

Octyl 1-(5-*tert*-butyl-1*H*-pyrazol-3-yl)-2-(4-chlorophenyl)-1*H*-benzimidazole-5-carboxylate: complex sheets built from N—H...N, C—H...N and C—H...O hydrogen bonds

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In the title compound, C₂₉H₃₅ClN₄O₂, the bond lengths provide evidence for aromatic delocalization in the pyrazole ring but bond fixation in the fused imidazole ring, and the octyl chain is folded, rather than adopting an all-*trans* chain-extended conformation. A combination of N—H...N, C—H...N and C—H...O hydrogen bonds links the molecules into sheets, in which the hydrogen bonds occupy the central layer with the *tert*-butyl and octyl groups arranged on either side, such that the closest contacts between adjacent sheets involve only the octyl groups. Comparisons are made with the supramolecular assembly in some simpler analogues.

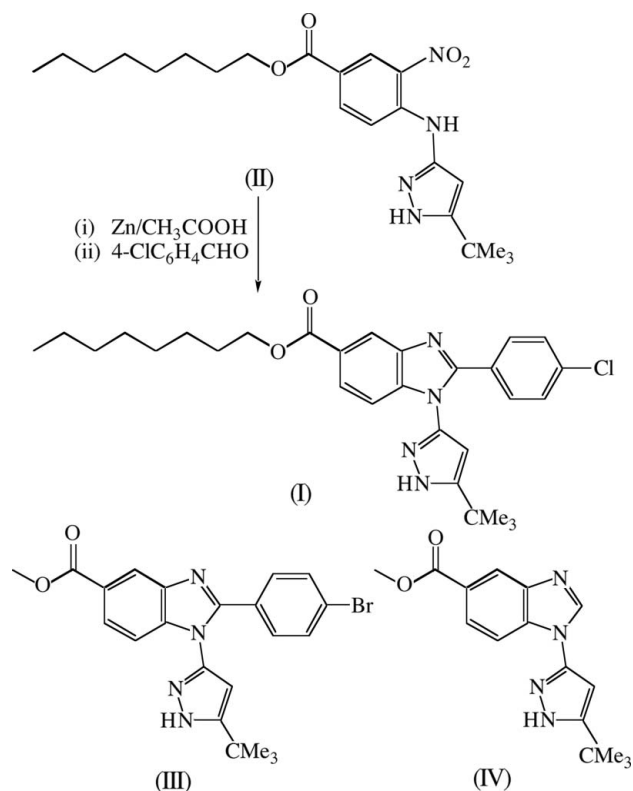
Keywords: crystal structure; hydrogen bonding; supramolecular assembly; benzimidazole carboxylic acid ester; antitumour activity.

1. Introduction

The imidazole nucleus is a common group in a large number of natural products and pharmacologically active compounds (Adams *et al.*, 1998). In particular, benzimidazoles may be considered as structural isosteres of nucleotide bases, owing to the fused heterocyclic nuclei in their structures, and they interact easily with biopolymers and possess potential activity for chemotherapeutic applications (Ören *et al.*, 1998). The benzimidazole group itself is a crucial pharmacophore in modern drug discovery (Tebbe *et al.*, 1997), owing to the broad spectrum of important biological and pharmacological properties exhibited for a large number of benzimidazole-containing compounds, such as anti-ulcerative and anti-hypertensive (Zarrinmayeh *et al.*, 1999), antifungal (Taggart *et al.*, 1998), antitumour (Zhou & Skibo, 1996; Craig *et al.*, 1999)

and anti-allergic actions (Nakano *et al.*, 2000), and acting as topoisomerase inhibitors (Kim *et al.*, 1996) and selective neuropeptide YY1 receptor antagonists (Zarrinmayeh *et al.*, 1998). In addition, some benzimidazole derivatives are effective against several human viruses, such as cytomegalovirus (HCMV) (Zhu *et al.*, 2000), HIV (Roth *et al.*, 1997) and herpes (HSV-1) (Migawa *et al.*, 1998).

