

Three closely-related cyclohexanols ($C_{35}H_{27}X_2N_3O_3$; $X = F, Cl$ or Br): similar molecular structures but different crystal structures

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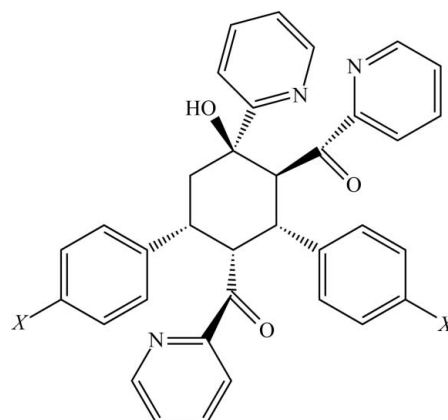
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Three highly-substituted cyclohexanol derivatives have been prepared from 2-acetylpyridine and 4-halogenobenzaldehydes under mild conditions. (1*RS*,2*SR*,3*SR*,4*RS*,5*RS*)-3,5-bis(4-fluorophenyl)-2,4-bis(pyridine-2-carbonyl)-1-(pyridin-2-yl)cyclohexanol, $C_{35}H_{27}F_2N_3O_3$, (I), (1*RS*,2*SR*,3*SR*,4*RS*,5*RS*)-3,5-bis(4-chlorophenyl)-2,4-bis(pyridine-2-carbonyl)-1-(pyridin-2-yl)cyclohexanol acetone 0.951-solvate, $C_{35}H_{27}Cl_2N_3O_3 \cdot 0.951C_3H_6O$, (II), and (1*RS*,2*SR*,3*SR*,4*RS*,5*RS*)-3,5-bis(4-bromophenyl)-2,4-bis(pyridine-2-carbonyl)-1-(pyridin-2-yl)cyclohexanol, $C_{35}H_{27}Br_2N_3O_3$, (III), all crystallize in different space groups, *viz.* *Pbca*, *Fdd2* and *P1*, respectively. In compound (II), the acetone molecule is disordered over two sets of atomic sites having occupancies of 0.690 (13) and 0.261 (13). Each of the cyclohexanol molecules contains an intramolecular O—H...N hydrogen bond and their overall molecular conformations are fairly similar. The molecules of (I) are linked by two independent C—H...O hydrogen bonds to form a $C(5)C(10)[R_2^2(15)]$ chain of rings, and those of (III) are linked by a combination of C—H...O and C—H...N hydrogen bonds, forming a chain of alternating $R_2^2(16)$ and $R_2^2(18)$ rings. The cyclohexanol molecules in (II) are linked by a single C—H...N hydrogen bond to form simple $C(4)$ chains and these chains are linked by a π – π stacking interaction to form sheets, to which the disordered acetone molecules are weakly linked *via* a number of C—H...O contacts.

Keywords: crystal structure; highly substituted cyclohexanols; supramolecular assembly; hydrogen bonding; Michael addition; condensation reactions.

1. Introduction

Chalcones, *i.e.* 1,3-disubstituted prop-2-en-1-one derivatives of the form $R^1COCH=CHR^2$, are versatile intermediates for organic synthesis which are readily prepared *via* Claisen reactions between acetyl compounds (R^1COCH_3) and aldehydes (R^2CHO). Their versatility stems from their dual modes of reactivity, involving either Michael-type addition across the C=C double bond or condensation reactions at the carbonyl group. When these two modes are active in tandem, new cyclic structures result which can be either carbocyclic (Tabba *et al.*, 1995; Ravindran *et al.*, 2008; Fischer *et al.*, 2008; Fun *et al.*, 2010*b*) or heterocyclic (Fun *et al.*, 2010*a*; Jasinski, Guild *et al.*, 2010; Jasinski, Pek *et al.*, 2010; Samshuddin *et al.*, 2010).



(I) $X = F$
(IIa) $X = Cl$
(III) $X = Br$
(IVa) $X = Ph$

(II) = (IIa)·0.951MeCOMe
(IV) = (IVa)·EtCOMe

Scheme 1

We now report the synthesis and structures of three closely related cyclohexanol derivatives, namely (1*RS*,2*SR*,3*SR*,4*RS*,5*RS*)-3,5-bis(4-fluorophenyl)-2,4-bis(pyridine-2-carbonyl)-1-(pyridin-2-yl)cyclohexanol, (I), (1*RS*,2*SR*,3*SR*,4*RS*,5*RS*)-3,5-bis(4-chlorophenyl)-2,4-bis(pyridine-2-carbonyl)-1-(pyridin-2-yl)cyclohexanol acetone 0.951-solvate, (II), and (1*RS*,2*SR*,3*SR*,4*RS*,5*RS*)-3,5-bis(4-bromophenyl)-2,4-bis(pyridine-2-carbonyl)-1-(pyridin-2-yl)cyclohexanol, (III) (see Scheme 1). These cyclohexanols were prepared, in a one-pot procedure exploiting the dual reactivity of chalcones and giving satisfactory yields, by the reaction of 3:2 molar ratios of 2-acetylpyridine with a 4-halogenobenzaldehyde in alkaline aqueous ethanol, without the need for any form of heating. The purposes of this study were the definition of the relative stereochemistry of the five stereogenic centres, the comparison of the molecular conformations, and the exploration of the supramolecular assembly. In addition, we compare the structures of compounds (I)–(III) with that of the recently reported analogue (IV) (Fun *et al.*, 2012) (see Scheme 1).

Table 1

Experimental details.

| | (I) | (II) | (III) |
|-------------------------------------------------------------------------------------------------------------------------|------------------------------------------------------------------------------|-------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------|-------------------------------------------------------------------------------|
| Crystal data | | | |
| Chemical formula | C ₃₅ H ₂₇ F ₂ N ₃ O ₃ | C ₃₅ H ₂₇ Cl ₂ N ₃ O ₃ ·0.951C ₃ H ₆ O | C ₃₅ H ₂₇ Br ₂ N ₃ O ₃ |
| <i>M_r</i> | 575.60 | 663.73 | 697.41 |
| Crystal system, space group | Orthorhombic, <i>Pbca</i> | Orthorhombic, <i>Fdd2</i> | Triclinic, <i>P</i> $\bar{1}$ |
| Temperature (K) | 200 | 200 | 200 |
| <i>a</i> , <i>b</i> , <i>c</i> (Å) | 21.8864 (9), 11.2268 (4), 24.2670 (9) | 16.5446 (6), 53.4204 (17), 15.5857 (4) | 9.5741 (4), 10.7061 (3), 15.9952 (6) |
| α , β , γ (°) | 90, 90, 90 | 90, 90, 90 | 92.863 (3), 97.443 (3), 103.618 (3) |
| <i>V</i> (Å ³) | 5962.7 (4) | 13774.9 (8) | 1574.49 (10) |
| <i>Z</i> | 8 | 16 | 2 |
| Radiation type | Cu <i>K</i> α | Cu <i>K</i> α | Cu <i>K</i> α |
| μ (mm ⁻¹) | 0.75 | 2.05 | 3.58 |
| Crystal size (mm) | 0.40 × 0.09 × 0.08 | 0.30 × 0.25 × 0.20 | 0.25 × 0.20 × 0.15 |
| Data collection | | | |
| Diffractometer | Agilent Eos Gemini diffractometer | Agilent Xcalibur Ruby Gemini diffractometer | Agilent Xcalibur Ruby Gemini diffractometer |
| Absorption correction | Multi-scan (<i>CrysAlis PRO</i> ; Agilent, 2012) | Multi-scan (<i>CrysAlis PRO</i> ; Agilent, 2012) | Multi-scan (<i>CrysAlis PRO</i> ; Agilent, 2012) |
| <i>T</i> _{min} , <i>T</i> _{max} | 0.693, 0.942 | 0.388, 0.664 | 0.109, 0.584 |
| No. of measured, independent and observed [<i>I</i> > 2 σ (<i>I</i>)] reflections | 37077, 5754, 4489 | 9544, 4224, 3490 | 11667, 5922, 4948 |
| <i>R</i> _{int} | 0.036 | 0.027 | 0.026 |
| (sin θ /λ) _{max} (Å ⁻¹) | 0.614 | 0.610 | 0.610 |
| Refinement | | | |
| <i>R</i> [<i>F</i> ² > 2 σ (<i>F</i> ²)], <i>wR</i> (<i>F</i> ²), <i>S</i> | 0.046, 0.131, 1.03 | 0.039, 0.109, 0.97 | 0.046, 0.141, 1.05 |
| No. of reflections | 5754 | 4224 | 5922 |
| No. of parameters | 388 | 436 | 388 |
| No. of restraints | 0 | 7 | 0 |
| H-atom treatment | H-atom parameters constrained | H-atom parameters constrained | H-atom parameters constrained |
| $\Delta\rho_{\max}$, $\Delta\rho_{\min}$ (e Å ⁻³) | 0.19, -0.20 | 0.16, -0.16 | 0.67, -0.64 |
| Absolute structure | — | Flack <i>x</i> determined using 613 quotients [(<i>I</i> ₊) - (<i>I</i> ₋)] / [(<i>I</i> ₊) + (<i>I</i> ₋)] (Parsons <i>et al.</i> , 2013). | — |
| Absolute structure parameter | — | 0.089 (18) | — |

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

2. Experimental

2.1. Synthesis and crystallization

For the synthesis of the solvent-free forms (I), (IIa) and (III) (see Scheme 1), 2-acetylpyridine (0.03 mol) and the appropriate 4-halogenobenzaldehyde (0.02 mol) were dissolved in ethanol (30 ml). Aqueous potassium hydroxide solution (10 ml of a 10% w/v solution) was added and the mixtures were stirred at 293 K for 4 h and then permitted to stand overnight at ambient temperature. The resulting colourless products were collected by filtration and dried in air. Data for compound (I): yield 64%, m.p. 493–495 K; NMR (dimethyl sulfoxide-*d*₆): δ (H) 1.69 (*m*, 2H, CH₂), 3.62 (*dd*, 1H, H-3), 4.04 (*m*, 1H, H-5), 4.40 (*dd*, 1H, H-4), 5.52 (*s*, 1H, OH), 6.04 (*d*, 1H, H-2), 6.61–8.44 (*m*, 20H, aryl and pyridyl); IR (KBr, cm⁻¹): 3430 (OH), 1682 (C=O); analysis found: C 72.9, H 4.7, N 6.5%; C₃₅H₂₇F₂N₃O₃ requires: C 73.0, H 4.7, N 6.6%. Data for compound (IIa): yield 66%, m.p. 416–419 K; NMR (dimethyl sulfoxide-*d*₆): δ (H) 1.75 (*m*, 2H, CH₂), 3.70 (*dd*, 1H, H-3), 4.05 (*m*, 1H, H-5), 4.45 (*dd*, 1H, H-4), 5.50 (*s*, 1H, OH), 6.05 (*d*, 1H, H-2), 6.84–8.44 (*m*, 20H, aryl and pyridyl); IR (KBr, cm⁻¹): 3434 (OH), 1689 (C=O); analysis found: C 68.9, H 4.5, N 6.9%; C₃₅H₂₇Cl₂N₃O₃ requires: C 69.3, H 4.5, N 6.9%. Data for compound (III): yield 72%, m.p. 508–510 K; NMR (chloroform-*d*₃): δ (H) 1.95 (*m*, 2H, CH₂), 3.50 (*dd*, 1H, H-3), 4.15 (*m*, 1H, H-5), 4.40 (*dd*, 1H, H-4), 5.50 (*s*, 1H, OH), 6.22

(*m*, 1H, H-2), 6.86–7.49 (*m*, 20H, aryl and pyridyl); δ (C) 37.9, 40.6, 47.7, 199.9, 120.9, 121.0, 121.6, 121.8, 126.0, 126.1, 126.5, 130.2, 130.7, 130.8, 136.0, 136.1, 139.7, 141.0, 146.9, 147.9, 148.0, 153.7, 153.9, 162.2, 203.0, 205.0; IR (KBr, cm⁻¹): 3429 (OH), 1682 (C=O); analysis found: C 60.2, H 3.9, N 6.0%; C₃₅H₂₇Br₂N₃O₃ requires: C 60.3, H 3.9, N 6.0%. Crystals of (I)–(III) suitable for single-crystal X-ray diffraction were grown by slow evaporation, at ambient temperature and in the presence of air, of solutions in acetone.

2.2. Refinement

Crystal data, data collection and structure refinement details are summarized in Table 1. All H atoms in the cyclohexanol molecules were located in difference maps and then treated as riding atoms. H atoms bonded to C atoms were treated as riding atoms in geometrically idealized positions, with C–H = 0.95 (aromatic and heteroaromatic), 0.99 (CH₂) or 1.00 Å (aliphatic), and with *U*_{iso}(H) = 1.2*U*_{eq}(C). H atoms bonded to O atoms were permitted to ride at the positions located in difference maps, with *U*_{iso}(H) = 1.5*U*_{eq}(O), giving the O–H distances shown in Table 2. Chloro compound (II) crystallizes as an acetone solvate where the solvent molecules are disordered over two sets of atomic sites. For the minor component, the bonded distances and the one-angle nonbonded distances were restrained to the corresponding

Table 2

Hydrogen bonds and short intermolecular contacts (Å, °) for compounds (I)–(III).

Cg1 represents the centroid of the C31–C36 ring.

| Compound | $D-H\cdots A$ | $D-H$ | $H\cdots A$ | $D\cdots A$ | $D-H\cdots A$ |
|----------|-------------------------------------|-------|-------------|-------------|---------------|
| (I) | O11–H11 \cdots N11 | 0.82 | 2.13 | 2.624 (2) | 119 |
| | C13–H13 \cdots O11 ⁱ | 0.95 | 2.54 | 3.385 (3) | 148 |
| | C55–H55 \cdots O27 ^j | 0.95 | 2.53 | 3.244 (2) | 132 |
| (I) | O11–H11 \cdots N11 | 0.88 | 1.92 | 2.587 (4) | 130 |
| | C14–H14 \cdots O71 | 0.95 | 2.62 | 3.517 (12) | 157 |
| | C14–H14 \cdots O81 | 0.95 | 2.72 | 3.499 (12) | 140 |
| | C43–H43 \cdots N41 ⁱⁱⁱ | 0.95 | 2.61 | 3.433 (4) | 145 |
| | C45–H45 \cdots O71 ⁱⁱⁱ | 0.95 | 2.57 | 3.251 (11) | 129 |
| | C16–H16 \cdots Cg1 ^{iv} | 0.95 | 3.00 | 3.869 (5) | 153 |
| (I) | O11–H11 \cdots N11 | 0.81 | 2.06 | 2.595 (4) | 123 |
| | C16–H16 \cdots O27 ^v | 0.95 | 2.46 | 3.385 (6) | 165 |
| | C53–H53 \cdots N41 ^{vi} | 0.95 | 2.57 | 3.473 (5) | 158 |

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

values in the major component, subject to variations of 0.005 and 0.01 Å, respectively. In addition, the anisotropic displacement parameters for atoms C71 and C81 were constrained to be identical, as were those of atoms O71 and O81, and those of methyl atoms C72, C73, C82 and C83. The H atoms of both components of the disordered acetone solvent molecule were included in calculated positions as riding atoms, with $C-H = 0.95$ Å and $U_{iso}(H) = 1.5U_{eq}(C)$. Subject to these conditions, the occupancies of the major and minor components refined to 0.690 (13) and 0.261 (13), respectively. The correct orientation of the structure of (II) with respect to the polar-axis direction was determined using the Flack x parameter (Flack, 1983), calculated using 613 quotients of the type $[(I+) - (I-)] / [(I+) + (I-)]$ (Parsons *et al.*, 2013), although this has no chemical significance. Examination of the refined structures using *PLATON* (Spek, 2009) showed that none of them contained any solvent-accessible voids.

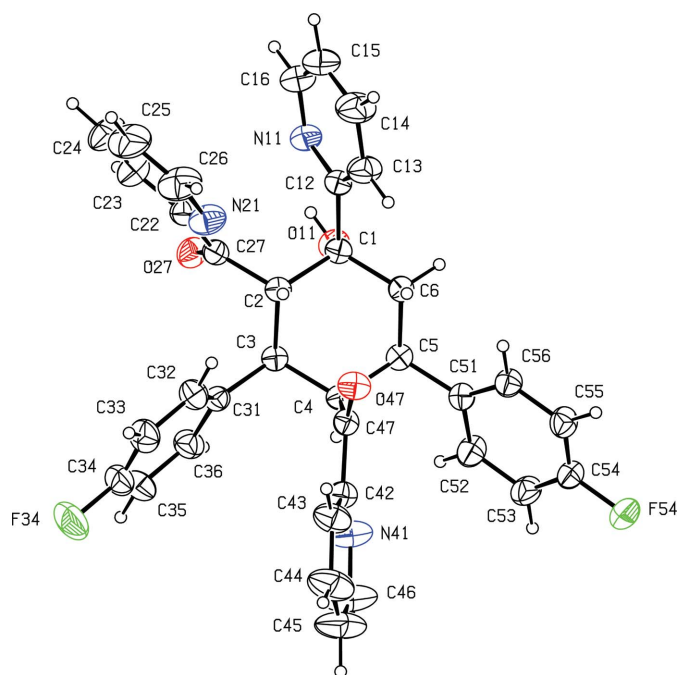
3. Results and discussion

Although all of the cyclohexanols reported here, (I)–(III), were recrystallized from acetone, fluoro and bromo derivatives (I) and (III) crystallized in the solvent-free form but chloro derivative (II) crystallized as a nonstoichiometric acetone solvate, in which the acetone solvent molecule is disordered over two adjacent sets of atomic sites having occupancies of 0.690 (13) and 0.261 (13) in the crystal selected for data collection. However, the s.u. values associated with these refined occupancies cannot definitively rule out the possibility that (II) might just, in fact, be a stoichiometric 1:1 solvate. In addition to the contrast between solvate (II) and solvent-free forms (I) and (III), all of these compounds crystallize in different space groups, *viz.* *Pbca*, *Fdd2* and *P1*, respectively, for compounds (I), (II) and (III), despite the very small differences in their overall molecular constitutions. This behaviour contrasts with the isomorphous behaviour sometimes seen in compounds which differ only in the identity of their halogen substituents (*e.g.* Glidewell *et al.*, 2005; Nayak *et al.*, 2014). [2,6-Bis(biphenyl-4-yl)-4-hydroxy-4-(pyridin-2-yl)-

cyclohexane-1,3-diyl]bis[(pyridin-2-yl)methanone]–butan-2-one (1/1), (IV), crystallizes in the space group *P2₁/c* as a stoichiometric 1:1 solvate with butanone, although the reported synthetic procedure for (IV) specifies that the compound was crystallized from acetone (Fun *et al.*, 2012).

