100 mg, 0.39 mmol) in ethanol (10 ml). This mixture was heated under reflux for 24 h and then the solvent and the excess of hydrazine were removed under reduced pressure. The solid product, 6,11-dimethyl-4-hydrazinyl-6,11-dihydro-5H-benzo[b]pyrimido[5,4-f]azepine, (B), was washed with water (2×50 ml), dried in air and used without further

Scheme 2

purification in the next step. 4-Chlorobenzaldehyde (68.3 mg, 0.49 mmol) and two drops of glacial acetic acid were added to a solution of intermediate (B) (99.6 mg, 0.39 mmol) in ethanol (3 ml). This mixture was heated under reflux for 4 h and then the solvent was removed under reduced pressure. The resulting crude product was purified by silica-gel column chromatography using hexane–ethyl acetate (50:50 v/v) as eluent to give the product (*RS*)-(*E*)-4-[2-(4-chlorobenzylidene)hydrazinyl]-6,11-dimethyl-6,11-dihydro-5H-benzo[b]pyrimido[5,4-f]azepine as a colourless solid [yield 96 mg, 66%; m.p. > 423 K (decomposition); $R_F = 0.43$ (33% ethyl acetate in hexane)]. NMR ($CDCl_3$): $\delta(^1H)$ 1.47 (d, $J = 7.0$ Hz, 3H, CH_3 -6), 2.68 (dd, $J = 15.6, 11.2$ Hz, 1H, H_{B-5}), 2.90 (dd, $J = 15.6, 2.2$ Hz, 1H, H_{A-5}), 3.52 (s, 3H, CH_3 -11), 3.67–3.75 (m, 1H, H-6), 7.13–7.19 (m, 2H, H-8, H-10), 7.22–7.27 (m, 2H, H-7, H-9), 7.31 (d, $J = 8.4$ Hz, 2H, H-3', H-5'), 7.58 (d, $J = 8.4$ Hz, 2H, H-2', H-6'), 7.79 (br s, 1H, $-N=CH$), 8.00 (br s, 1H,

Table 1

Experimental details.

For all structures: $C_{21}H_{30}ClN_5$, $M_r = 377.87$, $Z = 4$. Experiments were carried out at 100 K with Cu $K\alpha$ radiation using a Bruker D8 Venture. Absorption was corrected for by multi-scan methods (SADABS; Bruker, 2015). Refinement was on 250 parameters. H atoms were treated by a mixture of independent and constrained refinement.

	(I)	(II)
Crystal data		
Crystal system, space group	Monoclinic, Cc	Orthorhombic, $Pna2_1$
a, b, c (Å)	12.9010 (15), 20.055 (3), 8.7001 (13)	8.8623 (4), 14.4656 (7), 14.2723 (7)
α, β, γ (°)	90, 123.161 (7), 90	90, 90, 90
V (Å ³)	1884.4 (5)	1829.69 (15)
μ (mm ⁻¹)	1.91	1.97
Crystal size (mm)	0.11 × 0.10 × 0.06	0.12 × 0.12 × 0.07
Data collection		
T_{min}, T_{max}	0.707, 0.892	0.726, 0.871
No. of measured, independent and observed [$I > 2\sigma(I)$] reflections	11068, 3280, 2886	22910, 3083, 2669
R_{int}	0.063	0.062
$(\sin \theta/\lambda)_{max}$ (Å ⁻¹)	0.598	0.597
Refinement		
$R[F^2 > 2\sigma(F^2)], wR(F^2), S$	0.042, 0.105, 1.05	0.037, 0.089, 1.06
No. of reflections	3280	3083
No. of restraints	2	1
$\Delta\rho_{max}, \Delta\rho_{min}$ (e Å ⁻³)	0.26, -0.29	0.29, -0.23
Absolute structure	Flack x determined using 1264 quotients $[(I^+) - (I^-)]/$ $[(I^+) + (I^-)]$ (Parsons <i>et al.</i> , 2013)	Flack x determined using 1075 quotients $[(I^+) - (I^-)]/$ $[(I^+) + (I^-)]$ (Parsons <i>et al.</i> , 2013)
Absolute structure parameter	0.011 (11)	0.048 (9)

Computer programs: APEX2 (Bruker, 2014), SAINT (Bruker, 2013), SIR92 (Altomare *et al.*, 1994), SHELXL2014 (Sheldrick, 2015) and PLATON (Spek, 2009).

NH-4), 8.38 (s, 1H, H-2); $\delta(^{13}C)$ 18.8 (CH₃-6), 32.4 (C-6), 38.7 (C-5), 39.9 (CH₃-11), 98.6 (C-4a), 122.2 (C-10), 123.9 (C-7), 124.9 (C-8), 126.9 (C-9), 128.2 (C-2', C-6'), 128.9 (C-3', C-5'), 132.6 (C-1'), 135.2 (C-4'), 140.4 (C-6a), 141.4 (N=CH), 146.4 (C-10a), 154.5 (C-2), 157.9 (C-4), 160.2 (C-11a). HRMS (EI-MS) m/z found 375.1242 [$M - 2$]⁺, $C_{21}H_{18}^{35}ClN_5$ requires 375.1251. 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 hexane–ethyl acetate (50:50 v/v) derived from the chromatographic purification. Careful examination of the crystalline product showed the presence of two types of crystal, characterized by small differences in their crystal habits, *i.e.* one is slightly more needle-like and the other slightly more block-like. These two types were separated manually and an example of each type, coincidentally having very similar crystal dimensions (Table 1), was selected for data collection; the first type had the monoclinic space group Cc and is denoted as polymorph (I), and the other had the orthorhombic space group $Pna2_1$ and is denoted as polymorph (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. H atoms bonded to C atoms were subsequently treated as riding atoms in geometrically idealized positions, with C–H = 0.95 (aromatic and heteroaromatic), 0.98 (CH₃), 0.99 (CH₂) or 1.00 Å (aliphatic C–H), and with

$U_{iso}(H) = kU_{eq}(C)$, where $k = 1.5$ for the methyl groups which were allowed to rotate but not to tilt, and 1.2 for all other H atoms. For the H atoms bonded to N atoms, the atomic coordinates were refined with $U_{iso}(H) = 1.2U_{eq}(N)$, giving the N–H distances shown in Table 2. In the refinement of polymorph (II), one bad outlier reflection, *i.e.* 730, was omitted from the data set prior to the final refinements. For both polymorphs, the correct orientation of the structure with respect to the directions of the polar axes was determined using the Flack x parameter (Flack, 1983), calculated using quotients of the type $[(I^+) - (I^-)]/[(I^+) + (I^-)]$ (Parsons *et al.*, 2013). For monoclinic polymorph (I), the use of 1264 such quotients gave $x = 0.011$ (11) and for orthorhombic polymorph (II), the use of 1075 quotients gave $x = 0.048$ (9). The corresponding values of the Hooft y parameter (Hooft *et al.*, 2008) were $y = 0.007$ (12) for (I) and $y = 0.049$ (10) for (II).

3. Results and discussion

The synthesis of the title compound started with precursor (A). (RS)-4-Chloro-6,11-dimethyl-6,11-dihydro-5H-benzo[*b*]-pyrimido[5,4-*f*]azepine (see Scheme 1), whose synthesis (Acosta-Quintero *et al.*, 2015) and structure (Acosta *et al.*, 2015) were reported several years ago. Reaction of this precursor with hydrazine hydrate gives the hydrazino intermediate (B), by means of a nucleophilic substitution reaction, and, in a second reaction step, intermediate (B) undergoes an acid-catalysed condensation reaction with 4-chlorobenzaldehyde to give the title compound. The composition of the title

Table 2

Hydrogen-bond parameters ($\text{\AA}$, $^\circ$) for (I) and (II). $Cg1$ and $Cg2$ represent the centroids of the C6A/C7–C10/C10A and C431–C436 rings, respectively.