Continuing with our current studies on the synthesis of benzimidazole-based compounds with potential antitumour activity (Abonía *et al.*, 2010, 2011; Cortés *et al.*, 2011), we have now prepared octyl 1-(5-*tert*-butyl-1*H*-pyrazol-3-yl)-2-(4-chlorophenyl)-1*H*-benzimidazole-5-carboxylate, (I), through a two-step one-pot synthesis using the reduction of nitro derivative (II) {octyl 4-[(5-*tert*-butyl-1*H*-pyrazol-3-yl)amino]-3-nitrobenzoate; see Scheme} to a diamine followed by a condensation reaction with 4-chlorobenzaldehyde, without isolation of the intermediate diamine, and here we report the molecular and supramolecular structure of (I) which we compare with simpler analogues, *viz.* (III) [methyl 2-(4-bromophenyl)-1-(5-*tert*-butyl-1*H*-pyrazol-3-yl)-1*H*-benzimidazole-5-carboxylate; Cortés *et al.*, 2011] and (IV) [methyl 1-(5-*tert*-butyl-1*H*-pyrazol-3-yl)-1*H*-benzimidazole-5-carboxylate; Portilla *et al.*, 2007] (see Scheme), which had been prepared using a similar condensation reaction between a pre-formed diamine and 4-bromobenzaldehyde or trimethyl orthoformate, respectively.



2. Experimental

2.1. Synthesis and crystallization

A mixture of octyl 4-[(5-*tert*-butyl-1*H*-pyrazol-3-yl)amino]-3-nitrobenzoate, (II) (1 mmol) (see Scheme), zinc powder

Table 1
Experimental details.

Crystal data	
Chemical formula	C ₂₉ H ₃₅ ClN ₄ O ₂
<i>M_r</i>	507.06
Crystal system, space group	Monoclinic, <i>C2/c</i>
Temperature (K)	120
<i>a</i> , <i>b</i> , <i>c</i> (Å)	29.768 (4), 15.6022 (12), 11.8465 (15)
β (°)	93.247 (11)
<i>V</i> (Å ³)	5493.2 (11)
<i>Z</i>	8
Radiation type	Mo Kα
μ (mm ⁻¹)	0.17
Crystal size (mm)	0.30 × 0.30 × 0.24
Data collection	
Diffractometer	Bruker–Nonius KappaCCD area-detector diffractometer
Absorption correction	Multi-scan (<i>SADABS</i> ; Sheldrick, 2003)
<i>T_{min}</i> , <i>T_{max}</i>	0.904, 0.960
No. of measured, independent and observed [<i>I</i> > 2σ(<i>I</i>)] reflections	44941, 6303, 4127
<i>R_{int}</i>	0.076
(sin θ/λ) _{max} (Å ⁻¹)	0.650
Refinement	
<i>R</i> [<i>F</i> ² > 2σ(<i>F</i> ²)], <i>wR</i> (<i>F</i> ²), <i>S</i>	0.053, 0.116, 1.09
No. of reflections	6303
No. of parameters	329
H-atom treatment	H-atom parameters constrained
Δρ _{max} , Δρ _{min} (e Å ⁻³)	0.42, -0.32

Computer programs: *COLLECT* (Nonius, 1999), *DIRAX/LSQ* (Duisenberg *et al.*, 2000), *EVALCCD* (Duisenberg *et al.*, 2003), *SIR2004* (Burla *et al.*, 2005), *SHELXL97* (Sheldrick, 2008), *SHELXL2013* (Sheldrick, 2013) and *PLATON* (Spek, 2009).