The cyclohexanol molecules in compounds (I)–(III) contain five stereogenic centres and, for each compound, the reference molecule was selected as one having the *R* configuration at atom C1 (Figs. 1–3). On this basis, the reference molecules all have the configuration (1*R*,2*S*,3*S*,4*R*,5*R*) and the space groups confirm that all three compounds crystallize as racemic mixtures. Compound (IV) has exactly the same stereochemistry, although this aspect of its structure was not mentioned in the original structure report (Fun *et al.*, 2012). The isolated yields of the (1*RS*,2*SR*,3*SR*,4*RS*,5*RS*) forms for compounds (I)–(IV), in the range 64–74%, suggest a high degree of stereoselectivity in the formation of the substituted cyclohexane ring.

The formation of these polysubstituted cyclohexanols from very simple precursors can be envisaged as starting with a condensation reaction between the substituted benzaldehyde (ArCHO) and 2-acetylpyridine (MeCOPy) to form a chalcone intermediate (*A*) (see Scheme 2). This step is followed by two Michael additions, the first of which is addition of MeCOPy to chalcone (*A*) to form intermediate (*B*), and the second addition is that of (*B*) to a further molecule of (*A*) giving (*C*). Finally, an intramolecular aldol reaction converts intermediate (*C*) to the cyclohexanol product. The formation of intermediate (*B*) introduces a stereogenic centre, at the site which will eventually become atom C5 of the cyclohexane ring (*cf.* Figs. 1–3). Intermediate (*B*) is necessarily racemic, as no

**Figure 1**

The molecular structure of the (1*R*,2*S*,3*S*,4*R*,5*R*) enantiomer of compound (I), showing the atom-labelling scheme. Displacement ellipsoids are drawn at the 30% probability level.

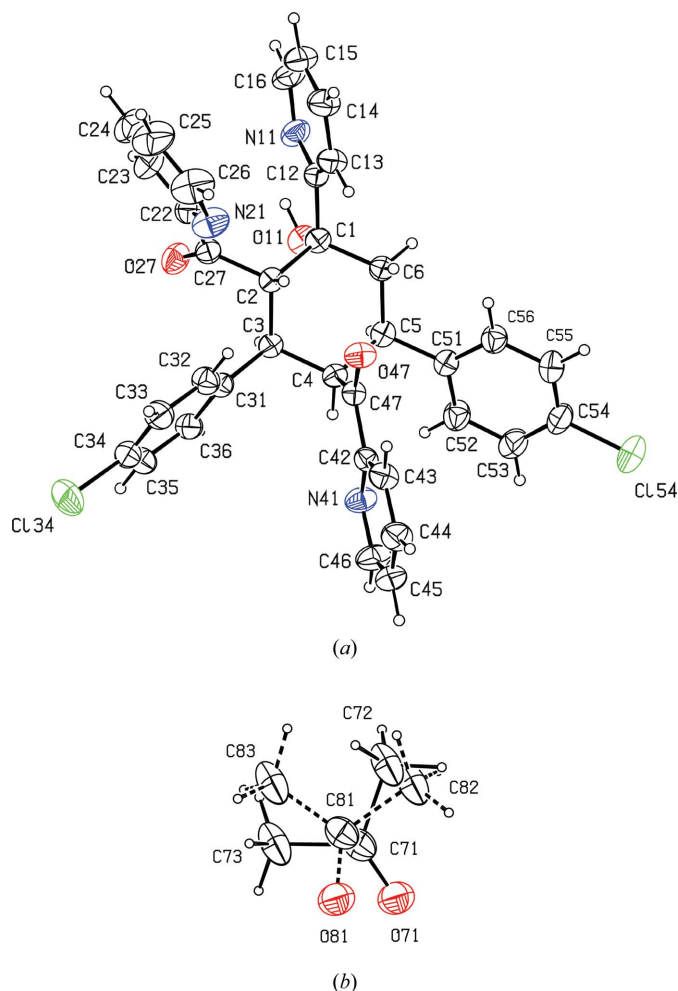


Figure 2
The independent molecular components of compound (II), showing the atom-labelling scheme, for (a) the (1*R*,2*S*,3*S*,4*R*,5*R*) enantiomer of the cyclohexanol molecule and (b) the disordered acetone solvent molecule. The occupancies of the two components of the disordered acetone molecule are 0.690 (13) and 0.261 (13). Displacement ellipsoids are drawn at the 30% probability level for part (a) and at the 10% probability level for part (b).

component in the initial reaction mixtures is capable of inducing enantioselectivity. However, the presence of a stereogenic centre in (B) appears to control the relative stereochemistry at the remaining stereogenic centres subsequently formed at the final positions C1, C2, C3 and C4. This reaction scheme accounts for the reaction stoichiometry, the formation of five adjacent stereogenic centres and the

Table 3
Selected dihedral angles ($^{\circ}$) for compounds (I)–(III).

| Compound | θ_1 | θ_2 | θ_3 | θ_4 | θ_5 |
|----------|------------|------------|------------|------------|------------|
| (I) | 30.80 (12) | 85.33 (11) | 44.19 (13) | 67.09 (13) | 28.94 (10) |
| (II) | 24.3 (2) | 88.0 (2) | 62.66 (19) | 57.3 (2) | 53.3 (2) |
| (III) | 31.5 (2) | 79.4 (2) | 63.9 (2) | 42.5 (2) | 49.05 (18) |

Notes: θ_1 represents the dihedral angle between the N11/C12–C16 and N21/C22–C26 planes; θ_2 represents the dihedral angle between the N21/C22–C26 and C31–C36 planes; θ_3 represents the dihedral angle between the C31–C36 and N41/C42–C46 planes; θ_4 represents the dihedral angle between the N41/C42–C46 and C51–C56 planes; θ_5 represents the dihedral angle between the C51–C56 and N11/C12–C16 planes.

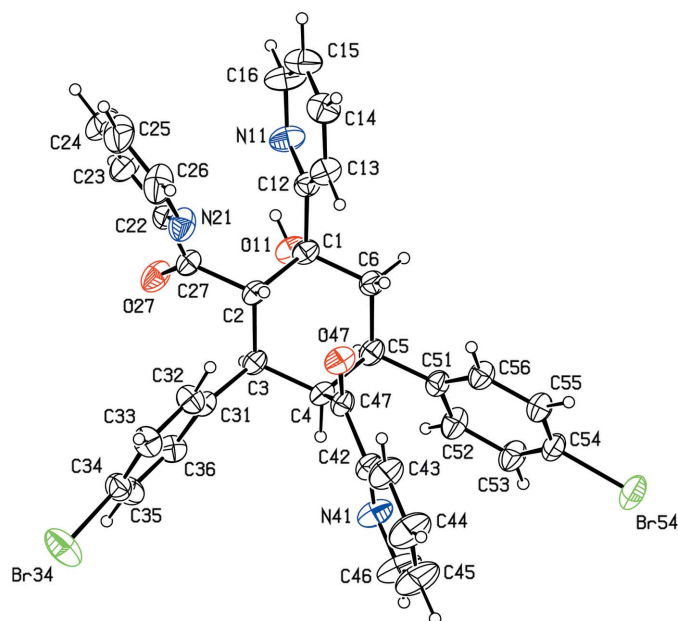
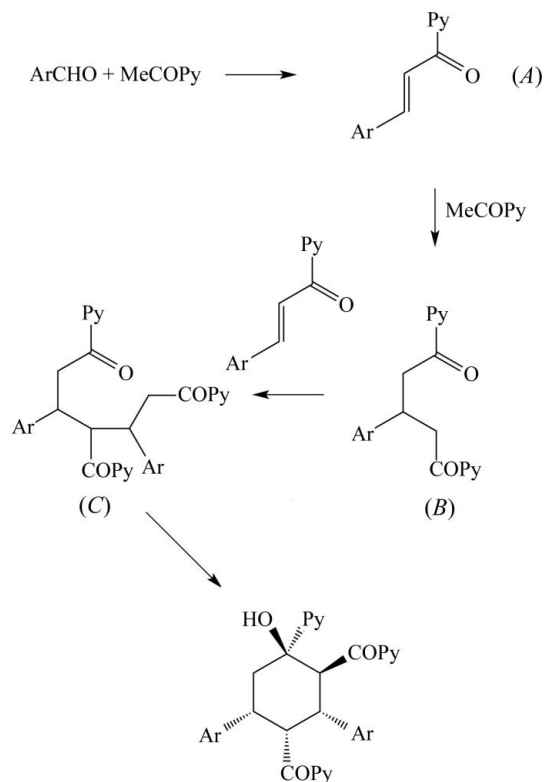


Figure 3
The molecular structure of the (1*R*,2*S*,3*S*,4*R*,5*R*) enantiomer of compound (III), showing the atom-labelling scheme. Displacement ellipsoids are drawn at the 30% probability level.

formation of the final products as racemic mixtures, but it must be emphasized that this scheme is largely conjectural, albeit firmly based on the straightforward application of simple organic processes.



Scheme 2

Within the cyclohexanol molecules, the cyclohexane rings all adopt chair conformations and the ring-puckering angles θ ,

calculated (Cremer & Pople, 1975) for the atom sequence C1–C2–C3–C4–C5–C6, are 5.36 (17), 5.5 (3) and 0.0 (3)° for compounds (I), (II) and (III), respectively; the corresponding value for compound (IV) is 4.69 (15)°. The ideal value for a perfect chair conformation is $\theta = 0.0^\circ$ (Boeyens, 1978). The organic substituents at atoms C1, C2, C3 and C5 all occupy equatorial sites, and both the hydroxy group at atom C1 and the acyl substituent at atom C4 occupy axial sites.

In each of compounds (I)–(III) there is an intramolecular O–H...N hydrogen bond (Table 2), which may serve effectively to lock the orientation of the pyridine ring bonded to atom C1. The overall molecular conformation can be conveniently summarized in terms of the dihedral angles between the successive rings bonded to the central cyclohexane ring (Table 3); the corresponding values for (I)–(III) are in general similar, although with some small differences in detail. The overall similarity between compounds (I)–(III) in terms of their molecular constitutions, stereochemistry and molecular conformations makes their marked differences in crystallization behaviour difficult to understand.

The supramolecular assembly in compounds (I)–(III) is fairly simple for molecules of this complexity. Thus, for example, despite the presence in each cyclohexanol molecule of five independent aryl or pyridyl rings, there are no π – π interactions in the structure of (I) and only one such interaction in each of (II) and (III). Similarly, there are no C–H... π interactions in the structures of (I) and (III), while the single interaction of this type in (II) has long H...Cg and C...Cg distances (Table 2), and it is not considered to be structurally significant. The principal intermolecular interactions are thus C–H...N and C–H...O hydrogen bonds, augmented by the π – π interactions in (II) and (III). In the structure of compound (I), a combination of two C–H...O hydrogen bonds (Table 2) links molecules related by a *b*-glide plane to form a $C(5)C(10)[R_2^2(15)]$ chain of rings (Bernstein *et al.*, 1995) running parallel to the [010] direction (Fig. 4).

There are several C–H...O contacts between the molecular components in compound (II) (Table 2). Within the selected asymmetric unit, the cyclohexanol molecule forms

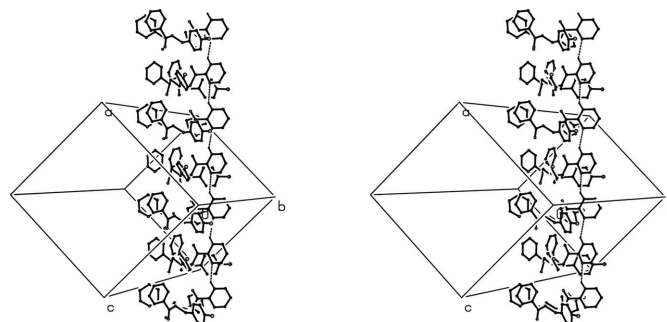


Figure 5

A stereoview of part of the crystal structure of compound (II), showing the formation of a hydrogen-bonded $C(4)$ chain parallel to $[10\bar{1}]$. Hydrogen bonds are shown as dashed lines and the disordered acetone molecules and H atoms not involved in the motif shown have been omitted.

rather long C–H...O contacts with the two partial-occupancy components of the disordered acetone molecule, one of them with an H...O distance beyond the sum (2.65 Å) of the van der Waals radii for H and O (Rowland & Taylor, 1996). A third such contact has a C–H...O angle of only 129°, so that this contact is probably not structurally significant (Wood *et al.*, 2009). The weak bonding of the acetone molecule to the cyclohexanol molecule may account for the nonstoichiometric nature of the solvation, for the positional disorder of the solvent molecule and for the relatively large displacement parameters of the solvent molecule. Subject to these provisos, and that mentioned above concerning the C–H... π contact, the sole significant intermolecular hydrogen bond, of C–H...N type, links cyclohexanol molecules related by the *d*-glide plane at $y = 0.375$ to form a simple $C(4)$ chain running parallel to the $[10\bar{1}]$ direction (Fig. 5). These simple chains are linked into sheets by a single π – π stacking interaction. The planes of the pyridine rings containing atoms N11 and N41 in the molecules at (x, y, z) and $(x + \frac{1}{2}, y, z + \frac{1}{2})$, respectively, make a dihedral angle of 4.7 (2)°. The ring-centroid separation is 3.846 (2) Å and the shortest perpendicular distance from the centroid of one ring to the plane of the other is 3.3909 (17) Å, corresponding to a nearly ideal ring-centroid offset of *ca* 1.52 Å (Fig. 6). This interaction links cyclohexanol molecules

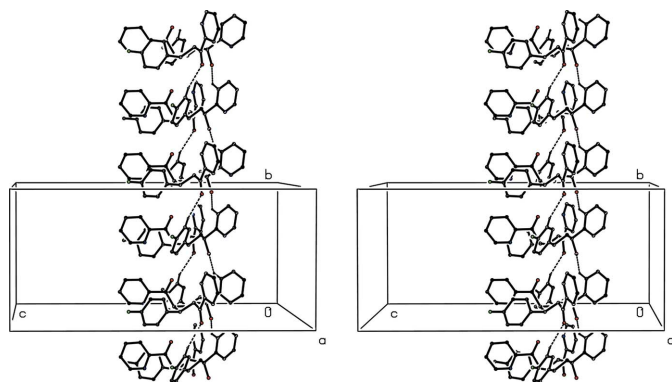


Figure 4

A stereoview of part of the crystal structure of compound (I), showing the formation of a hydrogen-bonded $C(5)C(10)[R_2^2(15)]$ chain of rings parallel to $[010]$. Hydrogen bonds are shown as dashed lines and H atoms not involved in the motifs shown have been omitted.

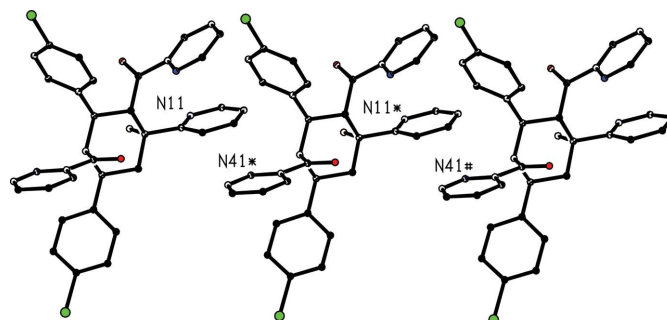
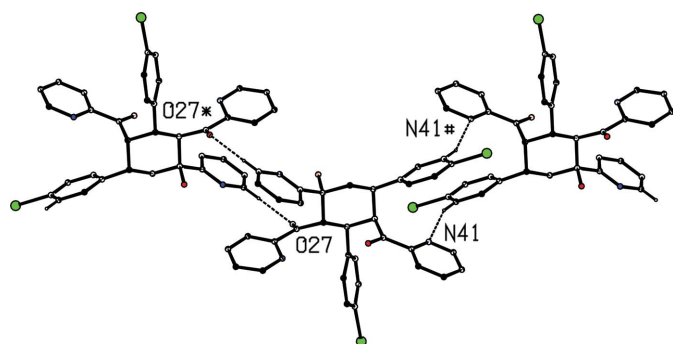


Figure 6

Part of the crystal structure of compound (II), showing the π – π stacking interaction which generates chains along $[101]$. For the sake of clarity, the H atoms, the solvent molecules and the unit-cell outline have been omitted. Atoms marked with an asterisk (*) or a hash (#) are at the symmetry positions $(x + \frac{1}{2}, y, z + \frac{1}{2})$ and $(x + 1, y, z + 1)$, respectively.