Compound	$D-H\cdots A$	$D-H$	$H\cdots A$	$D\cdots A$	$D-H\cdots A$
(I)	$N41-H41\cdots N3^i$	0.88 (4)	2.39 (5)	3.207 (5)	155 (4)
	$C5-H5A\cdots N42^i$	0.99	2.61	3.504 (7)	150
	$C43-H43\cdots N3^i$	0.95	2.45	3.295 (5)	148
	$C433-H433\cdots Cg1^{ii}$	0.95	2.68	3.378 (5)	131
(II)	$N41-H41\cdots N3^{iii}$	0.96 (4)	2.20 (4)	3.064 (4)	149 (3)
	$C43-H43\cdots N3^{iii}$	0.95	2.53	3.223 (4)	130
	$C6-H6\cdots Cg2^{iv}$	1.00	2.54	3.496 (3)	161

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

compound was confirmed by high-resolution mass spectrometry and its constitution was fully established from the 1H and ^{13}C NMR spectra (§2.1 above).

Crystallization of the title compound from hexane–ethyl acetate (50:50 v/v) yielded two types of crystal, in approximately equal abundance, having monoclinic space group Cc for polymorph (I) and orthorhombic space group $Pna2_1$ for polymorph (II) (Figs. 1 and 2). These two forms are thus concomitant polymorphs (Bernstein *et al.*, 1999; Bernstein, 2011) and their formation in approximately equal quantities requires both that their energies are very similar and that their rates of crystallization are very similar.

Although the two polymorphs crystallize in unit cells having similar volumes (Table 1) and each containing four molecules, there is no obvious relationship between the unit-cell dimensions of the two forms, regardless of whether the monoclinic polymorph is considered in the conventional Cc setting of space group No. 9 or in the alternative Ia setting; in particular, the unit-cell repeat vector b in the monoclinic form has no

Figure 1

The molecular structure of monoclinic polymorph (I), showing the atom-labelling scheme. Displacement ellipsoids are drawn at the 50% probability level.

Table 3

Selected geometric parameters ($\text{\AA}$, $^\circ$) for (I) and (II).

'Dihedral 1' represents the dihedral angle between the two rings fused to the azepine ring and 'dihedral 2' represents the dihedral angle between the pyrimidine ring and the chlorinated C431–C436 ring. Ring-puckering angles are calculated for the atom sequence N11–C10A–C6A–C6–C5–C4A–C11A.

Parameter	(I)	(II)
Torsion and dihedral angles		
$C4-N41-N42-C43$	177.2 (3)	−161.9 (3)
$N41-N42-C43-C431$	−177.9 (3)	−176.3 (3)
$N42-C43-C431-C432$	−1.4 (6)	14.0 (5)
Dihedral 1	65.35 (13)	50.60 (10)
Dihedral 2	16.64 (19)	36.26 (12)
Ring-puckering parameters		
Q	0.935 (5)	0.824 (3)
φ_2	31.8 (3)	37.9 (2)
φ_3	293.6 (10)	290.1 (6)

match in the orthorhombic form. The orthorhombic form has the higher density (Table 1) and for all of the hydrogen-bond types which the two polymorphs exhibit in common, the donor–acceptor ($D\cdots A$) distances are always shorter in the orthorhombic form (Table 2), thus accounting, at least in part, for the higher density of this form and suggesting that this polymorph is the more stable (Nelyubina *et al.*, 2010).

There is a stereogenic centre at atom C6 (Figs. 1 and 2) and, for each polymorph, the reference molecule was selected to be that having the *R* configuration at atom C6; the space groups confirm that the each polymorph has crystallized as a racemic mixture. The conformations of the molecules in the two forms differ slightly (Table 3); firstly, the orientation of the chlorinated ring relative to the adjacent pyrimidine ring differs, as

Figure 2

The molecular structure of orthorhombic polymorph (II), showing the atom-labelling scheme. Displacement ellipsoids are drawn at the 50% probability level.

Table 4

Geometric parameters ($\text{\AA}$, $^\circ$) for the $\text{C}-\text{Cl}\cdots\pi$ interaction in monoclinic polymorph (I).

$Cg2$ represents the centroid of the C431–C436 ring.

$\text{C}-\text{Cl}\cdots Cg$	$\text{C}-\text{Cl}$	$\text{Cl}\cdots Cg$	$\text{C}\cdots Cg$	$\text{C}-\text{Cl}\cdots Cg$
$\text{C434}-\text{Cl4}\cdots Cg2^i$	1.747 (4)	3.731 (3)	5.1356 (5)	136.1 (2)(4)

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

indicated in particular by the N42–C43–C431–C432 torsion angles and by the dihedral angles between the planes of the pyrimidine and chlorinated aryl rings. Secondly, the dihedral angles between the two rings fused to the central azepine unit differ by *ca* 15° ; this reflects the different conformations of the azepine ring in the two polymorphs. In monoclinic polymorph (I), the azepine ring adopts a conformation intermediate between the boat and twist-boat forms, whereas in orthorhombic polymorph (II), the conformation is dominated by the twist-boat form, with minor influences from the chair and twist-chair forms (Boessenkool & Boeyens, 1980; Evans & Boeyens, 1989).

The differences in the molecular conformations may perhaps be traceable to the differences in the direction-specific intermolecular interactions involving the aryl rings, as discussed in detail below. Thus, the fused C6A/C7–C10/C10A

aryl ring acts as a hydrogen-bond acceptor in polymorph (I) but not in polymorph (II). Similarly, the chlorinated C431–C436 aryl ring is involved in a $\text{C}-\text{H}\cdots\pi(\text{arene})$ hydrogen bond in polymorph (II), although not in polymorph (I). On the other hand, this ring is involved in a $\text{C}-\text{Cl}\cdots\pi(\text{arene})$ interaction in polymorph (I), although not in polymorph (II). Interactions of this type have been shown (Imai *et al.*, 2008) to be attractive and to be primarily electrostatic in origin.

The supramolecular assembly in monoclinic polymorph (I) is three-dimensional (3D), mediated by $\text{C}-\text{H}\cdots\text{N}$ and $\text{C}-\text{H}\cdots\pi(\text{arene})$ hydrogen bonds and $\text{C}-\text{Cl}\cdots\pi(\text{arene})$ interactions (Tables 2 and 4), but the formation of the 3D framework structure is readily analyzed in terms of simple substructures of lower dimensionality (Ferguson *et al.*, 1998*a,b*; Gregson *et al.*, 2000). Molecules of (I) which are related by the *c*-glide plane at $y = \frac{1}{2}$ are linked by the combined action of the two hydrogen bonds having atom N3 as the acceptor to form a $C(4)C(6)[R_2^1(6)]$ chain of rings (Etter, 1990; Etter *et al.*, 1990; Bernstein *et al.*, 1995) running parallel to the [001] direction (Fig. 3). The formation of this chain is weakly reinforced by a rather long hydrogen bond having atom N42 as the acceptor. A second substructure can be identified in which molecules, also related to one another by the *c*-glide plane at $y = \frac{1}{2}$, are linked by a $\text{C}-\text{H}\cdots\pi(\text{arene})$ hydrogen bond to form a chain running parallel to the [203] direction

Figure 3

Part of the crystal structure of monoclinic polymorph (I), showing the formation of a hydrogen-bonded chain of rings running parallel to the [001] direction. Hydrogen bonds are shown as dashed lines and, for the sake of clarity, H atoms not involved in the motif shown have been omitted. The Cl atoms marked with an asterisk (*), a hash (#), a dollar sign (\$) or an ampersand (&) are at the symmetry positions $(x, -y + 1, z + \frac{1}{2})$, $(x, -y + 1, z - \frac{1}{2})$, $(x, y, z + 1)$ and $(x, y, z - 1)$, respectively.