(5 mmol) and acetic acid (2 ml) was stirred at ambient temperature for 15 min. After complete disappearance of starting compound (II) [as monitored by thin-layer chromatography (TLC)], the by-product zinc acetate and the excess of zinc metal were removed by filtration. To the resulting solution, 4-chlorobenzaldehyde (1.05 mmol) was added, and the mixture was subjected to heating at 373 K for 1 h. After consumption of the starting materials (as monitored by TLC), the solution was allowed to cool to ambient temperature, the excess acetic acid was removed under reduced pressure and the resulting solid product was washed with ethanol (2 × 1 ml). Colourless crystals of (I) suitable for single-crystal X-ray diffraction were grown by slow evaporation, at ambient temperature and in the presence of air, from a solution in ethanol (yield 88%; m.p. 439 K). FT-IR (KBr, ν cm⁻¹): 3184

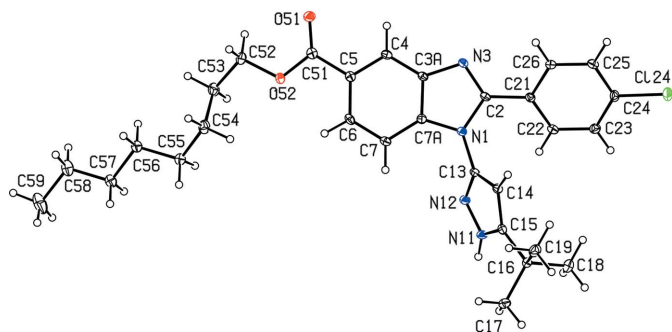


Figure 1
The molecular structure of (I), showing the atom-labelling scheme. Displacement ellipsoids are drawn at the 30% probability level.

(NH), 2959, 2854, 1710 (C=O), 1615 (C=C), 1570 (C=N), 1511, 1472, 1279 (C–O); EIMS (70 eV) *m/z* = 508/506 (26/68) [*M*⁺], 449 (21), 396/394 (33/86), 377 (52), 350 (100), 337 (12); analysis found: C 68.8, H 7.1, N 10.9%; C₂₉H₃₅ClN₄O₂ requires: C 68.7, H 7.0, N 11.1%.

2.2. Refinement

Crystal data, data collection and structure refinement details are summarized in Table 1. All H atoms were located in a difference map and then treated as riding atoms. C-bound H atoms were treated as riding in geometrically idealized positions, with C–H = 0.95 (aromatic and pyrazole), 0.98 (methyl) or 0.99 Å (methylene), and with *U*_{iso}(H) = *kU*_{eq}(C), where *k* = 1.5 for the methyl groups, which were permitted to rotate but not to tilt, and 1.2 for all other C-bound H atoms. The H atom bonded to atom N11 was permitted to ride at the position located in a difference map, with *U*_{iso}(H) = 1.2*U*_{eq}(N), giving the N···H distance shown in Table 3. Six low-angle reflections (202, 220, 221, 112, $\bar{3}$ 11 and 400), which had been wholly or partially attenuated by the beam stop, were omitted from the refinement. Examination of the refined structure using *PLATON* (Spek, 2009) showed the presence of four symmetry-related cavities per unit cell, each of volume *ca* 12 Å³, and centred at (0, 0, 0), ($\frac{1}{2}$, $\frac{1}{2}$, 0), ($\frac{1}{2}$, $\frac{1}{2}$, 0) and ($\frac{1}{2}$, $\frac{1}{2}$, $\frac{1}{2}$). These cavities are too small to accommodate any solvent species and, consistent with this, application of the SQUEEZE procedure in *PLATON* returned a count of zero additional electrons per unit cell; accordingly, no modification of the reflection file was required.

3. Results and discussion

Within the pyrazole ring of (I), the two independent C–C distances (C13–C14 and C14–C15) differ by less than 0.02 Å (Table 2), despite the fact that these bonds are formally single and double bonds, respectively. Similarly, the two independent C–N distances (N11–C15 and N12–C13) differ by less than 0.03 Å, although these two bonds are again formally single and double bonds, respectively. These observations indicate a degree of aromatic delocalization within this ring. By contrast, the bond lengths within the imidazole ring point to strong bond fixation in this ring.