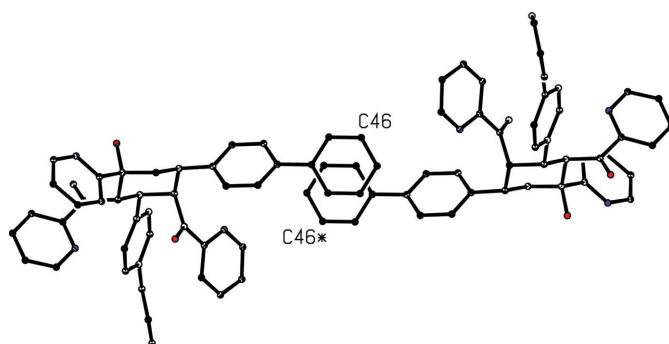
**Figure 7**

Part of the crystal structure of compound (III), showing the formation of the hydrogen-bonded $R_2^2(16)$ and $R_2^2(18)$ rings which generate a chain parallel to $[01\bar{1}]$. For the sake of clarity, H atoms not involved in the motifs shown and the unit-cell outline have been omitted. Atoms marked with an asterisk (*) or a hash (#) are at the symmetry positions $(-x, -y, -z + 1)$ and $(-x, -y + 1, -z)$, respectively.

related by translation to form a π -stacked chain running parallel to the $[101]$ direction. The combination of the hydrogen-bonded chains along $[10\bar{1}]$ and the π -stacked chains along $[101]$ links the cyclohexanol molecules into a sheet parallel to (010) to which the acetone molecules are linked only weakly, if at all.

A combination of one C—H...N hydrogen bond and one C—H...O hydrogen bond links the molecules of compound (III) into a chain of centrosymmetric rings running parallel to the $[01\bar{1}]$ direction (Fig. 7). Inversion-related pairs of C—H...N hydrogen bonds link pairs of molecules into $R_2^2(18)$ rings centred at $(0, \frac{1}{2} - n, n)$, where n represents an integer, and these rings alternate with $R_2^2(16)$ rings containing inversion-related pairs of C—H...O hydrogen bonds which are centred at $(0, n, \frac{1}{2} - n)$, where n again represents an integer. There is a single π – π interaction in this structure; the planes of the pyridine rings containing atom N21 in the molecules at (x, y, z) and $(-x + 1, -y, -z + 1)$ are parallel. The interplanar spacing is $3.555(2)$ Å, the ring-centroid separation is $3.680(3)$ Å and the ring-centroid offset is $0.951(3)$ Å; the effect of this interaction is to link the hydrogen-bonded chains into a sheet parallel to (011) .

In the structure of compound (III), there is a short intermolecular Br...Br contact between inversion-related molecules, with $\text{Br}54 \cdots \text{Br}54^i = 3.3802(6)$ Å and $\text{C}54 \cdots \text{Br}54^i = 159.23(9)^\circ$ [symmetry code: (i) $-x, -y + 1, -z$]. A database study of the angular distribution of such contacts (Ramasubbu *et al.*, 1986) has shown that the C—X...X angles (where X = Cl, Br or I) are clustered either around 100° or around 165° , and the angle observed in compound (III) is consistent with this finding. Although the observed Br...Br distance in (III) is shorter than the conventional sum of the van der Waals radii (3.70 Å; Rowland & Taylor, 1996), a database study of the nonbonded distances in such contacts (Nyburg & Faerman, 1985) found that atoms such as halogens bonded to C atoms do not behave in this context as though they were spherical but instead they behave as oblate ellipsoids, with the major axis normal to the direction of the C—X bond and the minor axis parallel to the C—X

**Figure 8**

Part of the crystal structure of compound (IV), showing the π – π stacking interaction which links hydrogen-bonded chains along $[001]$ into a sheet parallel to (100) . The original atomic coordinates (Fun *et al.*, 2012) have been used. For the sake of clarity, the H atoms, the solvent molecules and the unit-cell outline have been omitted. The atom marked with an asterisk (*) is at the symmetry position $(-x, -y, -z)$.

bond. For Br, these characteristic radii were found to be 2.01 and 1.64 Å, respectively, and, on this basis, the observed Br...Br distance in compound (III) does not seem to be exceptional.

In compound (IV) (Fun *et al.*, 2012), the supramolecular assembly consists of $C(5)$ chains containing molecules related by c -glide planes which are linked by a single C—H...O hydrogen bond, and the butanone solvent molecules are linked to these chains, also *via* C—H...O hydrogen bonds. Although the presence of a π – π stacking interaction was mentioned in the original structure report, no discussion of its action was given. In fact, this interaction involves a pair of inversion-related molecules (Fig. 8) and, in combination with the hydrogen-bonded chains, it generates a sheet lying parallel to (100) .

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supporting information

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Three closely-related cyclohexanols (C₃₅H₂₇X₂N₃O₃; X = F, Cl or Br): similar molecular structures but different crystal structures

Seranthimata Samshuddin, Jerry P. Jasinski, Ray J. Butcher, Elizabeth A. Neuhardt, Badiadka Narayana, Hemmige S. Yathirajan and Christopher Glidewell

Computing details

For all 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) (1*RS*,2*SR*,3*SR*,4*RS*,5*RS*)-3,5-Bis(4-fluorophenyl)-2,4-bis(pyridine-2-carbonyl)1-(pyridin-2-yl)cyclohexanol

Crystal data

C₃₅H₂₇F₂N₃O₃

M_r = 575.60

Orthorhombic, *Pbca*

a = 21.8864 (9) Å

b = 11.2268 (4) Å

c = 24.2670 (9) Å

V = 5962.7 (4) Å³

Z = 8

F(000) = 2400

D_x = 1.282 Mg m⁻³

Cu *Kα* radiation, λ = 1.54178 Å

Cell parameters from 5754 reflections

θ = 3.6–71.2°

μ = 0.75 mm⁻¹

T = 200 K

Needle, colourless

0.40 × 0.09 × 0.08 mm

Data collection

Agilent Eos Gemini

diffractometer

Radiation source: Enhance (Cu) X-ray Source

ω scans

Absorption correction: multi-scan

(*CrysAlis PRO*; Agilent, 2012)

T_{min} = 0.693, *T_{max}* = 0.942

37077 measured reflections

5754 independent reflections

4489 reflections with *I* > 2σ(*I*)

R_{int} = 0.036

θ_{max} = 71.2°, θ_{min} = 3.6°

h = −18→26

k = −13→13

l = −27→29

Refinement

Refinement on *F*²

Least-squares matrix: full

R [*F*² > 2σ(*F*²)] = 0.046

wR (*F*²) = 0.131

S = 1.03

5754 reflections

388 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

$$w = 1/[\sigma^2(F_o^2) + (0.0634P)^2 + 1.1285P]$$

where $P = (F_o^2 + 2F_c^2)/3$
 $(\Delta/\sigma)_{\max} < 0.001$

$$\Delta\rho_{\max} = 0.19 \text{ e } \text{\AA}^{-3}$$

$$\Delta\rho_{\min} = -0.20 \text{ e } \text{\AA}^{-3}$$

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 (\AA^2)

| | x | y | z | $U_{\text{iso}}^*/U_{\text{eq}}$ |
|-----|---------------|--------------|--------------|----------------------------------|
| C1 | 0.19695 (8) | 0.56058 (14) | 0.29755 (6) | 0.0469 (4) |
| O11 | 0.20061 (6) | 0.43914 (10) | 0.28039 (5) | 0.0587 (3) |
| H11 | 0.1716 | 0.4286 | 0.2598 | 0.088* |
| C2 | 0.15217 (7) | 0.57345 (13) | 0.34750 (6) | 0.0436 (3) |
| H2 | 0.1509 | 0.6589 | 0.3590 | 0.052* |
| C3 | 0.17385 (7) | 0.49773 (13) | 0.39661 (6) | 0.0434 (3) |
| H3 | 0.1731 | 0.4128 | 0.3842 | 0.052* |
| C4 | 0.24067 (7) | 0.52586 (13) | 0.41351 (6) | 0.0433 (3) |
| H4 | 0.2539 | 0.4617 | 0.4395 | 0.052* |
| C5 | 0.28430 (7) | 0.52110 (13) | 0.36324 (7) | 0.0463 (3) |
| H5 | 0.2842 | 0.4368 | 0.3500 | 0.056* |
| C6 | 0.26119 (7) | 0.59731 (15) | 0.31527 (7) | 0.0495 (4) |
| H6A | 0.2609 | 0.6821 | 0.3265 | 0.059* |
| H6B | 0.2894 | 0.5890 | 0.2836 | 0.059* |
| N11 | 0.13521 (8) | 0.57704 (16) | 0.21601 (6) | 0.0662 (4) |
| C12 | 0.17203 (8) | 0.63612 (16) | 0.25019 (7) | 0.0513 (4) |
| C13 | 0.18284 (11) | 0.75631 (19) | 0.24506 (9) | 0.0716 (5) |
| H13 | 0.2101 | 0.7960 | 0.2694 | 0.086* |
| C14 | 0.15306 (14) | 0.8180 (2) | 0.20361 (11) | 0.0942 (8) |
| H14 | 0.1597 | 0.9010 | 0.1990 | 0.113* |
| C15 | 0.11414 (13) | 0.7586 (3) | 0.16938 (10) | 0.0927 (8) |
| H15 | 0.0927 | 0.7995 | 0.1411 | 0.111* |
| C16 | 0.10686 (12) | 0.6393 (3) | 0.17684 (9) | 0.0853 (7) |
| H16 | 0.0800 | 0.5980 | 0.1527 | 0.102* |
| C27 | 0.08834 (8) | 0.53511 (15) | 0.33041 (7) | 0.0493 (4) |
| O27 | 0.07514 (6) | 0.43068 (11) | 0.32607 (6) | 0.0646 (3) |
| N21 | 0.05596 (9) | 0.74111 (16) | 0.32838 (8) | 0.0758 (5) |
| C22 | 0.04146 (8) | 0.62888 (18) | 0.31706 (7) | 0.0573 (4) |
| C23 | -0.01306 (10) | 0.5955 (3) | 0.29329 (10) | 0.0846 (7) |
| H23 | -0.0222 | 0.5142 | 0.2861 | 0.102* |
| C24 | -0.05428 (13) | 0.6857 (4) | 0.28028 (13) | 0.1123 (10) |
| H24 | -0.0920 | 0.6669 | 0.2630 | 0.135* |
| C25 | -0.04035 (15) | 0.8010 (3) | 0.29238 (13) | 0.1112 (10) |
| H25 | -0.0684 | 0.8633 | 0.2847 | 0.133* |
| C26 | 0.01477 (14) | 0.8246 (3) | 0.31575 (11) | 0.1002 (9) |
| H26 | 0.0246 | 0.9052 | 0.3236 | 0.120* |

| | | | | |
|-----|--------------|--------------|--------------|-------------|
| C31 | 0.13233 (7) | 0.50623 (14) | 0.44664 (7) | 0.0473 (4) |
| C32 | 0.10194 (9) | 0.60966 (17) | 0.46100 (8) | 0.0604 (4) |
| H32 | 0.1041 | 0.6769 | 0.4373 | 0.072* |
| C33 | 0.06841 (10) | 0.6169 (2) | 0.50932 (9) | 0.0737 (6) |
| H33 | 0.0479 | 0.6885 | 0.5190 | 0.088* |
| C34 | 0.06538 (10) | 0.5205 (2) | 0.54226 (9) | 0.0771 (6) |
| F34 | 0.03235 (8) | 0.52803 (18) | 0.58975 (6) | 0.1177 (6) |
| C35 | 0.09327 (12) | 0.4160 (2) | 0.52967 (9) | 0.0830 (7) |
| H35 | 0.0899 | 0.3491 | 0.5535 | 0.100* |
| C36 | 0.12679 (10) | 0.40895 (18) | 0.48118 (8) | 0.0649 (5) |
| H36 | 0.1462 | 0.3362 | 0.4716 | 0.078* |
| C47 | 0.24466 (7) | 0.64265 (13) | 0.44453 (7) | 0.0456 (3) |
| O47 | 0.23444 (6) | 0.73801 (9) | 0.42281 (5) | 0.0575 (3) |
| N41 | 0.28713 (11) | 0.54117 (16) | 0.52388 (8) | 0.0865 (6) |
| C42 | 0.26141 (9) | 0.63990 (15) | 0.50466 (7) | 0.0561 (4) |
| C43 | 0.25094 (12) | 0.73865 (19) | 0.53713 (8) | 0.0764 (6) |
| H43 | 0.2322 | 0.8079 | 0.5223 | 0.092* |
| C44 | 0.26832 (17) | 0.7342 (3) | 0.59181 (10) | 0.1086 (10) |
| H44 | 0.2610 | 0.8002 | 0.6154 | 0.130* |
| C45 | 0.29594 (18) | 0.6346 (3) | 0.61140 (11) | 0.1234 (12) |
| H45 | 0.3091 | 0.6302 | 0.6486 | 0.148* |
| C46 | 0.30429 (18) | 0.5414 (3) | 0.57659 (12) | 0.1228 (12) |
| H46 | 0.3236 | 0.4719 | 0.5907 | 0.147* |
| C51 | 0.34937 (7) | 0.54824 (14) | 0.38108 (7) | 0.0481 (4) |
| C52 | 0.37957 (9) | 0.46579 (17) | 0.41399 (9) | 0.0653 (5) |
| H52 | 0.3597 | 0.3934 | 0.4234 | 0.078* |
| C53 | 0.43805 (9) | 0.48691 (19) | 0.43340 (9) | 0.0705 (5) |
| H53 | 0.4584 | 0.4302 | 0.4560 | 0.085* |
| C54 | 0.46566 (8) | 0.59140 (18) | 0.41921 (8) | 0.0598 (4) |
| F54 | 0.52375 (5) | 0.61192 (12) | 0.43809 (5) | 0.0820 (4) |
| C55 | 0.43852 (8) | 0.67500 (17) | 0.38715 (8) | 0.0621 (5) |
| H55 | 0.4592 | 0.7468 | 0.3780 | 0.074* |
| C56 | 0.37968 (8) | 0.65291 (15) | 0.36802 (8) | 0.0550 (4) |
| H56 | 0.3599 | 0.7106 | 0.3456 | 0.066* |

Atomic displacement parameters (\AA^2)

| | U^{11} | U^{22} | U^{33} | U^{12} | U^{13} | U^{23} |
|-----|-------------|-------------|-------------|--------------|--------------|-------------|
| C1 | 0.0533 (9) | 0.0418 (8) | 0.0455 (8) | 0.0003 (6) | −0.0003 (7) | −0.0037 (7) |
| O11 | 0.0640 (7) | 0.0490 (6) | 0.0631 (7) | 0.0062 (5) | −0.0044 (6) | −0.0149 (6) |
| C2 | 0.0496 (8) | 0.0366 (7) | 0.0447 (8) | 0.0021 (6) | −0.0022 (6) | −0.0004 (6) |
| C3 | 0.0501 (8) | 0.0328 (7) | 0.0474 (8) | 0.0012 (6) | −0.0015 (6) | 0.0008 (6) |
| C4 | 0.0496 (8) | 0.0340 (7) | 0.0462 (8) | 0.0013 (6) | −0.0034 (6) | 0.0028 (6) |
| C5 | 0.0495 (9) | 0.0381 (7) | 0.0514 (8) | 0.0022 (6) | −0.0018 (7) | −0.0023 (6) |
| C6 | 0.0483 (9) | 0.0523 (9) | 0.0478 (8) | 0.0008 (7) | 0.0011 (7) | 0.0016 (7) |
| N11 | 0.0690 (10) | 0.0781 (11) | 0.0516 (8) | −0.0047 (8) | −0.0112 (7) | −0.0038 (8) |
| C12 | 0.0541 (9) | 0.0577 (10) | 0.0421 (8) | −0.0008 (7) | 0.0008 (7) | −0.0011 (7) |
| C13 | 0.0880 (14) | 0.0628 (12) | 0.0641 (12) | −0.0082 (10) | −0.0169 (10) | 0.0112 (9) |