Figure 4

Part of the crystal structure of polymorph (I), showing the formation of a hydrogen-bonded chain running parallel to the [203] direction. Hydrogen bonds are shown as dashed lines and, for the sake of clarity, H atoms not involved in the motif shown have been omitted. The Cl atoms marked with an asterisk (*), a hash (#), a dollar sign (\$) or an ampersand (&) are at the symmetry positions $(x - 1, -y + 1, z - \frac{3}{2})$, $(x + 1, -y + 1, z + \frac{3}{2})$, $(x - 2, y, z - 3)$ and $(x + 2, y, z + 3)$, respectively.

Figure 5

A projection down [010] of part of the crystal structure of polymorph (I), showing the formation of a hydrogen-bonded sheet lying parallel to (010). Hydrogen bonds are shown as dashed lines and, for the sake of clarity, H atoms not involved in the motif shown have been omitted.

(Fig. 4). The combination of these two chain motifs generates a complex sheet lying parallel to (010) and occupying the domain $\frac{1}{4} < y < \frac{3}{4}$ (Fig. 5). A second sheet of this type, related to the first by the C-centring operation, lies in the domain $-\frac{1}{4} < y < \frac{1}{4}$, and adjacent sheets are linked by the C—Cl $\cdots$ π (arene) interaction (Table 4; cf. Imai *et al.*, 2008). This interaction links molecules related by the *n*-glide plane at $y = \frac{1}{4}$ to form a chain running parallel to the [101] direction (Fig. 6), where alternate molecules lie in different hydrogen-bonded sheets; propagation of this interaction by the space group thus links all the sheets into a single 3D framework structure.

Figure 6

Part of the crystal structure of polymorph (I), showing the formation of a chain running parallel to the [101] direction and built from C—Cl $\cdots$ π (arene) interactions. The Cl $\cdots$ π contacts are shown as tapered lines and, for the sake of clarity, H atoms have all been omitted. The Cl atoms marked with an asterisk (*), a hash (#), a dollar sign (\$) or an ampersand (&) are at the symmetry positions $(x - \frac{1}{2}, -y + \frac{1}{2}, z - \frac{1}{2})$, $(x + \frac{1}{2}, -y + \frac{1}{2}, z + \frac{1}{2})$, $(x - 1, y, z - 1)$ and $(x + 1, y, z + 1)$, respectively.

Figure 7

Part of the crystal structure of orthorhombic polymorph (II), showing the formation of a hydrogen-bonded chain of rings running parallel to the [100] direction. Hydrogen bonds are shown as dashed lines and, for the sake of clarity, H atoms not involved in the motif shown have been omitted. The Cl atoms marked with an asterisk (*), a hash (#), a dollar sign (\$) or an ampersand (&) are at the symmetry positions $(x - \frac{1}{2}, -y + \frac{1}{2}, z)$, $(x + \frac{1}{2}, -y + \frac{1}{2}, z)$, $(x - 1, y, z)$ and $(x + 1, y, z)$, respectively.

There are no C—Cl $\cdots$ π (arene) interactions in the structure of orthorhombic polymorph (II), so that the two-dimensional (2D) supramolecular structure is built solely from hydrogen bonds, one each of the N—H $\cdots$ N, C—H $\cdots$ N and C—H $\cdots$ π (arene) types (Table 2). As in polymorph (I), the two hydrogen bonds having atom N3 as the acceptor form a $C(4)C(6)[R_2^1(6)]$ chain of rings, this time comprising molecules related by the *a*-glide plane at $y = \frac{1}{4}$ and running parallel to the [100] direction (Fig. 7). The C—H $\cdots$ π (arene) hydrogen bond links molecules which are related by the *n*-glide plane at $x = \frac{1}{4}$ to form a chain running parallel to the [011] direction (Fig. 8). The combination of chain motifs along [100] and [011] generates a rather complex sheet lying parallel to (01 $\bar{1}$), but there are no direction-specific interactions between adjacent sheets. Hence, the supramolecular assembly in the orthorhombic polymorph (II) is 2D, in contrast to the 3D assembly in monoclinic polymorph (I).

It is of interest briefly to compare the supramolecular assemblies in polymorphs (I) and (II) with those in some related compounds. In the structure of the precursor compound (A) (see Scheme 1), there are no hydrogen bonds of any kind, but instead inversion-related pairs molecules are linked into centrosymmetric dimers by a π – π stacking interaction involving pyrimidine rings (Acosta *et al.*, 2015); this structure also contains a C—Cl $\cdots$ π (pyrimidine) contact, again between inversion-related pairs of molecules. Compound (III) (see Scheme 2) is a hydrolysis product of the precursor (A) and inversion-related pairs molecules are linked by N—H $\cdots$ O hydrogen bonds to form centrosymmetric $R_2^2(8)$ dimers which

Figure 8

Part of the crystal structure of polymorph (II), showing the formation of a hydrogen-bonded chain running parallel to the [011] direction. Hydrogen bonds are shown as dashed lines and, for the sake of clarity, H atoms not involved in the motif shown have been omitted.

are themselves linked by C—H...N hydrogen bonds to form sheets containing equal numbers of $R_2^2(8)$ and $R_6^6(24)$ rings (Acosta Quintero, Palma *et al.*, 2016). In the structure of the *N*-methyl-*N*-phenylamino derivative, (IV), the only direction-specific interaction between the molecules is a C—H... π (pyrimidine) hydrogen bond, which links the molecules into simple chains (Acosta Quintero *et al.*, 2018). Finally, we note the tetracyclic analogues (V) and (VI) (Acosta Quintero, Burgos *et al.*, 2016) of the precursor compound (A). In (V), molecules are linked into chains by a C—H...N hydrogen bond, and inversion-related pairs of chains are linked by a π – π stacking interaction; by contrast, the molecules of (VI) are linked into sheets by a combination of a C—H... π (pyrimidine) hydrogen bond and two independent C—Cl... π interactions.

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supporting information

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Monoclinic and orthorhombic forms of (RS)-(E)-4-[2-(4-chlorobenzylidene)hydrazinyl]-6,11-dimethyl-6,11-dihydro-5H-benzo[*b*]pyrimido[5,4-*f*]azepine: synthesis, concomitant polymorphism and supramolecular assembly mediated by C—H $\cdots$ N, C—H $\cdots$ π (arene) and C—Cl $\cdots$ π (arene) interactions

Lina M. Acosta Quintero, Alirio Palma, Duane Choquesillo-Lazarte, Justo Cobo and Christopher Glidewell

Computing details

For both structures, data collection: *APEX2* (Bruker, 2014); cell refinement: *SAINT* (Bruker, 2013); data reduction: *SAINT* (Bruker, 2013); program(s) used to solve structure: *SIR92* (Altomare *et al.*, 1994); program(s) used to refine structure: *SHELXL2014* (Sheldrick, 2015); molecular graphics: *PLATON* (Spek, 2009); software used to prepare material for publication: *SHELXL2014* (Sheldrick, 2015) and *PLATON* (Spek, 2009).