The molecular conformation of (I) can be specified in terms of: (a) the dihedral angles between the imidazole ring and the two pendent rings (N11/N12/C13–C15 and C21–C26; Fig. 1), (b) the orientations of the *tert*-butyl and 4-chlorophenyl substituents relative to the adjacent rings, and (c) the folding of the octyl chain. The imidazole ring makes dihedral angles with the pyrazole ring and the chlorinated aryl ring of 60.01 (12) and 34.63 (11)°, respectively. The corresponding dihedral angles in (III) (Cortés *et al.*, 2011) are 83.30 (15) and 26.90 (14)°, respectively, while in (IV), which crystallizes with *Z'* = 2 (Portilla *et al.*, 2007), the dihedral angles between the imidazole and pyrazole rings in the two independent molecules are 5.5 (2) and 5.9 (2)°, indicating considerable flexibility about the N1–C13 and C2–C21 bonds. The relative

Table 2

Selected geometric parameters (Å, °).

N1—C2	1.381 (3)	N11—N12	1.358 (2)
C2—N3	1.324 (3)	N12—C13	1.326 (3)
N3—C3a	1.391 (3)	C13—C14	1.397 (3)
C3a—C7a	1.403 (3)	C14—C15	1.381 (3)
C7a—N1	1.386 (3)	C15—N11	1.354 (3)
C2—N1—C13—N12	−120.5 (2)	C4—C5—C51—O51	−9.4 (3)
C2—N1—C13—C14	58.7 (3)	C4—C5—C51—O52	168.98 (18)
C7a—N1—C13—N12	61.4 (3)	C5—C51—O52—C52	179.49 (18)
C7a—N1—C13—C14	−119.4 (2)	C51—O52—C52—C53	161.93 (19)
N1—C2—C21—C22	35.2 (3)	O52—C52—C53—C54	63.2 (3)
N1—C2—C21—C26	−146.5 (2)	C52—C53—C54—C55	−173.9 (2)
N3—C2—C21—C22	−144.6 (2)	C53—C54—C55—C56	−68.1 (3)
N3—C2—C21—C26	33.7 (3)	C54—C55—C56—C57	−170.9 (2)
C14—C15—C16—C17	143.4 (2)	C55—C56—C57—C58	179.0 (2)
C14—C15—C16—C18	−96.2 (3)	C56—C57—C58—C59	−173.3 (2)
C14—C15—C16—C19	22.5 (3)		

Table 3

Hydrogen-bond geometry (Å, °).

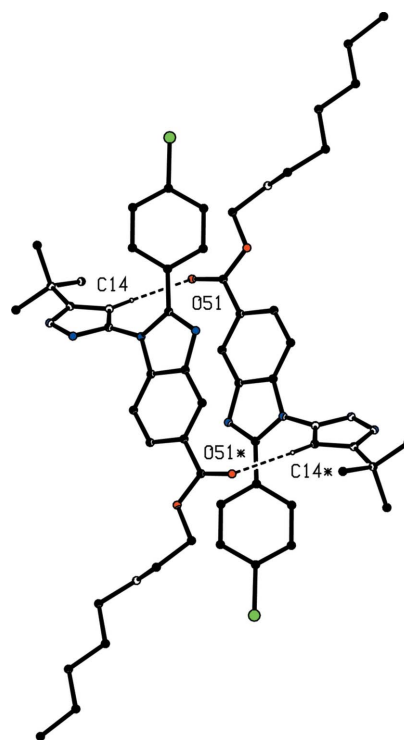
*C*_g1 is the centroid of the N11/N12/C13—C15 ring.

<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>
N11—H11...N3 ⁱ	0.86	2.16	3.011 (2)	169
C14—H14...O51 ⁱⁱ	0.95	2.31	3.249 (3)	168
C26—H26...N12 ⁱⁱⁱ	0.95	2.53	3.292 (3)	137
C22—H22... <i>C</i> _g 1	0.95	2.84	3.472 (3)	125

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

orientation of the pyrazole and chlorinated aryl rings in (I) may be influenced by the intramolecular C—H... π (pyrazole) contact (Table 3), although no such contact is apparent in (III) nor possible in (IV). The *tert*-butyl group adopts an orientation in which the projection of one of the C—Me bonds is almost orthogonal to the plane of the adjacent pyrazole ring, while the ester function is nearly coplanar with the fused aryl ring, as shown by the torsion angles within the fragment between atoms C4 and C52 (Table 2).