| | | | | | | |
|-----|-------------|-------------|-------------|--------------|--------------|--------------|
| C14 | 0.119 (2) | 0.0785 (15) | 0.0852 (16) | −0.0030 (14) | −0.0186 (15) | 0.0296 (13) |
| C15 | 0.0962 (18) | 0.116 (2) | 0.0661 (14) | 0.0048 (15) | −0.0201 (12) | 0.0294 (14) |
| C16 | 0.0844 (15) | 0.113 (2) | 0.0583 (12) | −0.0039 (14) | −0.0201 (11) | 0.0039 (12) |
| C27 | 0.0525 (9) | 0.0505 (9) | 0.0450 (8) | −0.0014 (7) | 0.0009 (7) | 0.0017 (7) |
| O27 | 0.0643 (8) | 0.0548 (7) | 0.0748 (8) | −0.0110 (6) | −0.0088 (6) | 0.0017 (6) |
| N21 | 0.0841 (12) | 0.0654 (11) | 0.0780 (11) | 0.0245 (9) | −0.0153 (9) | −0.0006 (9) |
| C22 | 0.0535 (9) | 0.0708 (12) | 0.0476 (9) | 0.0096 (8) | 0.0003 (7) | 0.0047 (8) |
| C23 | 0.0627 (12) | 0.1074 (18) | 0.0838 (15) | 0.0044 (12) | −0.0151 (11) | 0.0066 (13) |
| C24 | 0.0685 (15) | 0.160 (3) | 0.109 (2) | 0.0285 (18) | −0.0282 (14) | 0.014 (2) |
| C25 | 0.104 (2) | 0.126 (3) | 0.104 (2) | 0.058 (2) | −0.0170 (17) | 0.0143 (19) |
| C26 | 0.112 (2) | 0.0883 (17) | 0.1003 (18) | 0.0465 (16) | −0.0226 (16) | 0.0019 (14) |
| C31 | 0.0469 (8) | 0.0490 (8) | 0.0461 (8) | −0.0031 (7) | −0.0036 (7) | 0.0001 (7) |
| C32 | 0.0650 (11) | 0.0566 (10) | 0.0595 (10) | 0.0019 (8) | 0.0082 (8) | −0.0039 (8) |
| C33 | 0.0722 (13) | 0.0803 (14) | 0.0686 (12) | −0.0002 (11) | 0.0124 (10) | −0.0182 (11) |
| C34 | 0.0707 (13) | 0.1070 (18) | 0.0534 (11) | −0.0127 (12) | 0.0120 (9) | −0.0094 (11) |
| F34 | 0.1163 (12) | 0.1697 (16) | 0.0670 (8) | −0.0229 (11) | 0.0383 (8) | −0.0117 (9) |
| C35 | 0.0904 (16) | 0.0956 (17) | 0.0630 (12) | −0.0111 (13) | 0.0090 (11) | 0.0248 (12) |
| C36 | 0.0704 (12) | 0.0625 (11) | 0.0619 (11) | 0.0012 (9) | 0.0033 (9) | 0.0128 (9) |
| C47 | 0.0474 (8) | 0.0381 (8) | 0.0513 (8) | −0.0013 (6) | 0.0000 (7) | 0.0017 (7) |
| O47 | 0.0793 (8) | 0.0351 (6) | 0.0580 (7) | 0.0012 (5) | −0.0048 (6) | 0.0018 (5) |
| N41 | 0.1270 (17) | 0.0641 (11) | 0.0682 (11) | 0.0086 (10) | −0.0376 (11) | 0.0004 (9) |
| C42 | 0.0673 (11) | 0.0477 (9) | 0.0531 (9) | −0.0099 (8) | −0.0066 (8) | 0.0002 (7) |
| C43 | 0.1111 (18) | 0.0619 (12) | 0.0562 (11) | −0.0032 (11) | 0.0002 (11) | −0.0056 (9) |
| C44 | 0.173 (3) | 0.0959 (19) | 0.0572 (13) | −0.0161 (19) | −0.0056 (16) | −0.0175 (13) |
| C45 | 0.196 (4) | 0.112 (2) | 0.0613 (15) | −0.022 (2) | −0.0468 (19) | 0.0030 (15) |
| C46 | 0.196 (4) | 0.0907 (19) | 0.0821 (17) | 0.010 (2) | −0.066 (2) | 0.0076 (15) |
| C51 | 0.0480 (9) | 0.0433 (8) | 0.0529 (9) | 0.0031 (6) | 0.0018 (7) | −0.0014 (7) |
| C52 | 0.0575 (10) | 0.0523 (10) | 0.0862 (13) | −0.0029 (8) | −0.0101 (9) | 0.0141 (9) |
| C53 | 0.0605 (11) | 0.0714 (13) | 0.0795 (13) | 0.0020 (9) | −0.0142 (10) | 0.0209 (10) |
| C54 | 0.0480 (9) | 0.0718 (12) | 0.0597 (10) | −0.0051 (8) | −0.0060 (8) | −0.0029 (9) |
| F54 | 0.0588 (6) | 0.1041 (9) | 0.0831 (8) | −0.0149 (6) | −0.0181 (6) | 0.0077 (7) |
| C55 | 0.0576 (10) | 0.0542 (10) | 0.0744 (12) | −0.0093 (8) | −0.0008 (9) | 0.0043 (9) |
| C56 | 0.0523 (9) | 0.0492 (9) | 0.0634 (10) | 0.0012 (7) | −0.0025 (8) | 0.0062 (8) |

Geometric parameters (Å, °)

| | | | |
|---------|-------------|---------|-----------|
| C1—O11 | 1.4279 (19) | C25—C26 | 1.359 (4) |
| C1—C6 | 1.527 (2) | C25—H25 | 0.9500 |
| C1—C12 | 1.529 (2) | C26—H26 | 0.9500 |
| C1—C2 | 1.565 (2) | C31—C36 | 1.382 (2) |
| O11—H11 | 0.8158 | C31—C32 | 1.383 (2) |
| C2—C27 | 1.519 (2) | C32—C33 | 1.386 (3) |
| C2—C3 | 1.539 (2) | C32—H32 | 0.9500 |
| C2—H2 | 1.0000 | C33—C34 | 1.347 (3) |
| C3—C31 | 1.520 (2) | C33—H33 | 0.9500 |
| C3—C4 | 1.551 (2) | C34—C35 | 1.357 (4) |
| C3—H3 | 1.0000 | C34—F34 | 1.363 (2) |
| C4—C47 | 1.514 (2) | C35—C36 | 1.389 (3) |

| | | | |
|------------|-------------|-------------|-------------|
| C4—C5 | 1.550 (2) | C35—H35 | 0.9500 |
| C4—H4 | 1.0000 | C36—H36 | 0.9500 |
| C5—C51 | 1.519 (2) | C47—O47 | 1.2140 (19) |
| C5—C6 | 1.531 (2) | C47—C42 | 1.505 (2) |
| C5—H5 | 1.0000 | N41—C42 | 1.328 (3) |
| C6—H6A | 0.9900 | N41—C46 | 1.333 (3) |
| C6—H6B | 0.9900 | C42—C43 | 1.379 (3) |
| N11—C12 | 1.333 (2) | C43—C44 | 1.381 (3) |
| N11—C16 | 1.333 (3) | C43—H43 | 0.9500 |
| C12—C13 | 1.376 (3) | C44—C45 | 1.357 (4) |
| C13—C14 | 1.384 (3) | C44—H44 | 0.9500 |
| C13—H13 | 0.9500 | C45—C46 | 1.357 (4) |
| C14—C15 | 1.364 (4) | C45—H45 | 0.9500 |
| C14—H14 | 0.9500 | C46—H46 | 0.9500 |
| C15—C16 | 1.361 (4) | C51—C56 | 1.386 (2) |
| C15—H15 | 0.9500 | C51—C52 | 1.390 (2) |
| C16—H16 | 0.9500 | C52—C53 | 1.384 (3) |
| C27—O27 | 1.212 (2) | C52—H52 | 0.9500 |
| C27—C22 | 1.505 (2) | C53—C54 | 1.364 (3) |
| N21—C22 | 1.328 (3) | C53—H53 | 0.9500 |
| N21—C26 | 1.336 (3) | C54—C55 | 1.356 (3) |
| C22—C23 | 1.378 (3) | C54—F54 | 1.371 (2) |
| C23—C24 | 1.393 (4) | C55—C56 | 1.391 (2) |
| C23—H23 | 0.9500 | C55—H55 | 0.9500 |
| C24—C25 | 1.362 (4) | C56—H56 | 0.9500 |
| C24—H24 | 0.9500 | | |
| O11—C1—C6 | 106.76 (13) | C25—C24—H24 | 120.1 |
| O11—C1—C12 | 109.29 (13) | C23—C24—H24 | 120.1 |
| C6—C1—C12 | 112.97 (13) | C26—C25—C24 | 118.3 (2) |
| O11—C1—C2 | 110.43 (13) | C26—C25—H25 | 120.9 |
| C6—C1—C2 | 109.49 (13) | C24—C25—H25 | 120.9 |
| C12—C1—C2 | 107.91 (13) | N21—C26—C25 | 123.9 (3) |
| C1—O11—H11 | 105.9 | N21—C26—H26 | 118.0 |
| C27—C2—C3 | 109.78 (12) | C25—C26—H26 | 118.0 |
| C27—C2—C1 | 109.77 (13) | C36—C31—C32 | 117.94 (17) |
| C3—C2—C1 | 110.82 (12) | C36—C31—C3 | 119.17 (15) |
| C27—C2—H2 | 108.8 | C32—C31—C3 | 122.80 (15) |
| C3—C2—H2 | 108.8 | C31—C32—C33 | 121.13 (19) |
| C1—C2—H2 | 108.8 | C31—C32—H32 | 119.4 |
| C31—C3—C2 | 113.55 (13) | C33—C32—H32 | 119.4 |
| C31—C3—C4 | 109.86 (12) | C34—C33—C32 | 118.8 (2) |
| C2—C3—C4 | 112.52 (12) | C34—C33—H33 | 120.6 |
| C31—C3—H3 | 106.8 | C32—C33—H33 | 120.6 |
| C2—C3—H3 | 106.8 | C33—C34—C35 | 122.59 (19) |
| C4—C3—H3 | 106.8 | C33—C34—F34 | 118.6 (2) |
| C47—C4—C5 | 112.67 (12) | C35—C34—F34 | 118.9 (2) |
| C47—C4—C3 | 111.22 (12) | C34—C35—C36 | 118.5 (2) |

| | | | |
|---------------|--------------|-----------------|-------------|
| C5—C4—C3 | 111.44 (12) | C34—C35—H35 | 120.7 |
| C47—C4—H4 | 107.1 | C36—C35—H35 | 120.7 |
| C5—C4—H4 | 107.1 | C31—C36—C35 | 121.0 (2) |
| C3—C4—H4 | 107.1 | C31—C36—H36 | 119.5 |
| C51—C5—C6 | 114.48 (13) | C35—C36—H36 | 119.5 |
| C51—C5—C4 | 110.25 (13) | O47—C47—C42 | 118.94 (15) |
| C6—C5—C4 | 112.07 (13) | O47—C47—C4 | 122.49 (14) |
| C51—C5—H5 | 106.5 | C42—C47—C4 | 118.56 (13) |
| C6—C5—H5 | 106.5 | C42—N41—C46 | 117.1 (2) |
| C4—C5—H5 | 106.5 | N41—C42—C43 | 122.75 (18) |
| C1—C6—C5 | 111.55 (13) | N41—C42—C47 | 117.45 (16) |
| C1—C6—H6A | 109.3 | C43—C42—C47 | 119.79 (17) |
| C5—C6—H6A | 109.3 | C42—C43—C44 | 118.3 (2) |
| C1—C6—H6B | 109.3 | C42—C43—H43 | 120.9 |
| C5—C6—H6B | 109.3 | C44—C43—H43 | 120.9 |
| H6A—C6—H6B | 108.0 | C45—C44—C43 | 119.3 (3) |
| C12—N11—C16 | 117.64 (19) | C45—C44—H44 | 120.4 |
| N11—C12—C13 | 122.39 (17) | C43—C44—H44 | 120.4 |
| N11—C12—C1 | 114.04 (15) | C44—C45—C46 | 118.5 (2) |
| C13—C12—C1 | 123.42 (16) | C44—C45—H45 | 120.7 |
| C12—C13—C14 | 118.4 (2) | C46—C45—H45 | 120.7 |
| C12—C13—H13 | 120.8 | N41—C46—C45 | 124.1 (3) |
| C14—C13—H13 | 120.8 | N41—C46—H46 | 118.0 |
| C15—C14—C13 | 119.5 (2) | C45—C46—H46 | 118.0 |
| C15—C14—H14 | 120.3 | C56—C51—C52 | 117.92 (16) |
| C13—C14—H14 | 120.3 | C56—C51—C5 | 123.61 (15) |
| C16—C15—C14 | 118.2 (2) | C52—C51—C5 | 118.43 (15) |
| C16—C15—H15 | 120.9 | C53—C52—C51 | 121.41 (18) |
| C14—C15—H15 | 120.9 | C53—C52—H52 | 119.3 |
| N11—C16—C15 | 123.8 (2) | C51—C52—H52 | 119.3 |
| N11—C16—H16 | 118.1 | C54—C53—C52 | 118.12 (18) |
| C15—C16—H16 | 118.1 | C54—C53—H53 | 120.9 |
| O27—C27—C22 | 119.69 (16) | C52—C53—H53 | 120.9 |
| O27—C27—C2 | 121.13 (15) | C55—C54—C53 | 123.09 (17) |
| C22—C27—C2 | 119.16 (15) | C55—C54—F54 | 118.79 (17) |
| C22—N21—C26 | 117.2 (2) | C53—C54—F54 | 118.11 (17) |
| N21—C22—C23 | 123.49 (19) | C54—C55—C56 | 118.26 (17) |
| N21—C22—C27 | 117.14 (16) | C54—C55—H55 | 120.9 |
| C23—C22—C27 | 119.36 (19) | C56—C55—H55 | 120.9 |
| C22—C23—C24 | 117.3 (3) | C51—C56—C55 | 121.20 (16) |
| C22—C23—H23 | 121.4 | C51—C56—H56 | 119.4 |
| C24—C23—H23 | 121.4 | C55—C56—H56 | 119.4 |
| C25—C24—C23 | 119.8 (3) | | |
| O11—C1—C2—C27 | −61.80 (16) | C22—C23—C24—C25 | −1.5 (4) |
| C6—C1—C2—C27 | −179.08 (13) | C23—C24—C25—C26 | 1.7 (5) |
| C12—C1—C2—C27 | 57.59 (16) | C22—N21—C26—C25 | 0.1 (4) |
| O11—C1—C2—C3 | 59.62 (16) | C24—C25—C26—N21 | −1.0 (5) |

| | | | |
|-----------------|--------------|-----------------|--------------|
| C6—C1—C2—C3 | −57.65 (16) | C2—C3—C31—C36 | 148.77 (15) |
| C12—C1—C2—C3 | 179.02 (13) | C4—C3—C31—C36 | −84.24 (18) |
| C27—C2—C3—C31 | −58.61 (16) | C2—C3—C31—C32 | −34.7 (2) |
| C1—C2—C3—C31 | 179.97 (12) | C4—C3—C31—C32 | 92.30 (18) |
| C27—C2—C3—C4 | 175.80 (12) | C36—C31—C32—C33 | 1.9 (3) |
| C1—C2—C3—C4 | 54.37 (16) | C3—C31—C32—C33 | −174.72 (17) |
| C31—C3—C4—C47 | −51.99 (16) | C31—C32—C33—C34 | −0.5 (3) |
| C2—C3—C4—C47 | 75.59 (16) | C32—C33—C34—C35 | −0.8 (4) |
| C31—C3—C4—C5 | −178.62 (12) | C32—C33—C34—F34 | 180.0 (2) |
| C2—C3—C4—C5 | −51.05 (16) | C33—C34—C35—C36 | 0.7 (4) |
| C47—C4—C5—C51 | 54.51 (16) | F34—C34—C35—C36 | 179.9 (2) |
| C3—C4—C5—C51 | −179.66 (12) | C32—C31—C36—C35 | −1.9 (3) |
| C47—C4—C5—C6 | −74.26 (16) | C3—C31—C36—C35 | 174.78 (19) |
| C3—C4—C5—C6 | 51.57 (16) | C34—C35—C36—C31 | 0.7 (3) |
| O11—C1—C6—C5 | −60.66 (17) | C5—C4—C47—O47 | 58.7 (2) |
| C12—C1—C6—C5 | 179.18 (13) | C3—C4—C47—O47 | −67.30 (19) |
| C2—C1—C6—C5 | 58.90 (17) | C5—C4—C47—C42 | −121.88 (15) |
| C51—C5—C6—C1 | 176.87 (13) | C3—C4—C47—C42 | 112.16 (16) |
| C4—C5—C6—C1 | −56.61 (17) | C46—N41—C42—C43 | −1.6 (4) |
| C16—N11—C12—C13 | −2.1 (3) | C46—N41—C42—C47 | 177.1 (3) |
| C16—N11—C12—C1 | 173.54 (18) | O47—C47—C42—N41 | −163.26 (19) |
| O11—C1—C12—N11 | 28.5 (2) | C4—C47—C42—N41 | 17.3 (3) |
| C6—C1—C12—N11 | 147.25 (15) | O47—C47—C42—C43 | 15.5 (3) |
| C2—C1—C12—N11 | −91.57 (17) | C4—C47—C42—C43 | −164.01 (18) |
| O11—C1—C12—C13 | −155.82 (18) | N41—C42—C43—C44 | 0.3 (4) |
| C6—C1—C12—C13 | −37.1 (2) | C47—C42—C43—C44 | −178.3 (2) |
| C2—C1—C12—C13 | 84.1 (2) | C42—C43—C44—C45 | 1.2 (5) |
| N11—C12—C13—C14 | 1.6 (3) | C43—C44—C45—C46 | −1.4 (6) |
| C1—C12—C13—C14 | −173.7 (2) | C42—N41—C46—C45 | 1.4 (5) |
| C12—C13—C14—C15 | 0.1 (4) | C44—C45—C46—N41 | 0.1 (6) |
| C13—C14—C15—C16 | −1.1 (4) | C6—C5—C51—C56 | 18.5 (2) |
| C12—N11—C16—C15 | 1.0 (4) | C4—C5—C51—C56 | −108.96 (18) |
| C14—C15—C16—N11 | 0.6 (4) | C6—C5—C51—C52 | −163.96 (16) |
| C3—C2—C27—O27 | −45.1 (2) | C4—C5—C51—C52 | 68.6 (2) |
| C1—C2—C27—O27 | 76.93 (19) | C56—C51—C52—C53 | 0.1 (3) |
| C3—C2—C27—C22 | 136.74 (14) | C5—C51—C52—C53 | −177.57 (19) |
| C1—C2—C27—C22 | −101.21 (16) | C51—C52—C53—C54 | −0.2 (3) |
| C26—N21—C22—C23 | 0.1 (3) | C52—C53—C54—C55 | 0.0 (3) |
| C26—N21—C22—C27 | 179.0 (2) | C52—C53—C54—F54 | −179.53 (19) |
| O27—C27—C22—N21 | 172.63 (17) | C53—C54—C55—C56 | 0.2 (3) |
| C2—C27—C22—N21 | −9.2 (2) | F54—C54—C55—C56 | 179.70 (17) |
| O27—C27—C22—C23 | −8.4 (3) | C52—C51—C56—C55 | 0.1 (3) |
| C2—C27—C22—C23 | 169.76 (18) | C5—C51—C56—C55 | 177.62 (16) |
| N21—C22—C23—C24 | 0.6 (4) | C54—C55—C56—C51 | −0.2 (3) |
| C27—C22—C23—C24 | −178.2 (2) | | |