(RS)-(E)-4-[2-(4-Chlorobenzylidene)hydrazinyl]-6,11-dimethyl-6,11-dihydro-5H-benzo[*b*]pyrimido[5,4-*f*]azepine (I)

Crystal data

C₂₁H₂₀ClN₅

M_r = 377.87

Monoclinic, *Cc*

a = 12.9010 (15) Å

b = 20.055 (3) Å

c = 8.7001 (13) Å

β = 123.161 (7)°

V = 1884.4 (5) Å³

Z = 4

F(000) = 792

D_x = 1.332 Mg m⁻³

Cu *K* α radiation, λ = 1.54178 Å

Cell parameters from 3250 reflections

θ = 4.4–67.2°

μ = 1.91 mm⁻¹

T = 100 K

Plate, colourless

0.11 × 0.10 × 0.06 mm

Data collection

Bruker D8 Venture
diffractometer

Radiation source: INCOATEC high brilliance
microfocus sealed tube

Multilayer mirror monochromator

φ and ω scans

Absorption correction: multi-scan
(SADABS; Bruker, 2015)

T_{min} = 0.707, *T_{max}* = 0.892

11068 measured reflections

3280 independent reflections

2886 reflections with *I* > 2 σ (*I*)

R_{int} = 0.063

θ_{max} = 67.2°, θ_{min} = 4.4°

h = -15→15

k = -23→23

l = -10→10

*Refinement*Refinement on F^2

Least-squares matrix: full

 $R[F^2 > 2\sigma(F^2)] = 0.042$ $wR(F^2) = 0.105$ $S = 1.05$

3280 reflections

250 parameters

2 restraints

Primary atom site location: difference Fourier
map

Hydrogen site location: mixed

H atoms treated by a mixture of independent
and constrained refinement $w = 1/[\sigma^2(F_o^2) + (0.0435P)^2 + 0.640P]$ where $P = (F_o^2 + 2F_c^2)/3$ $(\Delta/\sigma)_{\max} < 0.001$ $\Delta\rho_{\max} = 0.26 \text{ e } \text{\AA}^{-3}$ $\Delta\rho_{\min} = -0.29 \text{ e } \text{\AA}^{-3}$

Extinction correction: SHELXL2014

(Sheldrick, 2015),

 $F_c^* = kF_c[1 + 0.001 \times F_c^2 \lambda^3 / \sin(2\theta)]^{-1/4}$

Extinction coefficient: 0.0033 (5)

Absolute structure: Flack x determined using1264 quotients $[(I^+)-(I^-)]/[(I^+)+(I^-)]$ (Parsons *et al.*, 2013)

Absolute structure parameter: 0.011 (11)

Special details

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

Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters ($\text{\AA}^2$)

	x	y	z	$U_{\text{iso}}^*/U_{\text{eq}}$
N1	0.5994 (3)	0.66938 (16)	0.4852 (5)	0.0322 (8)
C2	0.5047 (4)	0.6376 (2)	0.3464 (5)	0.0304 (9)
H2	0.4738	0.6560	0.2283	0.037*
N3	0.4468 (3)	0.58323 (17)	0.3493 (4)	0.0303 (8)
C4	0.4840 (3)	0.56256 (19)	0.5203 (5)	0.0272 (9)
C4A	0.5808 (3)	0.59193 (19)	0.6811 (5)	0.0264 (8)
C5	0.6061 (4)	0.5688 (2)	0.8646 (5)	0.0298 (9)
H5B	0.6215	0.5202	0.8744	0.036*
H5A	0.5302	0.5761	0.8644	0.036*
C6	0.7134 (4)	0.6016 (2)	1.0353 (6)	0.0303 (9)
H6	0.6987	0.6508	1.0241	0.036*
C6A	0.8297 (4)	0.58849 (19)	1.0391 (5)	0.0293 (9)
C7	0.9162 (4)	0.5405 (2)	1.1488 (6)	0.0359 (10)
H7	0.9036	0.5144	1.2283	0.043*
C8	1.0212 (4)	0.5298 (2)	1.1448 (6)	0.0411 (10)
H8	1.0783	0.4957	1.2180	0.049*
C9	1.0419 (4)	0.5690 (3)	1.0340 (7)	0.0452 (12)
H9	1.1158	0.5636	1.0361	0.054*
C10	0.9549 (4)	0.6165 (2)	0.9192 (6)	0.0404 (10)
H10	0.9684	0.6427	0.8407	0.049*
C10A	0.8489 (4)	0.6253 (2)	0.9200 (5)	0.0308 (9)
N11	0.7533 (3)	0.67116 (17)	0.7941 (5)	0.0339 (8)
C11A	0.6438 (4)	0.6435 (2)	0.6544 (5)	0.0289 (9)
N41	0.4196 (3)	0.50956 (17)	0.5290 (5)	0.0282 (7)
H41	0.437 (4)	0.496 (2)	0.637 (6)	0.034*
N42	0.3456 (3)	0.47120 (16)	0.3750 (4)	0.0279 (7)

C43	0.2932 (4)	0.42124 (19)	0.3977 (5)	0.0281 (9)
H43	0.3051	0.4142	0.5143	0.034*
C431	0.2160 (3)	0.37515 (19)	0.2485 (5)	0.0273 (8)
C432	0.1910 (4)	0.3823 (2)	0.0712 (6)	0.0324 (9)
H432	0.2276	0.4181	0.0457	0.039*
C433	0.1144 (4)	0.3382 (2)	−0.0670 (6)	0.0336 (9)
H433	0.0984	0.3436	−0.1866	0.040*
C434	0.0614 (4)	0.2864 (2)	−0.0296 (6)	0.0350 (10)
Cl4	−0.04196 (11)	0.23272 (5)	−0.20597 (16)	0.0488 (4)
C435	0.0849 (4)	0.2770 (2)	0.1440 (7)	0.0420 (11)
H435	0.0488	0.2407	0.1684	0.050*
C436	0.1622 (4)	0.3215 (2)	0.2820 (6)	0.0364 (10)
H436	0.1789	0.3153	0.4018	0.044*
C61	0.7195 (4)	0.5779 (2)	1.2067 (6)	0.0408 (10)
H61B	0.7283	0.5293	1.2162	0.061*
H61A	0.6433	0.5907	1.1983	0.061*
H61C	0.7907	0.5985	1.3156	0.061*
C111	0.7959 (5)	0.7324 (2)	0.7539 (6)	0.0466 (12)
H11A	0.8660	0.7508	0.8682	0.070*
H11C	0.7283	0.7649	0.6969	0.070*
H11B	0.8219	0.7223	0.6696	0.070*