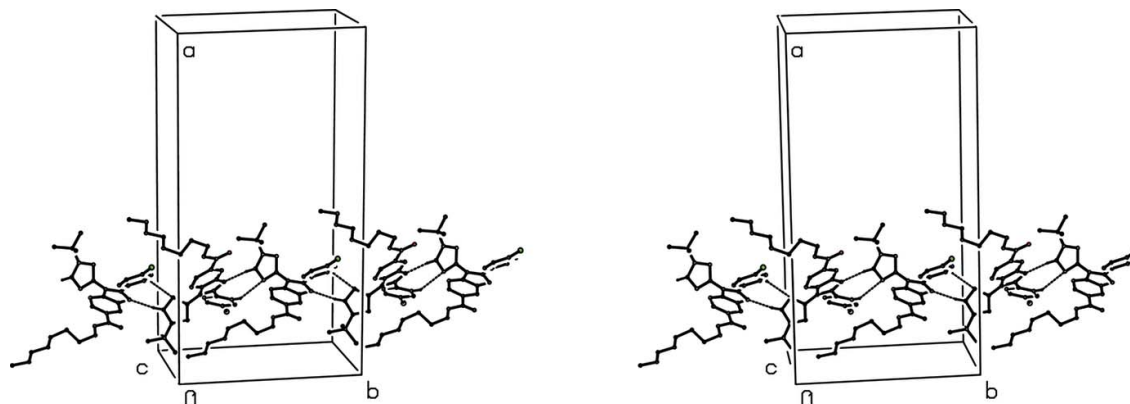
Perhaps the least expected aspect of the molecular conformation of (I) is the folding of the octyl chain. Instead of adopting an all-*trans* chain-extended conformation in which all of the C atoms are effectively coplanar, with the torsion

**Figure 2**

Part of the crystal structure of (I), showing the formation of a cyclic centrosymmetric $R_2^2(20)$ dimer built from C—H...O hydrogen bonds (dashed lines). For the sake of clarity, the unit-cell outline and H atoms not involved in the motif shown have been omitted. Atoms marked with an asterisk (*) are at the symmetry position $(-x + \frac{1}{2}, -y + \frac{3}{2}, -z + 1)$.

angles along the chain all close to 180° in each four-carbon fragment, the O52—C52—C53—C54 and C53—C54—C55—C56 torsion angles are close to $\pm 60^\circ$, indicating a synclinal arrangement about the C52—C53 and C54—C55 bonds, rather than the usual antiperiplanar arrangement. In view of the supramolecular arrangement discussed below, it seems possible that this chain folding represents the most effective means of accommodating the octyl substituents between the hydrogen-bonded sheets.

A combination of N—H...N, C—H...O and C—H...N hydrogen bonds (Table 3) links the molecules of (I) into

**Figure 3**

A stereoview of part of the crystal structure of (I), showing the formation of a $C(7)C(7)[R_2^2(8)]$ chain of rings along the $[010]$ direction. Dashed lines indicate hydrogen bonds. For the sake of clarity, H atoms not involved in the motifs shown have been omitted.