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> |
|-----------------------------------|-------------|---------------------|----------------------------|-------------------------------|
| O11—H11 \cdots N11 | 0.82 | 2.13 | 2.624 (2) | 119 |
| C13—H13 \cdots O11 ⁱ | 0.95 | 2.54 | 3.385 (3) | 148 |
| C55—H55 \cdots O27 ⁱ | 0.95 | 2.53 | 3.244 (2) | 132 |

Symmetry code: (i) $-x+1/2, y+1/2, z$.**(II) (1*RS*,2*SR*,3*SR*,4*RS*,5*RS*)-3,5-Bis(4-chlorophenyl)-2,4-bis(pyridine-2-carbonyl)-1-(pyridin-2-yl)cyclohexanol acetone 0.951-solvate***Crystal data* $C_{35}H_{27}Cl_2N_3O_3 \cdot 0.951C_3H_6O$ $M_r = 663.73$ Orthorhombic, *Fdd2* $a = 16.5446$ (6) Å $b = 53.4204$ (17) Å $c = 15.5857$ (4) Å $V = 13774.9$ (8) Å³ $Z = 16$ $F(000) = 5543$ $D_x = 1.280$ Mg m⁻³Cu $K\alpha$ radiation, $\lambda = 1.54178$ Å

Cell parameters from 4224 reflections

 $\theta = 4.6$ – 70.1° $\mu = 2.05$ mm⁻¹ $T = 200$ K

Block, colourless

 $0.30 \times 0.25 \times 0.20$ mm*Data collection*Agilent Xcalibur Ruby Gemini
diffractometer

Radiation source: Enhance (Cu) X-ray Source

 ω scans

Absorption correction: multi-scan

(CrysAlis PRO; Agilent, 2012)

 $T_{\min} = 0.388$, $T_{\max} = 0.664$

9544 measured reflections

4224 independent reflections

3490 reflections with $I > 2\sigma(I)$ $R_{\text{int}} = 0.027$ $\theta_{\max} = 70.1^\circ$, $\theta_{\min} = 4.6^\circ$ $h = -19 \rightarrow 20$ $k = -56 \rightarrow 64$ $l = -18 \rightarrow 6$ *Refinement*Refinement on F^2

Least-squares matrix: full

 $R[F^2 > 2\sigma(F^2)] = 0.039$ $wR(F^2) = 0.109$ $S = 0.97$

4224 reflections

436 parameters

7 restraints

Primary atom site location: structure-invariant
direct methodsSecondary atom site location: difference Fourier
mapHydrogen site location: inferred from
neighbouring sites

H-atom parameters constrained

 $w = 1/[\sigma^2(F_o^2) + (0.0744P)^2]$ where $P = (F_o^2 + 2F_c^2)/3$ $(\Delta/\sigma)_{\max} = 0.001$ $\Delta\rho_{\max} = 0.16$ e Å⁻³ $\Delta\rho_{\min} = -0.16$ e Å⁻³Absolute structure: Flack x determined using
613 quotients [(I+)-(I-)]/[(I+)+(I-)] (Parsons *et al.*, 2013).

Absolute structure parameter: 0.089 (18)

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 (\AA^2)

| | <i>x</i> | <i>y</i> | <i>z</i> | $U_{\text{iso}}^*/U_{\text{eq}}$ | Occ. (<1) |
|------|---------------|--------------|--------------|----------------------------------|-----------|
| C1 | 0.25172 (19) | 0.35490 (6) | 0.4632 (2) | 0.0505 (6) | |
| O11 | 0.20607 (15) | 0.35606 (5) | 0.54074 (15) | 0.0647 (6) | |
| H11 | 0.2379 | 0.3467 | 0.5731 | 0.097* | |
| C2 | 0.21280 (17) | 0.33568 (5) | 0.40064 (19) | 0.0481 (6) | |
| H2 | 0.2440 | 0.3357 | 0.3457 | 0.058* | |
| C3 | 0.12475 (17) | 0.34306 (5) | 0.38147 (19) | 0.0460 (6) | |
| H3 | 0.0962 | 0.3435 | 0.4380 | 0.055* | |
| C4 | 0.11812 (16) | 0.36986 (5) | 0.34352 (19) | 0.0454 (6) | |
| H4 | 0.0596 | 0.3745 | 0.3438 | 0.054* | |
| C5 | 0.16302 (18) | 0.38897 (5) | 0.4017 (2) | 0.0489 (6) | |
| H5 | 0.1336 | 0.3891 | 0.4577 | 0.059* | |
| C6 | 0.24983 (19) | 0.38087 (5) | 0.4218 (2) | 0.0526 (6) | |
| H6A | 0.2818 | 0.3806 | 0.3681 | 0.063* | |
| H6B | 0.2750 | 0.3932 | 0.4611 | 0.063* | |
| N11 | 0.3517 (2) | 0.33975 (6) | 0.5638 (2) | 0.0679 (7) | |
| C12 | 0.33845 (19) | 0.34663 (6) | 0.4829 (2) | 0.0546 (7) | |
| C13 | 0.3972 (2) | 0.34512 (7) | 0.4207 (3) | 0.0649 (8) | |
| H13 | 0.3865 | 0.3509 | 0.3642 | 0.078* | |
| C14 | 0.4712 (2) | 0.33528 (9) | 0.4409 (3) | 0.0809 (11) | |
| H14 | 0.5121 | 0.3338 | 0.3984 | 0.097* | |
| C15 | 0.4854 (3) | 0.32758 (9) | 0.5246 (4) | 0.0876 (13) | |
| H15 | 0.5356 | 0.3204 | 0.5407 | 0.105* | |
| C16 | 0.4251 (3) | 0.33070 (9) | 0.5827 (3) | 0.0862 (13) | |
| H16 | 0.4357 | 0.3262 | 0.6405 | 0.103* | |
| C27 | 0.21686 (19) | 0.30956 (6) | 0.4398 (2) | 0.0541 (7) | |
| O27 | 0.16848 (16) | 0.30235 (5) | 0.4917 (2) | 0.0735 (7) | |
| N21 | 0.3165 (2) | 0.29660 (7) | 0.3350 (3) | 0.0837 (10) | |
| C22 | 0.2864 (2) | 0.29305 (6) | 0.4138 (3) | 0.0620 (8) | |
| C23 | 0.3160 (3) | 0.27562 (7) | 0.4698 (4) | 0.0841 (12) | |
| H23 | 0.2924 | 0.2736 | 0.5249 | 0.101* | |
| C24 | 0.3807 (4) | 0.26106 (10) | 0.4446 (5) | 0.1104 (18) | |
| H24 | 0.4038 | 0.2492 | 0.4829 | 0.132* | |
| C25 | 0.4108 (4) | 0.26401 (11) | 0.3641 (5) | 0.116 (2) | |
| H25 | 0.4540 | 0.2537 | 0.3445 | 0.139* | |
| C26 | 0.3785 (3) | 0.28192 (12) | 0.3115 (4) | 0.1066 (17) | |
| H26 | 0.4009 | 0.2841 | 0.2559 | 0.128* | |
| C31 | 0.08089 (18) | 0.32368 (6) | 0.3270 (2) | 0.0513 (6) | |
| C32 | 0.1182 (2) | 0.31044 (7) | 0.2615 (3) | 0.0637 (8) | |
| H32 | 0.1729 | 0.3141 | 0.2477 | 0.076* | |
| C33 | 0.0783 (2) | 0.29211 (8) | 0.2158 (3) | 0.0746 (10) | |
| H33 | 0.1049 | 0.2832 | 0.1712 | 0.090* | |
| C34 | −0.0008 (3) | 0.28699 (7) | 0.2360 (3) | 0.0757 (10) | |
| Cl34 | −0.05239 (11) | 0.26346 (3) | 0.18053 (12) | 0.1225 (6) | |
| C35 | −0.0399 (2) | 0.29974 (8) | 0.2996 (3) | 0.0764 (11) | |
| H35 | −0.0946 | 0.2960 | 0.3126 | 0.092* | |

| | | | | | |
|------|--------------|-------------|--------------|-------------|------------|
| C36 | 0.0003 (2) | 0.31802 (7) | 0.3446 (3) | 0.0631 (8) | |
| H36 | −0.0272 | 0.3269 | 0.3884 | 0.076* | |
| C47 | 0.14717 (16) | 0.37140 (5) | 0.25098 (19) | 0.0451 (6) | |
| O47 | 0.21661 (12) | 0.36662 (5) | 0.23092 (16) | 0.0607 (6) | |
| N41 | 0.01329 (16) | 0.38537 (6) | 0.2066 (2) | 0.0646 (7) | |
| C42 | 0.08830 (17) | 0.37945 (5) | 0.1827 (2) | 0.0488 (6) | |
| C43 | 0.1135 (2) | 0.38102 (7) | 0.0983 (2) | 0.0618 (8) | |
| H43 | 0.1672 | 0.3765 | 0.0831 | 0.074* | |
| C44 | 0.0603 (2) | 0.38919 (8) | 0.0363 (3) | 0.0751 (10) | |
| H44 | 0.0768 | 0.3907 | −0.0218 | 0.090* | |
| C45 | −0.0167 (3) | 0.39508 (8) | 0.0603 (3) | 0.0782 (11) | |
| H45 | −0.0553 | 0.4005 | 0.0192 | 0.094* | |
| C46 | −0.0367 (2) | 0.39294 (9) | 0.1454 (3) | 0.0794 (11) | |
| H46 | −0.0903 | 0.3972 | 0.1616 | 0.095* | |
| C51 | 0.15672 (19) | 0.41541 (6) | 0.3660 (2) | 0.0508 (6) | |
| C52 | 0.0822 (2) | 0.42707 (7) | 0.3642 (3) | 0.0706 (10) | |
| H52 | 0.0362 | 0.4185 | 0.3856 | 0.085* | |
| C53 | 0.0733 (3) | 0.45099 (8) | 0.3318 (4) | 0.0804 (11) | |
| H53 | 0.0215 | 0.4587 | 0.3302 | 0.096* | |
| C54 | 0.1397 (3) | 0.46354 (7) | 0.3021 (3) | 0.0725 (10) | |
| Cl54 | 0.12896 (10) | 0.49384 (2) | 0.26117 (12) | 0.1142 (5) | |
| C55 | 0.2146 (3) | 0.45280 (7) | 0.3033 (3) | 0.0726 (10) | |
| H55 | 0.2603 | 0.4617 | 0.2825 | 0.087* | |
| C56 | 0.2225 (2) | 0.42862 (6) | 0.3355 (3) | 0.0623 (8) | |
| H56 | 0.2744 | 0.4210 | 0.3366 | 0.075* | |
| C71 | 0.6495 (16) | 0.2977 (7) | 0.2767 (10) | 0.125 (3) | 0.690 (13) |
| O71 | 0.5974 (5) | 0.3120 (2) | 0.2778 (8) | 0.159 (4) | 0.690 (13) |
| C72 | 0.7036 (14) | 0.2906 (3) | 0.2035 (9) | 0.174 (5) | 0.690 (13) |
| H72A | 0.7137 | 0.2726 | 0.2047 | 0.261* | 0.690 (13) |
| H72B | 0.7550 | 0.2996 | 0.2087 | 0.261* | 0.690 (13) |
| H72C | 0.6776 | 0.2951 | 0.1492 | 0.261* | 0.690 (13) |
| C73 | 0.6809 (14) | 0.2869 (3) | 0.3563 (8) | 0.174 (5) | 0.690 (13) |
| H73A | 0.7396 | 0.2893 | 0.3587 | 0.261* | 0.690 (13) |
| H73B | 0.6686 | 0.2690 | 0.3581 | 0.261* | 0.690 (13) |
| H73C | 0.6557 | 0.2953 | 0.4055 | 0.261* | 0.690 (13) |
| C81 | 0.664 (4) | 0.293 (2) | 0.285 (2) | 0.125 (3) | 0.261 (11) |
| O81 | 0.6093 (14) | 0.2987 (6) | 0.326 (2) | 0.159 (4) | 0.261 (11) |
| C82 | 0.680 (3) | 0.2969 (10) | 0.1916 (17) | 0.174 (5) | 0.261 (11) |
| H82A | 0.7179 | 0.2841 | 0.1711 | 0.261* | 0.261 (11) |
| H82B | 0.7035 | 0.3135 | 0.1825 | 0.261* | 0.261 (11) |
| H82C | 0.6291 | 0.2956 | 0.1599 | 0.261* | 0.261 (11) |
| C83 | 0.731 (2) | 0.2787 (7) | 0.323 (2) | 0.174 (5) | 0.261 (11) |
| H83A | 0.7726 | 0.2758 | 0.2799 | 0.261* | 0.261 (11) |
| H83B | 0.7101 | 0.2626 | 0.3440 | 0.261* | 0.261 (11) |
| H83C | 0.7539 | 0.2881 | 0.3714 | 0.261* | 0.261 (11) |

Atomic displacement parameters (\AA^2)

| | U^{11} | U^{22} | U^{33} | U^{12} | U^{13} | U^{23} |
|------|-------------|-------------|-------------|--------------|--------------|--------------|
| C1 | 0.0563 (14) | 0.0556 (15) | 0.0397 (13) | 0.0015 (13) | 0.0020 (13) | 0.0001 (12) |
| O11 | 0.0749 (13) | 0.0745 (14) | 0.0445 (12) | 0.0068 (12) | 0.0082 (11) | −0.0015 (11) |
| C2 | 0.0501 (13) | 0.0502 (13) | 0.0440 (14) | 0.0029 (12) | 0.0040 (12) | 0.0005 (12) |
| C3 | 0.0469 (13) | 0.0504 (13) | 0.0409 (13) | 0.0026 (11) | 0.0056 (11) | 0.0026 (11) |
| C4 | 0.0413 (12) | 0.0505 (14) | 0.0443 (14) | 0.0055 (11) | 0.0058 (11) | 0.0000 (12) |
| C5 | 0.0552 (14) | 0.0497 (13) | 0.0419 (13) | 0.0031 (12) | 0.0075 (13) | −0.0010 (11) |
| C6 | 0.0576 (15) | 0.0507 (14) | 0.0495 (15) | −0.0007 (13) | −0.0049 (13) | −0.0007 (13) |
| N11 | 0.0849 (19) | 0.0655 (15) | 0.0533 (15) | 0.0078 (15) | −0.0128 (16) | 0.0091 (13) |
| C12 | 0.0625 (16) | 0.0502 (14) | 0.0512 (16) | −0.0030 (13) | −0.0109 (15) | 0.0016 (13) |
| C13 | 0.0551 (16) | 0.080 (2) | 0.0597 (19) | −0.0013 (16) | −0.0068 (16) | 0.0029 (17) |
| C14 | 0.0621 (19) | 0.092 (3) | 0.088 (3) | 0.0039 (19) | −0.008 (2) | 0.002 (2) |
| C15 | 0.074 (2) | 0.086 (3) | 0.104 (3) | 0.015 (2) | −0.029 (3) | 0.006 (3) |
| C16 | 0.105 (3) | 0.084 (3) | 0.070 (2) | 0.019 (2) | −0.030 (3) | 0.015 (2) |
| C27 | 0.0583 (15) | 0.0555 (15) | 0.0485 (15) | −0.0016 (13) | −0.0029 (14) | 0.0026 (13) |
| O27 | 0.0774 (14) | 0.0687 (14) | 0.0743 (17) | 0.0041 (12) | 0.0120 (14) | 0.0199 (13) |
| N21 | 0.088 (2) | 0.093 (2) | 0.070 (2) | 0.0334 (19) | 0.0021 (18) | −0.0136 (18) |
| C22 | 0.0672 (17) | 0.0499 (15) | 0.069 (2) | 0.0054 (14) | −0.0081 (17) | −0.0079 (15) |
| C23 | 0.097 (3) | 0.0609 (19) | 0.094 (3) | 0.019 (2) | −0.003 (3) | 0.011 (2) |
| C24 | 0.123 (4) | 0.077 (3) | 0.131 (5) | 0.042 (3) | −0.014 (4) | 0.004 (3) |
| C25 | 0.122 (4) | 0.102 (4) | 0.123 (5) | 0.061 (3) | −0.013 (4) | −0.039 (4) |
| C26 | 0.110 (3) | 0.128 (4) | 0.081 (3) | 0.047 (3) | 0.011 (3) | −0.030 (3) |
| C31 | 0.0516 (14) | 0.0498 (14) | 0.0526 (16) | 0.0002 (12) | −0.0016 (13) | 0.0070 (13) |
| C32 | 0.0637 (16) | 0.0635 (17) | 0.064 (2) | 0.0005 (15) | −0.0012 (17) | −0.0067 (16) |
| C33 | 0.086 (2) | 0.067 (2) | 0.071 (2) | 0.0000 (18) | −0.016 (2) | −0.0121 (18) |
| C34 | 0.090 (2) | 0.0581 (17) | 0.079 (3) | −0.0081 (18) | −0.031 (2) | 0.0038 (18) |
| Cl34 | 0.1446 (11) | 0.0949 (8) | 0.1281 (12) | −0.0398 (8) | −0.0502 (10) | −0.0146 (8) |
| C35 | 0.0620 (18) | 0.081 (2) | 0.086 (3) | −0.0154 (19) | −0.0148 (19) | 0.014 (2) |
| C36 | 0.0564 (16) | 0.0667 (19) | 0.066 (2) | −0.0026 (15) | −0.0054 (16) | 0.0083 (17) |
| C47 | 0.0442 (13) | 0.0472 (12) | 0.0440 (15) | 0.0009 (11) | 0.0069 (12) | −0.0014 (11) |
| O47 | 0.0481 (10) | 0.0849 (15) | 0.0491 (11) | 0.0098 (10) | 0.0084 (10) | 0.0015 (11) |
| N41 | 0.0513 (13) | 0.0835 (18) | 0.0588 (16) | 0.0139 (13) | 0.0057 (13) | 0.0086 (15) |
| C42 | 0.0477 (13) | 0.0507 (13) | 0.0479 (15) | −0.0038 (11) | 0.0003 (13) | 0.0001 (12) |
| C43 | 0.0542 (16) | 0.082 (2) | 0.0494 (17) | −0.0068 (15) | 0.0071 (15) | 0.0027 (16) |
| C44 | 0.079 (2) | 0.093 (3) | 0.0528 (19) | −0.010 (2) | −0.0045 (18) | 0.0080 (19) |
| C45 | 0.080 (2) | 0.083 (2) | 0.072 (2) | 0.003 (2) | −0.022 (2) | 0.016 (2) |
| C46 | 0.0548 (17) | 0.101 (3) | 0.083 (3) | 0.0193 (19) | −0.0018 (19) | 0.014 (2) |
| C51 | 0.0590 (15) | 0.0487 (14) | 0.0448 (14) | 0.0031 (13) | 0.0035 (13) | −0.0028 (12) |
| C52 | 0.0645 (18) | 0.0581 (17) | 0.089 (3) | 0.0055 (16) | 0.0117 (19) | 0.0037 (18) |
| C53 | 0.076 (2) | 0.062 (2) | 0.103 (3) | 0.0158 (18) | −0.003 (2) | 0.008 (2) |
| C54 | 0.098 (3) | 0.0495 (16) | 0.070 (2) | 0.0066 (18) | −0.007 (2) | 0.0090 (16) |
| Cl54 | 0.1386 (10) | 0.0630 (5) | 0.1409 (12) | 0.0055 (6) | −0.0158 (10) | 0.0338 (6) |
| C55 | 0.084 (2) | 0.0572 (17) | 0.077 (2) | −0.0077 (18) | 0.006 (2) | 0.0091 (17) |
| C56 | 0.0596 (16) | 0.0565 (16) | 0.071 (2) | 0.0020 (14) | 0.0073 (17) | 0.0020 (16) |
| C71 | 0.138 (11) | 0.106 (16) | 0.132 (7) | −0.032 (6) | 0.022 (7) | 0.008 (6) |
| O71 | 0.130 (5) | 0.161 (8) | 0.186 (11) | 0.012 (5) | 0.014 (6) | 0.015 (7) |