Atomic displacement parameters (Å²)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
N1	0.035 (2)	0.0314 (18)	0.0330 (19)	0.0005 (15)	0.0206 (17)	0.0039 (15)
C2	0.031 (2)	0.032 (2)	0.027 (2)	−0.0020 (17)	0.0157 (18)	0.0018 (17)
N3	0.0325 (19)	0.0307 (18)	0.0297 (18)	0.0006 (15)	0.0183 (16)	0.0016 (15)
C4	0.023 (2)	0.030 (2)	0.032 (2)	0.0044 (16)	0.0171 (18)	0.0029 (17)
C4A	0.024 (2)	0.029 (2)	0.029 (2)	0.0007 (17)	0.0157 (18)	0.0005 (17)
C5	0.027 (2)	0.033 (2)	0.030 (2)	−0.0009 (17)	0.0161 (19)	0.0011 (17)
C6	0.032 (2)	0.031 (2)	0.031 (2)	−0.0015 (17)	0.0196 (19)	0.0011 (17)
C6A	0.025 (2)	0.031 (2)	0.030 (2)	−0.0031 (17)	0.0132 (18)	−0.0021 (17)
C7	0.031 (2)	0.035 (2)	0.035 (2)	−0.0024 (18)	0.014 (2)	−0.0018 (18)
C8	0.030 (2)	0.041 (2)	0.044 (3)	0.0067 (19)	0.016 (2)	−0.008 (2)
C9	0.029 (2)	0.064 (3)	0.045 (3)	−0.002 (2)	0.022 (2)	−0.014 (2)
C10	0.033 (2)	0.058 (3)	0.036 (2)	−0.010 (2)	0.022 (2)	−0.008 (2)
C10A	0.027 (2)	0.034 (2)	0.029 (2)	−0.0062 (17)	0.0139 (18)	−0.0036 (17)
N11	0.0336 (19)	0.0321 (19)	0.0304 (17)	−0.0067 (15)	0.0139 (16)	0.0012 (15)
C11A	0.028 (2)	0.031 (2)	0.029 (2)	−0.0032 (16)	0.0166 (19)	−0.0018 (17)
N41	0.0256 (18)	0.0329 (19)	0.0248 (17)	−0.0047 (14)	0.0129 (16)	−0.0009 (14)
N42	0.0215 (16)	0.0318 (18)	0.0275 (18)	−0.0004 (14)	0.0115 (15)	−0.0026 (14)
C43	0.025 (2)	0.032 (2)	0.031 (2)	0.0005 (17)	0.0182 (18)	0.0016 (18)
C431	0.0230 (19)	0.028 (2)	0.032 (2)	0.0030 (16)	0.0159 (18)	0.0047 (16)
C432	0.033 (2)	0.031 (2)	0.034 (2)	−0.0054 (17)	0.0182 (19)	0.0008 (18)
C433	0.031 (2)	0.034 (2)	0.031 (2)	−0.0020 (18)	0.0145 (19)	−0.0013 (18)
C434	0.030 (2)	0.025 (2)	0.043 (3)	0.0001 (17)	0.015 (2)	−0.0036 (18)
Cl4	0.0444 (7)	0.0354 (6)	0.0580 (7)	−0.0100 (5)	0.0225 (6)	−0.0138 (6)

C435	0.043 (3)	0.032 (2)	0.055 (3)	−0.011 (2)	0.029 (2)	−0.001 (2)
C436	0.038 (2)	0.035 (2)	0.042 (2)	−0.003 (2)	0.026 (2)	0.003 (2)
C61	0.042 (3)	0.050 (3)	0.033 (2)	−0.007 (2)	0.022 (2)	−0.002 (2)
C111	0.050 (3)	0.044 (3)	0.039 (3)	−0.019 (2)	0.020 (2)	0.003 (2)

Geometric parameters (Å, °)

N1—C2	1.320 (5)	C10A—N11	1.446 (5)
N1—C11A	1.358 (5)	N11—C11A	1.379 (5)
C2—N3	1.330 (5)	N11—C111	1.463 (5)
C2—H2	0.9500	N41—N42	1.378 (5)
N3—C4	1.354 (5)	N41—H41	0.88 (5)
C4—N41	1.377 (5)	N42—C43	1.283 (5)
C4—C4A	1.397 (5)	C43—C431	1.455 (6)
C4A—C11A	1.411 (5)	C43—H43	0.9500
C4A—C5	1.516 (5)	C431—C436	1.394 (5)
C5—C6	1.518 (6)	C431—C432	1.400 (5)
C5—H5B	0.9900	C432—C433	1.379 (6)
C5—H5A	0.9900	C432—H432	0.9500
C6—C6A	1.505 (5)	C433—C434	1.378 (6)
C6—C61	1.525 (6)	C433—H433	0.9500
C6—H6	1.0000	C434—C435	1.380 (6)
C6A—C7	1.384 (6)	C434—C14	1.747 (4)
C6A—C10A	1.400 (5)	C435—C436	1.387 (6)
C7—C8	1.390 (6)	C435—H435	0.9500
C7—H7	0.9500	C436—H436	0.9500
C8—C9	1.378 (7)	C61—H61B	0.9800
C8—H8	0.9500	C61—H61A	0.9800
C9—C10	1.392 (7)	C61—H61C	0.9800
C9—H9	0.9500	C111—H11A	0.9800
C10—C10A	1.383 (6)	C111—H11C	0.9800
C10—H10	0.9500	C111—H11B	0.9800
C2—N1—C11A	116.0 (3)	C11A—N11—C111	117.7 (3)
N1—C2—N3	128.8 (4)	C10A—N11—C111	116.0 (3)
N1—C2—H2	115.6	N1—C11A—N11	115.0 (3)
N3—C2—H2	115.6	N1—C11A—C4A	121.3 (4)
C2—N3—C4	114.0 (3)	N11—C11A—C4A	123.7 (3)
N3—C4—N41	115.8 (3)	C4—N41—N42	119.7 (3)
N3—C4—C4A	123.8 (3)	C4—N41—H41	119 (3)
N41—C4—C4A	120.4 (3)	N42—N41—H41	120 (3)
C4—C4A—C11A	115.1 (3)	C43—N42—N41	115.4 (3)
C4—C4A—C5	119.0 (3)	N42—C43—C431	121.3 (3)
C11A—C4A—C5	125.8 (3)	N42—C43—H43	119.3
C4A—C5—C6	117.0 (3)	C431—C43—H43	119.3
C4A—C5—H5B	108.0	C436—C431—C432	117.9 (4)
C6—C5—H5B	108.0	C436—C431—C43	118.7 (3)
C4A—C5—H5A	108.0	C432—C431—C43	123.4 (3)

C6—C5—H5A	108.0	C433—C432—C431	121.2 (4)
H5B—C5—H5A	107.3	C433—C432—H432	119.4
C6A—C6—C5	108.1 (3)	C431—C432—H432	119.4
C6A—C6—C61	114.0 (4)	C434—C433—C432	119.2 (4)
C5—C6—C61	110.7 (3)	C434—C433—H433	120.4
C6A—C6—H6	108.0	C432—C433—H433	120.4
C5—C6—H6	108.0	C433—C434—C435	121.4 (4)
C61—C6—H6	108.0	C433—C434—C14	119.7 (3)
C7—C6A—C10A	118.3 (3)	C435—C434—C14	118.8 (3)
C7—C6A—C6	123.7 (3)	C434—C435—C436	118.9 (4)
C10A—C6A—C6	118.0 (3)	C434—C435—H435	120.6
C6A—C7—C8	121.3 (4)	C436—C435—H435	120.6
C6A—C7—H7	119.4	C435—C436—C431	121.3 (4)
C8—C7—H7	119.4	C435—C436—H436	119.3
C9—C8—C7	119.6 (4)	C431—C436—H436	119.3
C9—C8—H8	120.2	C6—C61—H61B	109.5
C7—C8—H8	120.2	C6—C61—H61A	109.5
C8—C9—C10	120.2 (4)	H61B—C61—H61A	109.5
C8—C9—H9	119.9	C6—C61—H61C	109.5
C10—C9—H9	119.9	H61B—C61—H61C	109.5
C10A—C10—C9	119.6 (4)	H61A—C61—H61C	109.5
C10A—C10—H10	120.2	N11—C111—H11A	109.5
C9—C10—H10	120.2	N11—C111—H11C	109.5
C10—C10A—C6A	120.8 (4)	H11A—C111—H11C	109.5
C10—C10A—N11	120.9 (3)	N11—C111—H11B	109.5
C6A—C10A—N11	118.2 (3)	H11A—C111—H11B	109.5
C11A—N11—C10A	116.7 (3)	H11C—C111—H11B	109.5
C11A—N1—C2—N3	−0.3 (6)	C10—C10A—N11—C111	−36.3 (5)
N1—C2—N3—C4	6.9 (6)	C6A—C10A—N11—C111	145.6 (4)
C2—N3—C4—N41	175.1 (3)	C2—N1—C11A—N11	170.8 (3)
C2—N3—C4—C4A	−4.6 (5)	C2—N1—C11A—C4A	−9.0 (5)
N3—C4—C4A—C11A	−3.5 (5)	C10A—N11—C11A—N1	−133.2 (3)
N41—C4—C4A—C11A	176.8 (3)	C111—N11—C11A—N1	11.7 (5)
N3—C4—C4A—C5	174.2 (3)	C10A—N11—C11A—C4A	46.6 (5)
N41—C4—C4A—C5	−5.5 (5)	C111—N11—C11A—C4A	−168.5 (4)
C4—C4A—C5—C6	179.1 (3)	C4—C4A—C11A—N1	10.6 (5)
C11A—C4A—C5—C6	−3.5 (5)	C5—C4A—C11A—N1	−166.9 (4)
C4A—C5—C6—C6A	−59.8 (4)	C4—C4A—C11A—N11	−169.2 (3)
C4A—C5—C6—C61	174.7 (3)	C5—C4A—C11A—N11	13.3 (6)
C5—C6—C6A—C7	−101.8 (4)	N3—C4—N41—N42	15.6 (5)
C61—C6—C6A—C7	21.7 (6)	C4A—C4—N41—N42	−164.7 (3)
C5—C6—C6A—C10A	75.8 (4)	C4—N41—N42—C43	177.2 (3)
C61—C6—C6A—C10A	−160.7 (4)	N41—N42—C43—C431	−177.9 (3)
C10A—C6A—C7—C8	1.4 (6)	N42—C43—C431—C436	179.5 (4)
C6—C6A—C7—C8	179.0 (4)	N42—C43—C431—C432	−1.4 (6)
C6A—C7—C8—C9	2.1 (7)	C436—C431—C432—C433	0.9 (6)
C7—C8—C9—C10	−3.6 (7)	C43—C431—C432—C433	−178.2 (4)