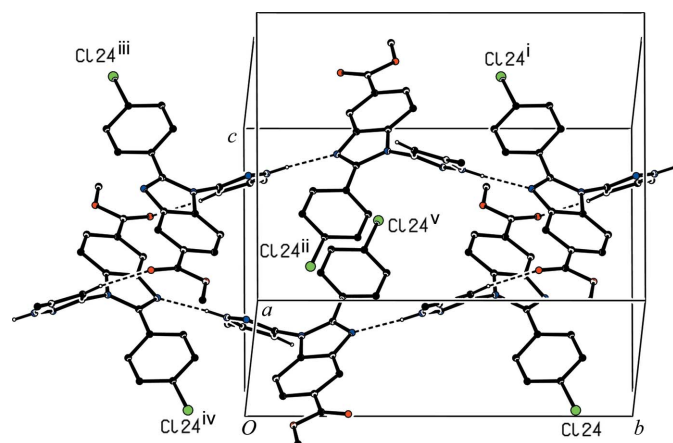


Figure 4
Part of the crystal structure of (I), showing the formation of a centrosymmetric hydrogen-bonded $R_6^c(36)$ ring lying within the (100) sheet and centred at $(\frac{1}{4}, \frac{1}{4}, \frac{1}{2})$. Dashed lines indicate hydrogen bonds. For the sake of clarity, H atoms not involved in the motif shown have been omitted, as have atoms C17–C19 and C53–C59. [Symmetry codes: (i) $-x + \frac{1}{2}, -y + \frac{3}{2}, -z + 1$; (ii) $x, -y + 1, z + \frac{1}{2}$; (iii) $-x + \frac{1}{2}, -y + \frac{1}{2}, -z + 1$; (iv) $x, y - 1, z$; (v) $-x + \frac{1}{2}, y - \frac{1}{2}, -z + \frac{1}{2}$]

complex sheets, the formation of which can readily be analysed in terms of two substructures (Ferguson *et al.*, 1998*a,b*; Gregson *et al.*, 2000); one of these substructures is finite and thus zero-dimensional, while the other is one-dimensional. In the finite substructure, inversion-related pairs of molecules are linked by C–H···O hydrogen bonds to form cyclic centrosymmetric dimers characterized by an $R_2^2(20)$ (Bernstein *et al.*, 1995) motif (Fig. 2), where the reference dimer is centred across $(\frac{1}{4}, \frac{3}{4}, \frac{1}{2})$. In the second substructure, molecules related by the 2_1 screw axis along $(\frac{1}{4}, y, \frac{1}{4})$ are linked by a combination of N–H···N and C–H···N hydrogen bonds to form a $C(7)C(7)[R_2^2(8)]$ chain of rings running parallel to the [010] direction (Fig. 3). Four chains of this type pass through each unit cell, associated with the screw axes along $(\frac{1}{4}, y, \frac{1}{4})$, $(\frac{1}{4}, y, \frac{3}{4})$, $(\frac{3}{4}, y, \frac{1}{4})$ and $(\frac{3}{4}, y, \frac{3}{4})$, and they link the $R_2^2(20)$ dimers into sheets. Thus, the reference dimer centred at $(\frac{1}{4}, \frac{3}{4}, \frac{1}{2})$ is directly linked to four other dimers centred at $(\frac{1}{4}, \frac{1}{4}, 0)$, $(\frac{1}{4}, \frac{1}{4}, 1)$, $(\frac{1}{4}, \frac{5}{4}, 0)$ and $(\frac{1}{4}, \frac{5}{4}, 1)$, respectively, so forming a sheet lying parallel to (100) and containing rings of $R_2^2(8)$, $R_2^2(20)$ and $R_6^c(36)$ types, where the interior of the $R_6^c(36)$ ring is occupied by an inversion-related pair of chlorinated aryl rings engaged in π – π stacking (Fig. 4), as discussed below.

This sheet lies in the domain $0 < x < \frac{1}{2}$ and a second sheet, related to the first by inversion, lies in the domain $\frac{1}{2} < x < 1.0$. Each sheet is effectively tripartite, with a central layer containing the hydrogen bonds, and with all of the octyl and *tert*-butyl groups arranged on either side of the central layer (Fig. 5). The only close contacts between adjacent sheets involve the octyl groups, so that there are no direction-specific interactions between adjacent sheets. The only C–H··· π contact in the structure is intramolecular (Table 3), but two intermolecular π – π stacking interactions are present. The chlorinated aryl rings in the molecules at (x, y, z) and $(-x + \frac{1}{2}, -y + \frac{3}{2}, -z)$ are strictly parallel, with an interplanar spacing of 3.2972 (9) Å; the ring-centroid separation is 3.6476 (13) Å,