| | | | | | | |
|-----|------------|------------|------------|------------|-----------|-----------|
| C72 | 0.286 (14) | 0.131 (8) | 0.104 (5) | −0.013 (8) | 0.028 (7) | 0.016 (4) |
| C73 | 0.286 (14) | 0.131 (8) | 0.104 (5) | −0.013 (8) | 0.028 (7) | 0.016 (4) |
| C81 | 0.138 (11) | 0.106 (16) | 0.132 (7) | −0.032 (6) | 0.022 (7) | 0.008 (6) |
| O81 | 0.130 (5) | 0.161 (8) | 0.186 (11) | 0.012 (5) | 0.014 (6) | 0.015 (7) |
| C82 | 0.286 (14) | 0.131 (8) | 0.104 (5) | −0.013 (8) | 0.028 (7) | 0.016 (4) |
| C83 | 0.286 (14) | 0.131 (8) | 0.104 (5) | −0.013 (8) | 0.028 (7) | 0.016 (4) |

Geometric parameters (Å, °)

| | | | |
|---------|------------|----------|------------|
| C1—O11 | 1.426 (4) | C34—C35 | 1.365 (7) |
| C1—C6 | 1.531 (4) | C34—C134 | 1.748 (4) |
| C1—C12 | 1.533 (4) | C35—C36 | 1.374 (6) |
| C1—C2 | 1.556 (4) | C35—H35 | 0.9500 |
| O11—H11 | 0.8847 | C36—H36 | 0.9500 |
| C2—C27 | 1.524 (4) | C47—O47 | 1.218 (3) |
| C2—C3 | 1.539 (4) | C47—C42 | 1.506 (4) |
| C2—H2 | 1.0000 | N41—C46 | 1.326 (5) |
| C3—C31 | 1.523 (4) | N41—C42 | 1.334 (4) |
| C3—C4 | 1.552 (4) | C42—C43 | 1.382 (5) |
| C3—H3 | 1.0000 | C43—C44 | 1.378 (5) |
| C4—C47 | 1.523 (4) | C43—H43 | 0.9500 |
| C4—C5 | 1.555 (4) | C44—C45 | 1.364 (6) |
| C4—H4 | 1.0000 | C44—H44 | 0.9500 |
| C5—C51 | 1.521 (4) | C45—C46 | 1.372 (7) |
| C5—C6 | 1.532 (4) | C45—H45 | 0.9500 |
| C5—H5 | 1.0000 | C46—H46 | 0.9500 |
| C6—H6A | 0.9900 | C51—C52 | 1.381 (5) |
| C6—H6B | 0.9900 | C51—C56 | 1.382 (5) |
| N11—C12 | 1.331 (5) | C52—C53 | 1.382 (5) |
| N11—C16 | 1.340 (5) | C52—H52 | 0.9500 |
| C12—C13 | 1.375 (5) | C53—C54 | 1.368 (6) |
| C13—C14 | 1.370 (6) | C53—H53 | 0.9500 |
| C13—H13 | 0.9500 | C54—C55 | 1.365 (6) |
| C14—C15 | 1.387 (8) | C54—C154 | 1.749 (4) |
| C14—H14 | 0.9500 | C55—C56 | 1.392 (5) |
| C15—C16 | 1.357 (7) | C55—H55 | 0.9500 |
| C15—H15 | 0.9500 | C56—H56 | 0.9500 |
| C16—H16 | 0.9500 | C71—O71 | 1.151 (13) |
| C27—O27 | 1.201 (4) | C71—C73 | 1.464 (17) |
| C27—C22 | 1.506 (5) | C71—C72 | 1.498 (14) |
| N21—C22 | 1.338 (6) | C72—H72A | 0.9800 |
| N21—C26 | 1.342 (5) | C72—H72B | 0.9800 |
| C22—C23 | 1.366 (6) | C72—H72C | 0.9800 |
| C23—C24 | 1.380 (7) | C73—H73A | 0.9800 |
| C23—H23 | 0.9500 | C73—H73B | 0.9800 |
| C24—C25 | 1.360 (10) | C73—H73C | 0.9800 |
| C24—H24 | 0.9500 | C81—O81 | 1.150 (13) |
| C25—C26 | 1.369 (9) | C81—C83 | 1.463 (18) |

| | | | |
|-------------|-----------|--------------|------------|
| C25—H25 | 0.9500 | C81—C82 | 1.497 (15) |
| C26—H26 | 0.9500 | C82—H82A | 0.9800 |
| C31—C32 | 1.386 (5) | C82—H82B | 0.9800 |
| C31—C36 | 1.394 (5) | C82—H82C | 0.9800 |
| C32—C33 | 1.380 (5) | C83—H83A | 0.9800 |
| C32—H32 | 0.9500 | C83—H83B | 0.9800 |
| C33—C34 | 1.373 (6) | C83—H83C | 0.9800 |
| C33—H33 | 0.9500 | | |
| O11—C1—C6 | 107.9 (2) | C34—C33—H33 | 120.7 |
| O11—C1—C12 | 109.8 (3) | C32—C33—H33 | 120.7 |
| C6—C1—C12 | 111.4 (3) | C35—C34—C33 | 121.2 (4) |
| O11—C1—C2 | 109.9 (2) | C35—C34—C134 | 119.1 (3) |
| C6—C1—C2 | 109.0 (2) | C33—C34—C134 | 119.6 (4) |
| C12—C1—C2 | 108.8 (2) | C34—C35—C36 | 119.7 (3) |
| C1—O11—H11 | 98.2 | C34—C35—H35 | 120.1 |
| C27—C2—C3 | 110.7 (2) | C36—C35—H35 | 120.1 |
| C27—C2—C1 | 109.6 (2) | C35—C36—C31 | 121.1 (4) |
| C3—C2—C1 | 110.1 (2) | C35—C36—H36 | 119.5 |
| C27—C2—H2 | 108.8 | C31—C36—H36 | 119.5 |
| C3—C2—H2 | 108.8 | O47—C47—C42 | 119.2 (3) |
| C1—C2—H2 | 108.8 | O47—C47—C4 | 122.0 (3) |
| C31—C3—C2 | 112.6 (2) | C42—C47—C4 | 118.8 (2) |
| C31—C3—C4 | 112.4 (2) | C46—N41—C42 | 116.8 (3) |
| C2—C3—C4 | 112.2 (2) | N41—C42—C43 | 122.2 (3) |
| C31—C3—H3 | 106.4 | N41—C42—C47 | 118.1 (3) |
| C2—C3—H3 | 106.4 | C43—C42—C47 | 119.6 (3) |
| C4—C3—H3 | 106.4 | C44—C43—C42 | 119.5 (3) |
| C47—C4—C3 | 112.9 (2) | C44—C43—H43 | 120.2 |
| C47—C4—C5 | 111.5 (2) | C42—C43—H43 | 120.2 |
| C3—C4—C5 | 110.5 (2) | C45—C44—C43 | 118.6 (4) |
| C47—C4—H4 | 107.2 | C45—C44—H44 | 120.7 |
| C3—C4—H4 | 107.2 | C43—C44—H44 | 120.7 |
| C5—C4—H4 | 107.2 | C44—C45—C46 | 118.1 (4) |
| C51—C5—C6 | 113.7 (2) | C44—C45—H45 | 121.0 |
| C51—C5—C4 | 111.3 (2) | C46—C45—H45 | 121.0 |
| C6—C5—C4 | 112.4 (2) | N41—C46—C45 | 124.8 (4) |
| C51—C5—H5 | 106.3 | N41—C46—H46 | 117.6 |
| C6—C5—H5 | 106.3 | C45—C46—H46 | 117.6 |
| C4—C5—H5 | 106.3 | C52—C51—C56 | 117.7 (3) |
| C1—C6—C5 | 111.2 (2) | C52—C51—C5 | 119.2 (3) |
| C1—C6—H6A | 109.4 | C56—C51—C5 | 123.1 (3) |
| C5—C6—H6A | 109.4 | C51—C52—C53 | 121.4 (4) |
| C1—C6—H6B | 109.4 | C51—C52—H52 | 119.3 |
| C5—C6—H6B | 109.4 | C53—C52—H52 | 119.3 |
| H6A—C6—H6B | 108.0 | C54—C53—C52 | 119.4 (4) |
| C12—N11—C16 | 117.2 (4) | C54—C53—H53 | 120.3 |
| N11—C12—C13 | 122.3 (3) | C52—C53—H53 | 120.3 |

| | | | |
|---------------|-----------|-----------------|------------|
| N11—C12—C1 | 115.1 (3) | C55—C54—C53 | 121.2 (3) |
| C13—C12—C1 | 122.5 (3) | C55—C54—C154 | 119.1 (3) |
| C14—C13—C12 | 119.5 (4) | C53—C54—C154 | 119.7 (3) |
| C14—C13—H13 | 120.3 | C54—C55—C56 | 118.7 (4) |
| C12—C13—H13 | 120.3 | C54—C55—H55 | 120.6 |
| C13—C14—C15 | 118.7 (5) | C56—C55—H55 | 120.6 |
| C13—C14—H14 | 120.6 | C51—C56—C55 | 121.6 (3) |
| C15—C14—H14 | 120.6 | C51—C56—H56 | 119.2 |
| C16—C15—C14 | 117.8 (4) | C55—C56—H56 | 119.2 |
| C16—C15—H15 | 121.1 | O71—C71—C73 | 120.9 (14) |
| C14—C15—H15 | 121.1 | O71—C71—C72 | 128.7 (13) |
| N11—C16—C15 | 124.3 (4) | C73—C71—C72 | 109.5 (11) |
| N11—C16—H16 | 117.8 | C71—C72—H72A | 109.5 |
| C15—C16—H16 | 117.8 | C71—C72—H72B | 109.5 |
| O27—C27—C22 | 120.2 (3) | H72A—C72—H72B | 109.5 |
| O27—C27—C2 | 122.2 (3) | C71—C72—H72C | 109.5 |
| C22—C27—C2 | 117.5 (3) | H72A—C72—H72C | 109.5 |
| C22—N21—C26 | 116.8 (4) | H72B—C72—H72C | 109.5 |
| N21—C22—C23 | 123.3 (4) | C71—C73—H73A | 109.5 |
| N21—C22—C27 | 116.6 (3) | C71—C73—H73B | 109.5 |
| C23—C22—C27 | 120.1 (4) | H73A—C73—H73B | 109.5 |
| C22—C23—C24 | 118.7 (5) | C71—C73—H73C | 109.5 |
| C22—C23—H23 | 120.6 | H73A—C73—H73C | 109.5 |
| C24—C23—H23 | 120.6 | H73B—C73—H73C | 109.5 |
| C25—C24—C23 | 118.8 (5) | O81—C81—C83 | 120.7 (17) |
| C25—C24—H24 | 120.6 | O81—C81—C82 | 129.5 (16) |
| C23—C24—H24 | 120.6 | C83—C81—C82 | 109.7 (13) |
| C24—C25—C26 | 119.3 (5) | C81—C82—H82A | 109.5 |
| C24—C25—H25 | 120.3 | C81—C82—H82B | 109.5 |
| C26—C25—H25 | 120.3 | H82A—C82—H82B | 109.5 |
| N21—C26—C25 | 123.0 (6) | C81—C82—H82C | 109.5 |
| N21—C26—H26 | 118.5 | H82A—C82—H82C | 109.5 |
| C25—C26—H26 | 118.5 | H82B—C82—H82C | 109.5 |
| C32—C31—C36 | 117.4 (3) | C81—C83—H83A | 109.5 |
| C32—C31—C3 | 123.0 (3) | C81—C83—H83B | 109.5 |
| C36—C31—C3 | 119.5 (3) | H83A—C83—H83B | 109.5 |
| C33—C32—C31 | 121.9 (3) | C81—C83—H83C | 109.5 |
| C33—C32—H32 | 119.0 | H83A—C83—H83C | 109.5 |
| C31—C32—H32 | 119.0 | H83B—C83—H83C | 109.5 |
| C34—C33—C32 | 118.6 (4) | | |
| O11—C1—C2—C27 | −63.9 (3) | C22—C23—C24—C25 | −2.2 (8) |
| C6—C1—C2—C27 | 178.1 (2) | C23—C24—C25—C26 | 2.5 (10) |
| C12—C1—C2—C27 | 56.4 (3) | C22—N21—C26—C25 | 0.0 (8) |
| O11—C1—C2—C3 | 58.2 (3) | C24—C25—C26—N21 | −1.4 (10) |
| C6—C1—C2—C3 | −59.9 (3) | C2—C3—C31—C32 | −36.8 (4) |
| C12—C1—C2—C3 | 178.5 (2) | C4—C3—C31—C32 | 91.0 (4) |
| C27—C2—C3—C31 | −53.4 (3) | C2—C3—C31—C36 | 140.7 (3) |

| | | | |
|-----------------|------------|------------------|------------|
| C1—C2—C3—C31 | −174.8 (2) | C4—C3—C31—C36 | −91.4 (3) |
| C27—C2—C3—C4 | 178.6 (2) | C36—C31—C32—C33 | −0.8 (5) |
| C1—C2—C3—C4 | 57.3 (3) | C3—C31—C32—C33 | 176.8 (3) |
| C31—C3—C4—C47 | −55.0 (3) | C31—C32—C33—C34 | 0.2 (6) |
| C2—C3—C4—C47 | 73.1 (3) | C32—C33—C34—C35 | 0.3 (6) |
| C31—C3—C4—C5 | 179.5 (2) | C32—C33—C34—C134 | −178.8 (3) |
| C2—C3—C4—C5 | −52.4 (3) | C33—C34—C35—C36 | −0.1 (6) |
| C47—C4—C5—C51 | 54.1 (3) | C134—C34—C35—C36 | 179.0 (3) |
| C3—C4—C5—C51 | −179.6 (2) | C34—C35—C36—C31 | −0.6 (6) |
| C47—C4—C5—C6 | −74.7 (3) | C32—C31—C36—C35 | 1.0 (5) |
| C3—C4—C5—C6 | 51.6 (3) | C3—C31—C36—C35 | −176.7 (3) |
| O11—C1—C6—C5 | −59.7 (3) | C3—C4—C47—O47 | −61.9 (4) |
| C12—C1—C6—C5 | 179.7 (3) | C5—C4—C47—O47 | 63.1 (4) |
| C2—C1—C6—C5 | 59.6 (3) | C3—C4—C47—C42 | 119.0 (3) |
| C51—C5—C6—C1 | 176.0 (3) | C5—C4—C47—C42 | −116.0 (3) |
| C4—C5—C6—C1 | −56.4 (3) | C46—N41—C42—C43 | −0.1 (5) |
| C16—N11—C12—C13 | −1.2 (5) | C46—N41—C42—C47 | 178.5 (3) |
| C16—N11—C12—C1 | 175.4 (3) | O47—C47—C42—N41 | −177.8 (3) |
| O11—C1—C12—N11 | 6.8 (4) | C4—C47—C42—N41 | 1.3 (4) |
| C6—C1—C12—N11 | 126.3 (3) | O47—C47—C42—C43 | 0.8 (4) |
| C2—C1—C12—N11 | −113.6 (3) | C4—C47—C42—C43 | 179.9 (3) |
| O11—C1—C12—C13 | −176.6 (3) | N41—C42—C43—C44 | 0.7 (5) |
| C6—C1—C12—C13 | −57.1 (4) | C47—C42—C43—C44 | −177.9 (3) |
| C2—C1—C12—C13 | 63.1 (4) | C42—C43—C44—C45 | −1.1 (6) |
| N11—C12—C13—C14 | 2.7 (6) | C43—C44—C45—C46 | 1.0 (7) |
| C1—C12—C13—C14 | −173.7 (4) | C42—N41—C46—C45 | 0.0 (7) |
| C12—C13—C14—C15 | −1.4 (7) | C44—C45—C46—N41 | −0.5 (7) |
| C13—C14—C15—C16 | −1.3 (7) | C6—C5—C51—C52 | −165.0 (3) |
| C12—N11—C16—C15 | −1.7 (7) | C4—C5—C51—C52 | 66.9 (4) |
| C14—C15—C16—N11 | 2.9 (8) | C6—C5—C51—C56 | 14.5 (4) |
| C3—C2—C27—O27 | −39.9 (4) | C4—C5—C51—C56 | −113.6 (3) |
| C1—C2—C27—O27 | 81.8 (4) | C56—C51—C52—C53 | 1.0 (6) |
| C3—C2—C27—C22 | 142.5 (3) | C5—C51—C52—C53 | −179.5 (4) |
| C1—C2—C27—C22 | −95.8 (3) | C51—C52—C53—C54 | −0.9 (7) |
| C26—N21—C22—C23 | 0.3 (7) | C52—C53—C54—C55 | 0.4 (7) |
| C26—N21—C22—C27 | −179.9 (4) | C52—C53—C54—C154 | −179.9 (4) |
| O27—C27—C22—N21 | 152.5 (4) | C53—C54—C55—C56 | 0.0 (7) |
| C2—C27—C22—N21 | −29.9 (5) | C154—C54—C55—C56 | −179.7 (3) |
| O27—C27—C22—C23 | −27.8 (5) | C52—C51—C56—C55 | −0.5 (6) |
| C2—C27—C22—C23 | 149.9 (4) | C5—C51—C56—C55 | 180.0 (4) |
| N21—C22—C23—C24 | 0.8 (7) | C54—C55—C56—C51 | 0.0 (6) |
| C27—C22—C23—C24 | −178.9 (4) | | |