C8—C9—C10—C10A	1.5 (7)	C431—C432—C433—C434	0.1 (6)
C9—C10—C10A—C6A	2.0 (6)	C432—C433—C434—C435	−1.1 (6)
C9—C10—C10A—N11	−176.0 (4)	C432—C433—C434—C14	176.8 (3)
C7—C6A—C10A—C10	−3.5 (6)	C433—C434—C435—C436	1.0 (6)
C6—C6A—C10A—C10	178.8 (4)	C14—C434—C435—C436	−176.9 (3)
C7—C6A—C10A—N11	174.7 (4)	C434—C435—C436—C431	0.1 (6)
C6—C6A—C10A—N11	−3.1 (5)	C432—C431—C436—C435	−1.0 (6)
C10—C10A—N11—C11A	109.3 (4)	C43—C431—C436—C435	178.2 (4)
C6A—C10A—N11—C11A	−68.9 (5)		

Hydrogen-bond geometry ($\text{\AA}$, $^\circ$)

$D\cdots H\cdots A$	$D\cdots H$	$H\cdots A$	$D\cdots A$	$D\cdots H\cdots A$
N41—H41 $\cdots$ N3 ⁱ	0.88 (4)	2.39 (5)	3.207 (5)	155 (4)
C5—H5A $\cdots$ N42 ⁱ	0.99	2.61	3.504 (7)	150
C43—H43 $\cdots$ N3 ⁱ	0.95	2.45	3.295 (5)	148
C433—H433 $\cdots$ Cg1 ⁱⁱ	0.95	2.68	3.378 (5)	131

Symmetry codes: (i) $x, -y+1, z+1/2$; (ii) $x-1, -y+1, z-3/2$.

(RS)-(E)-4-[2-(4-Chlorobenzylidene)hydrazinyl]-6,11-dimethyl-6,11-dihydro-5H-benzo[b]pyrimido[5,4-f]azepine (II)

Crystal data

$\text{C}_{21}\text{H}_{20}\text{ClN}_5$

$M_r = 377.87$

Orthorhombic, $Pna2_1$

$a = 8.8623$ (4) $\text{\AA}$

$b = 14.4656$ (7) $\text{\AA}$

$c = 14.2723$ (7) $\text{\AA}$

$V = 1829.69$ (15) $\text{\AA}^3$

$Z = 4$

$F(000) = 792$

$D_x = 1.372$ Mg m^{-3}

Cu $K\alpha$ radiation, $\lambda = 1.54178$ $\text{\AA}$

Cell parameters from 3084 reflections

$\theta = 4.4\text{--}67.0^\circ$

$\mu = 1.97$ mm^{-1}

$T = 100$ K

Plate, colourless

$0.12 \times 0.12 \times 0.07$ mm

Data collection

Bruker D8 Venture
diffractometer

Radiation source: INCOATEC high brilliance
microfocus sealed tube

Multilayer mirror monochromator
 φ and ω scans

Absorption correction: multi-scan
(SADABS; Bruker, 2015)

$T_{\min} = 0.726$, $T_{\max} = 0.871$

22910 measured reflections

3083 independent reflections

2669 reflections with $I > 2\sigma(I)$

$R_{\text{int}} = 0.062$

$\theta_{\max} = 66.9^\circ$, $\theta_{\min} = 4.4^\circ$

$h = -9 \rightarrow 10$

$k = -17 \rightarrow 17$

$l = -15 \rightarrow 16$

Refinement

Refinement on F^2

Least-squares matrix: full

$R[F^2 > 2\sigma(F^2)] = 0.037$

$wR(F^2) = 0.089$

$S = 1.06$

3083 reflections

250 parameters

1 restraint

Primary atom site location: difference Fourier
map

Hydrogen site location: mixed

H atoms treated by a mixture of independent
and constrained refinement

$$w = 1/[\sigma^2(F_o^2) + (0.0509P)^2]$$

$$\text{where } P = (F_o^2 + 2F_c^2)/3$$

$$(\Delta/\sigma)_{\max} < 0.001$$

$$\Delta\rho_{\max} = 0.29 \text{ e } \text{\AA}^{-3}$$

$$\Delta\rho_{\min} = -0.23 \text{ e } \text{\AA}^{-3}$$

Extinction correction: SHELXL,

$$F_c^* = k F_c [1 + 0.001 x F_c^2 \lambda^3 / \sin(2\theta)]^{-1/4}$$

Extinction coefficient: 0.0057 (6)

Absolute structure: Flack x determined using

1075 quotients $[(I^+)-(I^-)]/[(I^+)+(I^-)]$ (Parsons *et al.*, 2013)

Absolute structure parameter: 0.048 (9)

Special details

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

Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters ($\text{\AA}^2$)