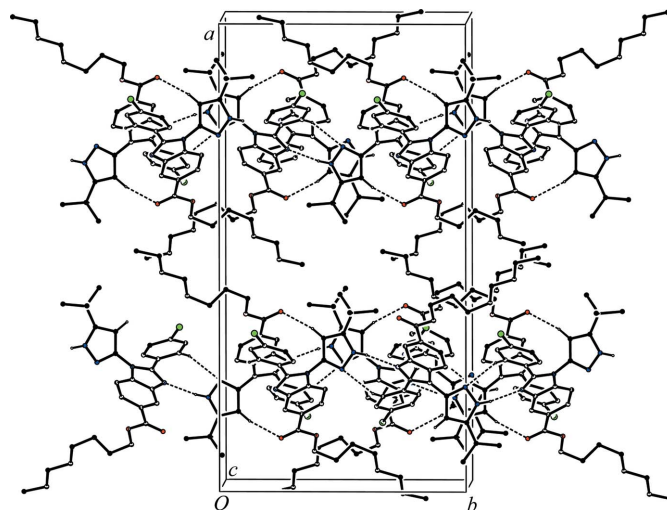


Figure 5
Part of the crystal structure of (I), viewed approximately along [001], showing the tripartite nature of two adjacent sheets comprising central hydrogen-bonded layers and exterior layers of octyl groups. Dashed lines indicate hydrogen bonds. For the sake of clarity, H atoms not involved in hydrogen bonding have been omitted.

corresponding to a ring-centroid offset of 1.560 Å. In addition, the imidazole ring of the molecule at (x, y, z) and the fused aryl ring in the molecule at $(-x + \frac{1}{2}, -y + \frac{3}{2}, -z + 1)$ make a dihedral angle of only 1.94 (11)°; the ring-centroid separation here is 3.6881 (13) Å and the shortest perpendicular distance from the centroid of one ring to the plane of the other is 3.4489 (9) Å, corresponding to a ring-centroid offset of *ca* 1.31 Å. Both of these interactions involve molecules in the same hydrogen-bonded sheet and, indeed, the first of them lies within the hydrogen-bonded $R_2^2(20)$ dimer (*cf.* Fig. 2).

It is of interest briefly to compare the rather complex sheet structure in (I) with the supramolecular assembly in (III) (Cortés *et al.*, 2011) and (IV) (Portilla *et al.*, 2007). In (III), a combination of N–H···O and C–H··· π (arene) hydrogen bonds links the molecules into a chain of centrosymmetric edge-fused rings. Compound (IV), where there is no pendent aryl group, crystallizes ($Z' = 2$) with no direction-specific interactions between the two independent molecules. Each type of molecule forms a hydrogen-bonded sheet, in which molecules related by translation only are linked by a combination of N–H···N and C–H···O hydrogen bonds to form a single type of $R_4^4(28)$ ring. In each of (I), (III) and (IV), atoms N11 and C14 of the pyrazole ring act as hydrogen-bond donors, but the two acceptors in these two hydrogen bonds are not always the same. In (I) and (IV), the acceptors from the pyrazole donors are, respectively, the two-coordinate N atom of the imidazole ring and the carbonyl O atom of the ester group, but in (III) these acceptors are, respectively, the carbonyl O atom of the ester group and the pendent aryl ring. However, the assembly in (I) and (IV) differs in the relationship between the molecules within the hydrogen-bonded sheet, *i.e.* translation only in (IV), but a combination of inversion and translation in (I), where there is also an additional hydrogen bond involving the pyrazole ring as an

acceptor, rather than as a donor. Only in (III) is there an intermolecular C—H $\cdots\pi$ hydrogen bond.

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Supporting information for this paper is available from the IUCr electronic archives (Reference: FG3321).