Hydrogen-bond geometry (Å, °)

| <i>D</i> —H··· <i>A</i> | <i>D</i> —H | H··· <i>A</i> | <i>D</i> ··· <i>A</i> | <i>D</i> —H··· <i>A</i> |
|-------------------------|-------------|---------------|-----------------------|-------------------------|
| O11—H11···N11 | 0.88 | 1.92 | 2.587 (4) | 130 |
| C14—H14···O71 | 0.95 | 2.62 | 3.517 (12) | 157 |

| | | | | |
|-------------------------------------|------|------|------------|-----|
| C14—H14 \cdots O81 | 0.95 | 2.72 | 3.499 (12) | 140 |
| C43—H43 \cdots N41 ⁱ | 0.95 | 2.61 | 3.433 (4) | 145 |
| C45—H45 \cdots O71 ⁱⁱ | 0.95 | 2.57 | 3.251 (11) | 129 |
| C16—H16 \cdots Cg1 ⁱⁱⁱ | 0.95 | 3.00 | 3.869 (5) | 153 |

Symmetry codes: (i) $x+1/4, -y+3/4, z-1/4$; (ii) $x-3/4, -y+3/4, z-1/4$; (iii) $x+1/2, y, z+1/2$.

(III) (1*RS*,2*SR*,3*SR*,4*RS*,5*RS*)- 3,5-Bis(4-bromophenyl)-2,4-bis(pyridine-2-carbonyl)-1-(pyridin-2-yl)cyclohexanol

Crystal data

| | |
|----------------------------------|---------------------------------------------------------|
| $C_{35}H_{27}Br_2N_3O_3$ | $Z = 2$ |
| $M_r = 697.41$ | $F(000) = 704$ |
| Triclinic, $P\bar{1}$ | $D_x = 1.471 \text{ Mg m}^{-3}$ |
| $a = 9.5741 (4) \text{ \AA}$ | Cu $K\alpha$ radiation, $\lambda = 1.54178 \text{ \AA}$ |
| $b = 10.7061 (3) \text{ \AA}$ | Cell parameters from 5922 reflections |
| $c = 15.9952 (6) \text{ \AA}$ | $\theta = 4.8\text{--}70.0^\circ$ |
| $\alpha = 92.863 (3)^\circ$ | $\mu = 3.58 \text{ mm}^{-1}$ |
| $\beta = 97.443 (3)^\circ$ | $T = 200 \text{ K}$ |
| $\gamma = 103.618 (3)^\circ$ | Block, colourless |
| $V = 1574.49 (10) \text{ \AA}^3$ | $0.25 \times 0.20 \times 0.15 \text{ mm}$ |

Data collection

| | |
|-----------------------------------------------------------------|---------------------------------------------------------------------|
| Agilent Xcalibur Ruby Gemini diffractometer | 5922 independent reflections |
| Radiation source: Enhance (Cu) X-ray Source | 4948 reflections with $I > 2\sigma(I)$ |
| ω scans | $R_{\text{int}} = 0.026$ |
| Absorption correction: multi-scan (CrysAlis PRO; Agilent, 2012) | $\theta_{\text{max}} = 70.0^\circ, \theta_{\text{min}} = 4.8^\circ$ |
| $T_{\text{min}} = 0.109, T_{\text{max}} = 0.584$ | $h = -10 \rightarrow 11$ |
| 11667 measured reflections | $k = -13 \rightarrow 13$ |
| | $l = -19 \rightarrow 19$ |

Refinement

| | |
|----------------------------------------------------------------|----------------------------------------------------------|
| Refinement on F^2 | Secondary atom site location: difference Fourier map |
| Least-squares matrix: full | Hydrogen site location: inferred from neighbouring sites |
| $R[F^2 > 2\sigma(F^2)] = 0.046$ | H-atom parameters constrained |
| $wR(F^2) = 0.141$ | $w = 1/[\sigma^2(F_o^2) + (0.0808P)^2 + 0.8269P]$ |
| $S = 1.05$ | where $P = (F_o^2 + 2F_c^2)/3$ |
| 5922 reflections | $(\Delta/\sigma)_{\text{max}} < 0.001$ |
| 388 parameters | $\Delta\rho_{\text{max}} = 0.67 \text{ e \AA}^{-3}$ |
| 0 restraints | $\Delta\rho_{\text{min}} = -0.64 \text{ e \AA}^{-3}$ |
| Primary atom site location: structure-invariant direct methods | |

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 (\AA^2)

| | x | y | z | $U_{\text{iso}}^*/U_{\text{eq}}$ |
|-----|-------------|------------|--------------|----------------------------------|
| C1 | 0.1094 (3) | 0.2890 (3) | 0.37522 (18) | 0.0469 (6) |
| O11 | -0.0179 (2) | 0.1914 (2) | 0.34356 (14) | 0.0597 (5) |

| | | | | |
|------|-------------|-------------|--------------|-------------|
| H11 | −0.0388 | 0.1511 | 0.3839 | 0.075* |
| C2 | 0.2459 (3) | 0.2500 (3) | 0.34883 (17) | 0.0431 (6) |
| H2 | 0.3345 | 0.3181 | 0.3736 | 0.052* |
| C3 | 0.2393 (3) | 0.2382 (2) | 0.25268 (17) | 0.0423 (5) |
| H3 | 0.1509 | 0.1686 | 0.2300 | 0.051* |
| C4 | 0.2191 (3) | 0.3631 (3) | 0.21229 (17) | 0.0428 (6) |
| H4 | 0.2020 | 0.3448 | 0.1494 | 0.051* |
| C5 | 0.0830 (3) | 0.3990 (3) | 0.23934 (18) | 0.0474 (6) |
| H5 | −0.0014 | 0.3245 | 0.2185 | 0.057* |
| C6 | 0.0928 (3) | 0.4136 (3) | 0.33570 (19) | 0.0505 (6) |
| H6A | 0.0040 | 0.4358 | 0.3508 | 0.061* |
| H6B | 0.1771 | 0.4851 | 0.3592 | 0.061* |
| N11 | 0.0326 (3) | 0.2241 (3) | 0.50752 (18) | 0.0679 (8) |
| C12 | 0.1245 (3) | 0.3091 (3) | 0.47110 (19) | 0.0496 (6) |
| C13 | 0.2307 (4) | 0.4069 (4) | 0.5184 (2) | 0.0618 (8) |
| H13 | 0.2964 | 0.4669 | 0.4914 | 0.074* |
| C14 | 0.2392 (4) | 0.4156 (4) | 0.6059 (2) | 0.0722 (9) |
| H14 | 0.3110 | 0.4819 | 0.6396 | 0.087* |
| C15 | 0.1442 (4) | 0.3286 (5) | 0.6429 (2) | 0.0778 (11) |
| H15 | 0.1477 | 0.3333 | 0.7026 | 0.093* |
| C16 | 0.0443 (5) | 0.2349 (5) | 0.5928 (2) | 0.0857 (13) |
| H16 | −0.0211 | 0.1735 | 0.6190 | 0.103* |
| C27 | 0.2561 (3) | 0.1226 (3) | 0.38517 (19) | 0.0489 (6) |
| O27 | 0.1950 (3) | 0.0192 (2) | 0.34738 (15) | 0.0666 (6) |
| N21 | 0.4626 (4) | 0.2257 (3) | 0.4895 (2) | 0.0679 (8) |
| C22 | 0.3450 (4) | 0.1270 (3) | 0.4699 (2) | 0.0541 (7) |
| C23 | 0.3069 (5) | 0.0303 (4) | 0.5227 (3) | 0.0768 (11) |
| H23 | 0.2229 | −0.0384 | 0.5068 | 0.092* |
| C24 | 0.3957 (7) | 0.0364 (6) | 0.6000 (3) | 0.1017 (17) |
| H24 | 0.3722 | −0.0276 | 0.6384 | 0.122* |
| C25 | 0.5172 (7) | 0.1359 (5) | 0.6197 (3) | 0.0977 (17) |
| H25 | 0.5802 | 0.1416 | 0.6715 | 0.117* |
| C26 | 0.5455 (6) | 0.2268 (4) | 0.5633 (3) | 0.0884 (14) |
| H26 | 0.6300 | 0.2954 | 0.5776 | 0.106* |
| C31 | 0.3678 (3) | 0.1972 (2) | 0.22351 (17) | 0.0439 (6) |
| C32 | 0.5090 (3) | 0.2443 (3) | 0.2641 (2) | 0.0550 (7) |
| H32 | 0.5266 | 0.2992 | 0.3148 | 0.066* |
| C33 | 0.6256 (3) | 0.2124 (3) | 0.2318 (2) | 0.0597 (8) |
| H33 | 0.7222 | 0.2468 | 0.2593 | 0.072* |
| C34 | 0.5991 (4) | 0.1310 (3) | 0.1601 (2) | 0.0575 (7) |
| Br34 | 0.75694 (5) | 0.09296 (5) | 0.11223 (4) | 0.0979 (2) |
| C35 | 0.4591 (4) | 0.0767 (4) | 0.1205 (2) | 0.0655 (9) |
| H35 | 0.4417 | 0.0171 | 0.0721 | 0.079* |
| C36 | 0.3452 (4) | 0.1110 (3) | 0.1528 (2) | 0.0561 (7) |
| H36 | 0.2487 | 0.0745 | 0.1257 | 0.067* |
| C47 | 0.3521 (3) | 0.4760 (3) | 0.23542 (18) | 0.0441 (6) |
| O47 | 0.4088 (2) | 0.5068 (2) | 0.30802 (13) | 0.0568 (5) |
| N41 | 0.3478 (4) | 0.5267 (3) | 0.0881 (2) | 0.0725 (8) |

| | | | | |
|------|--------------|-------------|--------------|--------------|
| C42 | 0.4133 (3) | 0.5553 (3) | 0.1677 (2) | 0.0512 (6) |
| C43 | 0.5344 (4) | 0.6559 (4) | 0.1917 (3) | 0.0752 (10) |
| H43 | 0.5767 | 0.6742 | 0.2495 | 0.090* |
| C44 | 0.5924 (6) | 0.7290 (5) | 0.1310 (4) | 0.1031 (17) |
| H44 | 0.6775 | 0.7971 | 0.1456 | 0.124* |
| C45 | 0.5261 (6) | 0.7024 (6) | 0.0496 (4) | 0.113 (2) |
| H45 | 0.5621 | 0.7530 | 0.0064 | 0.135* |
| C46 | 0.4060 (6) | 0.6008 (6) | 0.0310 (3) | 0.1027 (17) |
| H46 | 0.3615 | 0.5822 | −0.0263 | 0.123* |
| C51 | 0.0525 (3) | 0.5151 (3) | 0.19609 (18) | 0.0466 (6) |
| C52 | −0.0392 (4) | 0.4954 (3) | 0.1203 (2) | 0.0611 (8) |
| H52 | −0.0860 | 0.4096 | 0.0980 | 0.073* |
| C53 | −0.0653 (4) | 0.5979 (3) | 0.0755 (2) | 0.0643 (8) |
| H53 | −0.1278 | 0.5828 | 0.0229 | 0.077* |
| C54 | 0.0009 (3) | 0.7206 (3) | 0.1089 (2) | 0.0544 (7) |
| Br54 | −0.03457 (5) | 0.86020 (4) | 0.04693 (3) | 0.07606 (16) |
| C55 | 0.0917 (4) | 0.7454 (3) | 0.1847 (2) | 0.0577 (7) |
| H55 | 0.1369 | 0.8315 | 0.2068 | 0.069* |
| C56 | 0.1159 (4) | 0.6418 (3) | 0.2283 (2) | 0.0553 (7) |
| H56 | 0.1772 | 0.6578 | 0.2813 | 0.066* |

Atomic displacement parameters (Å²)

| | U^{11} | U^{22} | U^{33} | U^{12} | U^{13} | U^{23} |
|-----|-------------|-------------|-------------|--------------|--------------|--------------|
| C1 | 0.0392 (13) | 0.0497 (15) | 0.0488 (15) | 0.0037 (11) | 0.0059 (11) | 0.0116 (11) |
| O11 | 0.0459 (11) | 0.0660 (13) | 0.0585 (12) | −0.0037 (10) | 0.0042 (9) | 0.0149 (10) |
| C2 | 0.0421 (13) | 0.0399 (13) | 0.0450 (14) | 0.0050 (10) | 0.0043 (10) | 0.0108 (10) |
| C3 | 0.0393 (13) | 0.0383 (12) | 0.0457 (14) | 0.0030 (10) | 0.0023 (10) | 0.0102 (10) |
| C4 | 0.0433 (13) | 0.0421 (13) | 0.0408 (13) | 0.0061 (11) | 0.0027 (10) | 0.0114 (10) |
| C5 | 0.0409 (14) | 0.0458 (14) | 0.0525 (15) | 0.0062 (11) | 0.0005 (11) | 0.0126 (11) |
| C6 | 0.0473 (15) | 0.0552 (16) | 0.0536 (16) | 0.0161 (12) | 0.0129 (12) | 0.0159 (13) |
| N11 | 0.0625 (17) | 0.0764 (19) | 0.0571 (16) | −0.0042 (14) | 0.0157 (13) | 0.0159 (13) |
| C12 | 0.0454 (15) | 0.0543 (16) | 0.0517 (16) | 0.0126 (12) | 0.0119 (12) | 0.0139 (12) |
| C13 | 0.0581 (18) | 0.0651 (19) | 0.0566 (18) | 0.0054 (15) | 0.0049 (14) | 0.0089 (14) |
| C14 | 0.063 (2) | 0.085 (3) | 0.063 (2) | 0.0140 (18) | 0.0011 (16) | −0.0032 (18) |
| C15 | 0.068 (2) | 0.114 (3) | 0.0501 (19) | 0.018 (2) | 0.0123 (16) | 0.0069 (19) |
| C16 | 0.079 (3) | 0.113 (3) | 0.057 (2) | −0.004 (2) | 0.0232 (19) | 0.022 (2) |
| C27 | 0.0526 (16) | 0.0413 (14) | 0.0510 (15) | 0.0072 (12) | 0.0066 (12) | 0.0116 (11) |
| O27 | 0.0818 (16) | 0.0433 (11) | 0.0637 (14) | −0.0001 (11) | −0.0038 (12) | 0.0116 (10) |
| N21 | 0.077 (2) | 0.0548 (15) | 0.0665 (18) | 0.0189 (14) | −0.0131 (15) | 0.0022 (13) |
| C22 | 0.0646 (19) | 0.0483 (15) | 0.0513 (16) | 0.0208 (14) | 0.0012 (13) | 0.0073 (12) |
| C23 | 0.096 (3) | 0.068 (2) | 0.067 (2) | 0.020 (2) | 0.0048 (19) | 0.0260 (18) |
| C24 | 0.148 (5) | 0.104 (4) | 0.064 (2) | 0.053 (4) | 0.004 (3) | 0.037 (2) |
| C25 | 0.133 (4) | 0.095 (3) | 0.066 (2) | 0.056 (3) | −0.031 (3) | −0.006 (2) |
| C26 | 0.102 (3) | 0.069 (2) | 0.083 (3) | 0.028 (2) | −0.033 (2) | −0.008 (2) |
| C31 | 0.0465 (14) | 0.0387 (13) | 0.0453 (14) | 0.0083 (11) | 0.0038 (11) | 0.0105 (10) |
| C32 | 0.0480 (16) | 0.0565 (17) | 0.0559 (17) | 0.0096 (13) | 0.0012 (12) | −0.0086 (13) |
| C33 | 0.0432 (15) | 0.0594 (18) | 0.073 (2) | 0.0076 (13) | 0.0068 (14) | −0.0022 (15) |