	<i>x</i>	<i>y</i>	<i>z</i>	$U_{\text{iso}}^*/U_{\text{eq}}$
N1	0.6254 (3)	0.4527 (2)	0.6504 (2)	0.0276 (7)
C2	0.6661 (4)	0.4156 (2)	0.5697 (2)	0.0316 (8)
H2	0.7591	0.4371	0.5446	0.038*
N3	0.5950 (3)	0.35249 (19)	0.51894 (18)	0.0272 (7)
C4	0.4589 (4)	0.3292 (2)	0.5520 (2)	0.0249 (8)
C4A	0.3975 (4)	0.3621 (2)	0.6370 (2)	0.0252 (7)
C5	0.2391 (4)	0.3341 (2)	0.6622 (2)	0.0287 (8)
H5A	0.2395	0.2673	0.6772	0.034*
H5B	0.1748	0.3425	0.6061	0.034*
C6	0.1651 (4)	0.3856 (2)	0.7439 (2)	0.0280 (8)
H6	0.1737	0.4533	0.7308	0.034*
C6A	0.2487 (4)	0.3665 (2)	0.8338 (2)	0.0284 (8)
C7	0.1855 (5)	0.3138 (2)	0.9061 (3)	0.0337 (9)
H7	0.0893	0.2862	0.8975	0.040*
C8	0.2625 (5)	0.3013 (2)	0.9908 (3)	0.0361 (9)
H8	0.2185	0.2655	1.0395	0.043*
C9	0.4011 (4)	0.3408 (2)	1.0032 (3)	0.0361 (9)
H9	0.4524	0.3333	1.0611	0.043*
C10	0.4676 (5)	0.3918 (3)	0.9322 (3)	0.0338 (9)
H10	0.5644	0.4185	0.9415	0.041*
C10A	0.3925 (4)	0.4041 (2)	0.8469 (2)	0.0268 (8)
N11	0.4618 (3)	0.4585 (2)	0.7752 (2)	0.0269 (7)
C11A	0.4935 (4)	0.4224 (2)	0.6864 (2)	0.0245 (8)
N41	0.3745 (3)	0.27030 (18)	0.4969 (2)	0.0289 (6)
H41	0.274 (5)	0.253 (2)	0.514 (3)	0.035*
N42	0.4331 (3)	0.23699 (19)	0.41314 (19)	0.0277 (7)
C43	0.3317 (4)	0.2050 (2)	0.3577 (2)	0.0264 (8)
H43	0.2286	0.2097	0.3753	0.032*
C431	0.3700 (4)	0.1616 (2)	0.2683 (2)	0.0257 (8)
C432	0.5153 (5)	0.1333 (3)	0.2439 (3)	0.0290 (8)
H432	0.5966	0.1451	0.2857	0.035*
C433	0.5433 (4)	0.0887 (2)	0.1602 (2)	0.0299 (8)

H433	0.6427	0.0697	0.1443	0.036*
C434	0.4238 (4)	0.0719 (2)	0.0994 (2)	0.0295 (8)
Cl4	0.45257 (10)	0.01049 (6)	−0.00398 (7)	0.0372 (3)
C435	0.2793 (5)	0.0993 (2)	0.1208 (2)	0.0313 (8)
H435	0.1988	0.0876	0.0785	0.038*
C436	0.2525 (4)	0.1446 (2)	0.2059 (2)	0.0294 (8)
H436	0.1530	0.1640	0.2211	0.035*
C61	−0.0023 (5)	0.3618 (3)	0.7470 (3)	0.0311 (8)
H61A	−0.0502	0.3952	0.7989	0.047*
H61B	−0.0145	0.2952	0.7565	0.047*
H61C	−0.0498	0.3799	0.6878	0.047*
C111	0.5616 (4)	0.5329 (3)	0.8079 (3)	0.0337 (9)
H11A	0.5775	0.5775	0.7571	0.051*
H11C	0.6588	0.5067	0.8269	0.051*
H11B	0.5150	0.5643	0.8614	0.051*

Atomic displacement parameters (Å²)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
N1	0.0238 (17)	0.0353 (15)	0.0238 (15)	−0.0030 (13)	0.0007 (13)	−0.0023 (13)
C2	0.027 (2)	0.0346 (19)	0.033 (2)	−0.0032 (15)	0.0018 (16)	0.0028 (16)
N3	0.0212 (16)	0.0349 (15)	0.0257 (17)	−0.0033 (12)	0.0016 (12)	0.0017 (12)
C4	0.0206 (19)	0.0264 (17)	0.0275 (18)	−0.0001 (14)	−0.0022 (15)	0.0024 (15)
C4A	0.0247 (19)	0.0272 (16)	0.0238 (17)	0.0021 (14)	−0.0005 (15)	0.0018 (14)
C5	0.022 (2)	0.037 (2)	0.026 (2)	−0.0011 (15)	0.0008 (15)	−0.0001 (16)
C6	0.027 (2)	0.0320 (18)	0.0254 (18)	0.0005 (16)	0.0005 (16)	0.0006 (15)
C6A	0.030 (2)	0.0311 (18)	0.0242 (18)	0.0026 (16)	0.0024 (15)	0.0008 (15)
C7	0.035 (2)	0.0345 (19)	0.032 (2)	−0.0035 (17)	0.0017 (17)	0.0010 (16)
C8	0.046 (2)	0.0351 (18)	0.0273 (19)	0.0043 (16)	0.0028 (18)	0.0070 (19)
C9	0.042 (2)	0.044 (2)	0.0225 (18)	0.0095 (17)	−0.0022 (19)	0.0027 (18)
C10	0.029 (2)	0.045 (2)	0.0277 (19)	0.0009 (17)	−0.0028 (16)	−0.0058 (17)
C10A	0.027 (2)	0.0301 (18)	0.0228 (18)	0.0024 (15)	0.0005 (15)	0.0007 (15)
N11	0.0248 (17)	0.0318 (15)	0.0239 (16)	−0.0037 (13)	0.0000 (12)	−0.0040 (13)
C11A	0.0220 (19)	0.0285 (18)	0.0231 (18)	0.0021 (14)	0.0002 (14)	0.0005 (14)
N41	0.0236 (16)	0.0388 (15)	0.0242 (14)	−0.0023 (13)	0.0050 (14)	−0.0041 (15)
N42	0.0262 (18)	0.0323 (16)	0.0247 (16)	0.0000 (13)	0.0046 (13)	−0.0023 (13)
C43	0.0224 (18)	0.0313 (17)	0.0255 (19)	−0.0005 (15)	0.0037 (15)	0.0014 (15)
C431	0.026 (2)	0.0269 (18)	0.0238 (19)	−0.0019 (14)	0.0003 (15)	0.0028 (14)
C432	0.025 (2)	0.034 (2)	0.0275 (18)	−0.0010 (17)	0.0027 (16)	−0.0014 (16)
C433	0.026 (2)	0.0342 (19)	0.029 (2)	−0.0002 (15)	0.0051 (15)	0.0013 (15)
C434	0.036 (2)	0.0298 (19)	0.0230 (19)	0.0025 (16)	0.0051 (15)	0.0017 (16)
Cl4	0.0421 (6)	0.0447 (5)	0.0249 (4)	0.0037 (4)	0.0013 (5)	−0.0060 (4)
C435	0.036 (2)	0.0329 (18)	0.0253 (19)	0.0019 (16)	−0.0042 (16)	0.0025 (15)
C436	0.028 (2)	0.0338 (19)	0.0268 (18)	0.0022 (16)	0.0020 (16)	0.0011 (16)
C61	0.0257 (19)	0.040 (2)	0.0272 (17)	−0.0001 (19)	0.0022 (15)	−0.0020 (17)
C111	0.030 (2)	0.038 (2)	0.033 (2)	−0.0064 (17)	−0.0003 (17)	−0.0089 (17)

Geometric parameters (Å, °)