| | | | | | | |
|------|-------------|-------------|-------------|--------------|--------------|--------------|
| C34 | 0.0583 (18) | 0.0496 (16) | 0.0683 (19) | 0.0139 (13) | 0.0215 (15) | 0.0060 (14) |
| Br34 | 0.0719 (3) | 0.0935 (3) | 0.1280 (4) | 0.0138 (2) | 0.0402 (3) | −0.0285 (3) |
| C35 | 0.070 (2) | 0.0626 (19) | 0.0597 (19) | 0.0105 (16) | 0.0115 (16) | −0.0109 (15) |
| C36 | 0.0533 (17) | 0.0572 (17) | 0.0509 (16) | 0.0043 (13) | 0.0014 (13) | −0.0014 (13) |
| C47 | 0.0407 (13) | 0.0398 (13) | 0.0507 (16) | 0.0072 (10) | 0.0049 (11) | 0.0102 (11) |
| O47 | 0.0561 (12) | 0.0521 (11) | 0.0518 (12) | −0.0030 (9) | −0.0009 (9) | 0.0071 (9) |
| N41 | 0.0667 (18) | 0.081 (2) | 0.0631 (18) | 0.0009 (15) | 0.0096 (14) | 0.0287 (15) |
| C42 | 0.0459 (15) | 0.0511 (15) | 0.0564 (17) | 0.0085 (12) | 0.0079 (12) | 0.0181 (13) |
| C43 | 0.064 (2) | 0.068 (2) | 0.084 (3) | −0.0065 (17) | 0.0105 (18) | 0.0255 (19) |
| C44 | 0.085 (3) | 0.093 (3) | 0.115 (4) | −0.020 (3) | 0.021 (3) | 0.045 (3) |
| C45 | 0.098 (4) | 0.121 (4) | 0.113 (4) | −0.007 (3) | 0.033 (3) | 0.068 (3) |
| C46 | 0.099 (3) | 0.128 (4) | 0.071 (3) | −0.002 (3) | 0.013 (2) | 0.049 (3) |
| C51 | 0.0423 (14) | 0.0468 (14) | 0.0518 (15) | 0.0126 (11) | 0.0049 (11) | 0.0117 (11) |
| C52 | 0.065 (2) | 0.0478 (16) | 0.0630 (19) | 0.0093 (14) | −0.0101 (15) | 0.0076 (14) |
| C53 | 0.071 (2) | 0.0616 (19) | 0.0572 (18) | 0.0187 (16) | −0.0089 (15) | 0.0128 (15) |
| C54 | 0.0542 (17) | 0.0510 (16) | 0.0645 (18) | 0.0192 (13) | 0.0126 (14) | 0.0249 (14) |
| Br54 | 0.0745 (3) | 0.0655 (2) | 0.0962 (3) | 0.02530 (19) | 0.0135 (2) | 0.0409 (2) |
| C55 | 0.0626 (19) | 0.0443 (15) | 0.0655 (19) | 0.0107 (13) | 0.0079 (15) | 0.0117 (13) |
| C56 | 0.0569 (17) | 0.0517 (16) | 0.0535 (17) | 0.0111 (13) | −0.0026 (13) | 0.0080 (13) |

Geometric parameters (Å, °)

| | | | |
|---------|-----------|----------|-----------|
| C1—O11 | 1.422 (3) | C25—C26 | 1.364 (7) |
| C1—C12 | 1.521 (4) | C25—H25 | 0.9500 |
| C1—C6 | 1.537 (4) | C26—H26 | 0.9500 |
| C1—C2 | 1.563 (4) | C31—C36 | 1.384 (4) |
| O11—H11 | 0.8144 | C31—C32 | 1.387 (4) |
| C2—C27 | 1.528 (4) | C32—C33 | 1.394 (4) |
| C2—C3 | 1.529 (4) | C32—H32 | 0.9500 |
| C2—H2 | 1.0000 | C33—C34 | 1.363 (5) |
| C3—C31 | 1.519 (4) | C33—H33 | 0.9500 |
| C3—C4 | 1.555 (3) | C34—C35 | 1.383 (5) |
| C3—H3 | 1.0000 | C34—Br34 | 1.896 (3) |
| C4—C47 | 1.526 (4) | C35—C36 | 1.381 (5) |
| C4—C5 | 1.548 (4) | C35—H35 | 0.9500 |
| C4—H4 | 1.0000 | C36—H36 | 0.9500 |
| C5—C51 | 1.521 (4) | C47—O47 | 1.211 (4) |
| C5—C6 | 1.530 (4) | C47—C42 | 1.503 (4) |
| C5—H5 | 1.0000 | N41—C46 | 1.330 (5) |
| C6—H6A | 0.9900 | N41—C42 | 1.331 (4) |
| C6—H6B | 0.9900 | C42—C43 | 1.382 (5) |
| N11—C12 | 1.322 (4) | C43—C44 | 1.369 (6) |
| N11—C16 | 1.351 (5) | C43—H43 | 0.9500 |
| C12—C13 | 1.387 (5) | C44—C45 | 1.358 (8) |
| C13—C14 | 1.388 (5) | C44—H44 | 0.9500 |
| C13—H13 | 0.9500 | C45—C46 | 1.373 (7) |
| C14—C15 | 1.357 (6) | C45—H45 | 0.9500 |
| C14—H14 | 0.9500 | C46—H46 | 0.9500 |

| | | | |
|------------|-----------|--------------|-----------|
| C15—C16 | 1.353 (6) | C51—C52 | 1.377 (4) |
| C15—H15 | 0.9500 | C51—C56 | 1.391 (4) |
| C16—H16 | 0.9500 | C52—C53 | 1.394 (4) |
| C27—O27 | 1.213 (4) | C52—H52 | 0.9500 |
| C27—C22 | 1.496 (4) | C53—C54 | 1.364 (5) |
| N21—C26 | 1.333 (5) | C53—H53 | 0.9500 |
| N21—C22 | 1.341 (5) | C54—C55 | 1.372 (5) |
| C22—C23 | 1.381 (5) | C54—Br54 | 1.905 (3) |
| C23—C24 | 1.397 (6) | C55—C56 | 1.388 (4) |
| C23—H23 | 0.9500 | C55—H55 | 0.9500 |
| C24—C25 | 1.369 (8) | C56—H56 | 0.9500 |
| C24—H24 | 0.9500 | | |
| O11—C1—C12 | 110.1 (2) | C25—C24—H24 | 120.5 |
| O11—C1—C6 | 107.2 (2) | C23—C24—H24 | 120.5 |
| C12—C1—C6 | 109.9 (2) | C26—C25—C24 | 118.5 (4) |
| O11—C1—C2 | 109.9 (2) | C26—C25—H25 | 120.7 |
| C12—C1—C2 | 110.0 (2) | C24—C25—H25 | 120.7 |
| C6—C1—C2 | 109.7 (2) | N21—C26—C25 | 124.4 (4) |
| C1—O11—H11 | 105.3 | N21—C26—H26 | 117.8 |
| C27—C2—C3 | 110.6 (2) | C25—C26—H26 | 117.8 |
| C27—C2—C1 | 108.8 (2) | C36—C31—C32 | 117.9 (3) |
| C3—C2—C1 | 111.4 (2) | C36—C31—C3 | 119.4 (3) |
| C27—C2—H2 | 108.6 | C32—C31—C3 | 122.7 (3) |
| C3—C2—H2 | 108.6 | C31—C32—C33 | 121.1 (3) |
| C1—C2—H2 | 108.6 | C31—C32—H32 | 119.4 |
| C31—C3—C2 | 113.6 (2) | C33—C32—H32 | 119.4 |
| C31—C3—C4 | 110.4 (2) | C34—C33—C32 | 119.0 (3) |
| C2—C3—C4 | 112.4 (2) | C34—C33—H33 | 120.5 |
| C31—C3—H3 | 106.7 | C32—C33—H33 | 120.5 |
| C2—C3—H3 | 106.7 | C33—C34—C35 | 121.4 (3) |
| C4—C3—H3 | 106.7 | C33—C34—Br34 | 119.6 (3) |
| C47—C4—C5 | 110.4 (2) | C35—C34—Br34 | 119.0 (3) |
| C47—C4—C3 | 112.7 (2) | C36—C35—C34 | 118.6 (3) |
| C5—C4—C3 | 109.4 (2) | C36—C35—H35 | 120.7 |
| C47—C4—H4 | 108.1 | C34—C35—H35 | 120.7 |
| C5—C4—H4 | 108.1 | C35—C36—C31 | 121.8 (3) |
| C3—C4—H4 | 108.1 | C35—C36—H36 | 119.1 |
| C51—C5—C6 | 113.8 (3) | C31—C36—H36 | 119.1 |
| C51—C5—C4 | 111.2 (2) | O47—C47—C42 | 118.1 (2) |
| C6—C5—C4 | 111.4 (2) | O47—C47—C4 | 121.7 (2) |
| C51—C5—H5 | 106.6 | C42—C47—C4 | 120.1 (2) |
| C6—C5—H5 | 106.6 | C46—N41—C42 | 116.2 (4) |
| C4—C5—H5 | 106.6 | N41—C42—C43 | 123.2 (3) |
| C5—C6—C1 | 111.5 (3) | N41—C42—C47 | 118.9 (3) |
| C5—C6—H6A | 109.3 | C43—C42—C47 | 117.9 (3) |
| C1—C6—H6A | 109.3 | C44—C43—C42 | 118.9 (4) |
| C5—C6—H6B | 109.3 | C44—C43—H43 | 120.6 |

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|---------------|------------|------------------|------------|
| C1—C6—H6B | 109.3 | C42—C43—H43 | 120.6 |
| H6A—C6—H6B | 108.0 | C45—C44—C43 | 118.7 (4) |
| C12—N11—C16 | 118.2 (3) | C45—C44—H44 | 120.6 |
| N11—C12—C13 | 121.5 (3) | C43—C44—H44 | 120.6 |
| N11—C12—C1 | 115.7 (3) | C44—C45—C46 | 118.7 (4) |
| C13—C12—C1 | 122.7 (3) | C44—C45—H45 | 120.7 |
| C12—C13—C14 | 118.8 (3) | C46—C45—H45 | 120.7 |
| C12—C13—H13 | 120.6 | N41—C46—C45 | 124.2 (5) |
| C14—C13—H13 | 120.6 | N41—C46—H46 | 117.9 |
| C15—C14—C13 | 119.4 (4) | C45—C46—H46 | 117.9 |
| C15—C14—H14 | 120.3 | C52—C51—C56 | 117.8 (3) |
| C13—C14—H14 | 120.3 | C52—C51—C5 | 119.1 (3) |
| C16—C15—C14 | 118.5 (4) | C56—C51—C5 | 123.2 (3) |
| C16—C15—H15 | 120.7 | C51—C52—C53 | 121.7 (3) |
| C14—C15—H15 | 120.7 | C51—C52—H52 | 119.2 |
| N11—C16—C15 | 123.5 (4) | C53—C52—H52 | 119.2 |
| N11—C16—H16 | 118.2 | C54—C53—C52 | 118.6 (3) |
| C15—C16—H16 | 118.2 | C54—C53—H53 | 120.7 |
| O27—C27—C22 | 119.5 (3) | C52—C53—H53 | 120.7 |
| O27—C27—C2 | 122.0 (3) | C53—C54—C55 | 122.0 (3) |
| C22—C27—C2 | 118.4 (2) | C53—C54—Br54 | 118.3 (2) |
| C26—N21—C22 | 116.9 (4) | C55—C54—Br54 | 119.8 (2) |
| N21—C22—C23 | 123.1 (3) | C54—C55—C56 | 118.5 (3) |
| N21—C22—C27 | 116.8 (3) | C54—C55—H55 | 120.7 |
| C23—C22—C27 | 120.1 (3) | C56—C55—H55 | 120.7 |
| C22—C23—C24 | 118.1 (4) | C55—C56—C51 | 121.5 (3) |
| C22—C23—H23 | 121.0 | C55—C56—H56 | 119.3 |
| C24—C23—H23 | 121.0 | C51—C56—H56 | 119.3 |
| C25—C24—C23 | 119.0 (4) | | |
| O11—C1—C2—C27 | −59.6 (3) | C22—C23—C24—C25 | −1.0 (8) |
| C12—C1—C2—C27 | 61.8 (3) | C23—C24—C25—C26 | 1.0 (8) |
| C6—C1—C2—C27 | −177.2 (2) | C22—N21—C26—C25 | −0.9 (7) |
| O11—C1—C2—C3 | 62.6 (3) | C24—C25—C26—N21 | 0.0 (8) |
| C12—C1—C2—C3 | −176.0 (2) | C2—C3—C31—C36 | 140.5 (3) |
| C6—C1—C2—C3 | −55.0 (3) | C4—C3—C31—C36 | −92.2 (3) |
| C27—C2—C3—C31 | −57.4 (3) | C2—C3—C31—C32 | −40.6 (4) |
| C1—C2—C3—C31 | −178.5 (2) | C4—C3—C31—C32 | 86.7 (3) |
| C27—C2—C3—C4 | 176.4 (2) | C36—C31—C32—C33 | 4.0 (5) |
| C1—C2—C3—C4 | 55.2 (3) | C3—C31—C32—C33 | −174.9 (3) |
| C31—C3—C4—C47 | −59.7 (3) | C31—C32—C33—C34 | −1.6 (5) |
| C2—C3—C4—C47 | 68.3 (3) | C32—C33—C34—C35 | −1.9 (5) |
| C31—C3—C4—C5 | 177.1 (2) | C32—C33—C34—Br34 | 177.0 (3) |
| C2—C3—C4—C5 | −54.9 (3) | C33—C34—C35—C36 | 2.9 (6) |
| C47—C4—C5—C51 | 59.7 (3) | Br34—C34—C35—C36 | −176.1 (3) |
| C3—C4—C5—C51 | −175.8 (2) | C34—C35—C36—C31 | −0.3 (5) |
| C47—C4—C5—C6 | −68.5 (3) | C32—C31—C36—C35 | −3.0 (5) |
| C3—C4—C5—C6 | 56.0 (3) | C3—C31—C36—C35 | 175.9 (3) |

| | | | |
|-----------------|------------|------------------|------------|
| C51—C5—C6—C1 | 174.7 (2) | C5—C4—C47—O47 | 72.3 (3) |
| C4—C5—C6—C1 | −58.6 (3) | C3—C4—C47—O47 | −50.3 (4) |
| O11—C1—C6—C5 | −62.5 (3) | C5—C4—C47—C42 | −105.5 (3) |
| C12—C1—C6—C5 | 177.9 (2) | C3—C4—C47—C42 | 131.9 (3) |
| C2—C1—C6—C5 | 56.8 (3) | C46—N41—C42—C43 | 0.4 (6) |
| C16—N11—C12—C13 | 0.1 (6) | C46—N41—C42—C47 | 179.4 (4) |
| C16—N11—C12—C1 | 177.9 (4) | O47—C47—C42—N41 | −176.7 (3) |
| O11—C1—C12—N11 | 8.8 (4) | C4—C47—C42—N41 | 1.3 (4) |
| C6—C1—C12—N11 | 126.6 (3) | O47—C47—C42—C43 | 2.5 (5) |
| C2—C1—C12—N11 | −112.5 (3) | C4—C47—C42—C43 | −179.6 (3) |
| O11—C1—C12—C13 | −173.5 (3) | N41—C42—C43—C44 | −1.3 (7) |
| C6—C1—C12—C13 | −55.7 (4) | C47—C42—C43—C44 | 179.7 (4) |
| C2—C1—C12—C13 | 65.2 (4) | C42—C43—C44—C45 | 2.0 (9) |
| N11—C12—C13—C14 | −0.4 (5) | C43—C44—C45—C46 | −1.9 (10) |
| C1—C12—C13—C14 | −178.0 (3) | C42—N41—C46—C45 | −0.3 (9) |
| C12—C13—C14—C15 | 0.1 (6) | C44—C45—C46—N41 | 1.1 (11) |
| C13—C14—C15—C16 | 0.5 (7) | C6—C5—C51—C52 | −141.5 (3) |
| C12—N11—C16—C15 | 0.6 (7) | C4—C5—C51—C52 | 91.7 (3) |
| C14—C15—C16—N11 | −0.9 (8) | C6—C5—C51—C56 | 40.2 (4) |
| C3—C2—C27—O27 | −34.8 (4) | C4—C5—C51—C56 | −86.7 (4) |
| C1—C2—C27—O27 | 88.0 (4) | C56—C51—C52—C53 | 1.9 (5) |
| C3—C2—C27—C22 | 145.0 (3) | C5—C51—C52—C53 | −176.6 (3) |
| C1—C2—C27—C22 | −92.3 (3) | C51—C52—C53—C54 | −0.9 (6) |
| C26—N21—C22—C23 | 0.9 (6) | C52—C53—C54—C55 | 0.0 (6) |
| C26—N21—C22—C27 | −177.2 (4) | C52—C53—C54—Br54 | 179.7 (3) |
| O27—C27—C22—N21 | 146.8 (3) | C53—C54—C55—C56 | −0.1 (5) |
| C2—C27—C22—N21 | −32.9 (4) | Br54—C54—C55—C56 | −179.8 (3) |
| O27—C27—C22—C23 | −31.3 (5) | C54—C55—C56—C51 | 1.1 (5) |
| C2—C27—C22—C23 | 148.9 (3) | C52—C51—C56—C55 | −2.0 (5) |
| N21—C22—C23—C24 | 0.1 (7) | C5—C51—C56—C55 | 176.4 (3) |
| C27—C22—C23—C24 | 178.1 (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> |
|------------------------------------|-------------|---------------------|----------------------------|-------------------------------|
| O11—H11 \cdots N11 | 0.81 | 2.06 | 2.595 (4) | 123 |
| C16—H16 \cdots O27 ⁱ | 0.95 | 2.46 | 3.385 (6) | 165 |
| C53—H53 \cdots N41 ⁱⁱ | 0.95 | 2.57 | 3.473 (5) | 158 |

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