N1—C2	1.322 (5)	C10A—N11	1.430 (4)
N1—C11A	1.350 (5)	N11—C11A	1.400 (4)
C2—N3	1.324 (4)	N11—C111	1.469 (5)
C2—H2	0.9500	N41—N42	1.390 (4)
N3—C4	1.338 (4)	N41—H41	0.96 (4)
C4—N41	1.380 (4)	N42—C43	1.284 (4)
C4—C4A	1.413 (5)	C43—C431	1.461 (5)
C4A—C11A	1.408 (5)	C43—H43	0.9500
C4A—C5	1.505 (5)	C431—C436	1.393 (5)
C5—C6	1.531 (5)	C431—C432	1.396 (5)
C5—H5A	0.9900	C432—C433	1.381 (5)
C5—H5B	0.9900	C432—H432	0.9500
C6—C6A	1.507 (5)	C433—C434	1.390 (5)
C6—C61	1.523 (5)	C433—H433	0.9500
C6—H6	1.0000	C434—C435	1.375 (5)
C6A—C10A	1.398 (5)	C434—C14	1.741 (4)
C6A—C7	1.400 (5)	C435—C436	1.400 (5)
C7—C8	1.401 (5)	C435—H435	0.9500
C7—H7	0.9500	C436—H436	0.9500
C8—C9	1.366 (5)	C61—H61A	0.9800
C8—H8	0.9500	C61—H61B	0.9800
C9—C10	1.385 (5)	C61—H61C	0.9800
C9—H9	0.9500	C111—H11A	0.9800
C10—C10A	1.399 (5)	C111—H11C	0.9800
C10—H10	0.9500	C111—H11B	0.9800
C2—N1—C11A	115.9 (3)	C11A—N11—C111	116.1 (3)
N1—C2—N3	128.8 (3)	C10A—N11—C111	115.8 (3)
N1—C2—H2	115.6	N1—C11A—N11	113.4 (3)
N3—C2—H2	115.6	N1—C11A—C4A	122.3 (3)
C2—N3—C4	114.2 (3)	N11—C11A—C4A	124.3 (3)
N3—C4—N41	116.4 (3)	C4—N41—N42	120.1 (3)
N3—C4—C4A	124.4 (3)	C4—N41—H41	122 (2)
N41—C4—C4A	119.2 (3)	N42—N41—H41	118 (2)
C11A—C4A—C4	114.0 (3)	C43—N42—N41	113.1 (3)
C11A—C4A—C5	127.7 (3)	N42—C43—C431	122.0 (3)
C4—C4A—C5	118.3 (3)	N42—C43—H43	119.0
C4A—C5—C6	116.8 (3)	C431—C43—H43	119.0
C4A—C5—H5A	108.1	C436—C431—C432	118.6 (3)
C6—C5—H5A	108.1	C436—C431—C43	117.4 (3)
C4A—C5—H5B	108.1	C432—C431—C43	123.9 (3)
C6—C5—H5B	108.1	C433—C432—C431	121.3 (4)
H5A—C5—H5B	107.3	C433—C432—H432	119.4
C6A—C6—C61	114.4 (3)	C431—C432—H432	119.4
C6A—C6—C5	110.4 (3)	C432—C433—C434	119.0 (3)
C61—C6—C5	109.3 (3)	C432—C433—H433	120.5

C6A—C6—H6	107.5	C434—C433—H433	120.5
C61—C6—H6	107.5	C435—C434—C433	121.4 (3)
C5—C6—H6	107.5	C435—C434—C14	118.2 (3)
C10A—C6A—C7	118.5 (3)	C433—C434—C14	120.4 (3)
C10A—C6A—C6	119.4 (3)	C434—C435—C436	119.1 (4)
C7—C6A—C6	122.0 (3)	C434—C435—H435	120.5
C6A—C7—C8	120.8 (4)	C436—C435—H435	120.5
C6A—C7—H7	119.6	C431—C436—C435	120.7 (3)
C8—C7—H7	119.6	C431—C436—H436	119.6
C9—C8—C7	119.7 (4)	C435—C436—H436	119.6
C9—C8—H8	120.2	C6—C61—H61A	109.5
C7—C8—H8	120.2	C6—C61—H61B	109.5
C8—C9—C10	120.8 (4)	H61A—C61—H61B	109.5
C8—C9—H9	119.6	C6—C61—H61C	109.5
C10—C9—H9	119.6	H61A—C61—H61C	109.5
C9—C10—C10A	120.1 (4)	H61B—C61—H61C	109.5
C9—C10—H10	119.9	N11—C111—H11A	109.5
C10A—C10—H10	119.9	N11—C111—H11C	109.5
C6A—C10A—C10	120.1 (3)	H11A—C111—H11C	109.5
C6A—C10A—N11	120.6 (3)	N11—C111—H11B	109.5
C10—C10A—N11	119.2 (3)	H11A—C111—H11B	109.5
C11A—N11—C10A	121.9 (3)	H11C—C111—H11B	109.5
C11A—N1—C2—N3	0.0 (5)	C6A—C10A—N11—C111	147.7 (3)
N1—C2—N3—C4	5.2 (5)	C10—C10A—N11—C111	−29.8 (5)
C2—N3—C4—N41	174.1 (3)	C2—N1—C11A—N11	175.3 (3)
C2—N3—C4—C4A	−4.6 (5)	C2—N1—C11A—C4A	−6.1 (5)
N3—C4—C4A—C11A	−0.6 (5)	C10A—N11—C11A—N1	−141.9 (3)
N41—C4—C4A—C11A	−179.3 (3)	C111—N11—C11A—N1	9.3 (4)
N3—C4—C4A—C5	176.4 (3)	C10A—N11—C11A—C4A	39.6 (5)
N41—C4—C4A—C5	−2.2 (5)	C111—N11—C11A—C4A	−169.3 (3)
C11A—C4A—C5—C6	8.2 (5)	C4—C4A—C11A—N1	6.3 (5)
C4—C4A—C5—C6	−168.3 (3)	C5—C4A—C11A—N1	−170.4 (3)
C4A—C5—C6—C6A	−64.2 (4)	C4—C4A—C11A—N11	−175.2 (3)
C4A—C5—C6—C61	169.1 (3)	C5—C4A—C11A—N11	8.1 (6)
C61—C6—C6A—C10A	−165.6 (3)	N3—C4—N41—N42	1.4 (4)
C5—C6—C6A—C10A	70.6 (4)	C4A—C4—N41—N42	−179.8 (3)
C61—C6—C6A—C7	12.9 (5)	C4—N41—N42—C43	−161.9 (3)
C5—C6—C6A—C7	−110.9 (4)	N41—N42—C43—C431	−176.3 (3)
C10A—C6A—C7—C8	1.9 (5)	N42—C43—C431—C436	−168.5 (3)
C6—C6A—C7—C8	−176.5 (3)	N42—C43—C431—C432	14.0 (5)
C6A—C7—C8—C9	−0.1 (5)	C436—C431—C432—C433	−0.6 (5)
C7—C8—C9—C10	−1.2 (5)	C43—C431—C432—C433	176.9 (3)
C8—C9—C10—C10A	0.6 (5)	C431—C432—C433—C434	0.1 (5)
C7—C6A—C10A—C10	−2.5 (5)	C432—C433—C434—C435	0.3 (5)
C6—C6A—C10A—C10	176.0 (3)	C432—C433—C434—C14	−176.6 (3)
C7—C6A—C10A—N11	−179.9 (3)	C433—C434—C435—C436	−0.2 (5)
C6—C6A—C10A—N11	−1.4 (5)	C14—C434—C435—C436	176.8 (3)

C9—C10—C10A—C6A	1.3 (5)	C432—C431—C436—C435	0.7 (5)
C9—C10—C10A—N11	178.7 (3)	C43—C431—C436—C435	−176.9 (3)
C6A—C10A—N11—C11A	−61.1 (5)	C434—C435—C436—C431	−0.3 (5)
C10—C10A—N11—C11A	121.5 (4)		

Hydrogen-bond geometry (Å, °)

<i>D</i> —H $\cdots$ <i>A</i>	<i>D</i> —H	H $\cdots$ <i>A</i>	<i>D</i> $\cdots$ <i>A</i>	<i>D</i> —H $\cdots$ <i>A</i>
N41—H41 $\cdots$ N3 ⁱ	0.96 (4)	2.20 (4)	3.064 (4)	149 (3)
C43—H43 $\cdots$ N3 ⁱ	0.95	2.53	3.223 (4)	130
C6—H6 $\cdots$ Cg2 ⁱⁱ	1.00	2.54	3.496 (3)	161

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