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supplementary materials

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Octyl 1-(5-*tert*-butyl-1*H*-pyrazol-3-yl)-2-(4-chlorophenyl)-1*H*-benzimidazole-5-carboxylate: complex sheets built from N—H⋯N, C—H⋯N and C—H⋯O hydrogen bonds

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Computing details

Data collection: *COLLECT* (Nonius, 1999); cell refinement: *DIRAX/LSQ* (Duisenberg *et al.*, 2000); data reduction: *EVALCCD* (Duisenberg *et al.*, 2003); program(s) used to solve structure: *SIR2004* (Burla *et al.*, 2005); program(s) used to refine structure: *SHELXL97* (Sheldrick, 2008) and *SHELXL2013* (Sheldrick, 2013); molecular graphics: *PLATON* (Spek, 2009); software used to prepare material for publication: *SHELXL97* (Sheldrick, 2008), *SHELXL2013* (Sheldrick, 2013) and *PLATON* (Spek, 2009).

Octyl 1-(5-(*tert*-butyl)-1*H*-pyrazol-3-yl)-2-(4-chlorophenyl)-1*H*-benzo[*d*]imidazole-5-carboxylate

Crystal data

$C_{29}H_{35}ClN_4O_2$	$F(000) = 2160$
$M_r = 507.06$	$D_x = 1.226 \text{ Mg m}^{-3}$
Monoclinic, $C2/c$	Mo $K\alpha$ radiation, $\lambda = 0.71073 \text{ \AA}$
Hall symbol: $-C 2yc$	Cell parameters from 6308 reflections
$a = 29.768 (4) \text{ \AA}$	$\theta = 2.7\text{--}27.5^\circ$
$b = 15.6022 (12) \text{ \AA}$	$\mu = 0.17 \text{ mm}^{-1}$
$c = 11.8465 (15) \text{ \AA}$	$T = 120 \text{ K}$
$\beta = 93.247 (11)^\circ$	Block, colourless
$V = 5493.2 (11) \text{ \AA}^3$	$0.30 \times 0.30 \times 0.24 \text{ mm}$
$Z = 8$	

Data collection

Bruker Nonius KappaCCD area-detector diffractometer	$T_{\min} = 0.904, T_{\max} = 0.960$
Radiation source: Bruker Nonius FR591 rotating anode	44941 measured reflections
Graphite monochromator	6303 independent reflections
Detector resolution: $9.091 \text{ pixels mm}^{-1}$	4127 reflections with $I > 2\sigma(I)$
φ and ω scans	$R_{\text{int}} = 0.076$
Absorption correction: multi-scan (<i>SADABS</i> ; Sheldrick, 2003)	$\theta_{\max} = 27.5^\circ, \theta_{\min} = 3.1^\circ$
	$h = -38 \rightarrow 38$
	$k = -20 \rightarrow 20$
	$l = -12 \rightarrow 15$

Refinement

Refinement on F^2	6303 reflections
Least-squares matrix: full	329 parameters
$R[F^2 > 2\sigma(F^2)] = 0.053$	0 restraints
$wR(F^2) = 0.116$	Primary atom site location: structure-invariant
$S = 1.09$	direct methods

Secondary atom site location: difference Fourier map
 Hydrogen site location: inferred from neighbouring sites
 H-atom parameters constrained

$$w = 1/[\sigma^2(F_o^2) + (0.0289P)^2 + 10.0795P]$$

where $P = (F_o^2 + 2F_c^2)/3$
 $(\Delta/\sigma)_{\max} = 0.001$
 $\Delta\rho_{\max} = 0.42 \text{ e } \text{Å}^{-3}$
 $\Delta\rho_{\min} = -0.32 \text{ e } \text{Å}^{-3}$

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

	<i>x</i>	<i>y</i>	<i>z</i>	<i>U</i> _{iso} */ <i>U</i> _{eq}
N1	0.25787 (6)	0.63868 (10)	0.31816 (15)	0.0163 (4)
C2	0.25340 (7)	0.71904 (13)	0.26995 (17)	0.0153 (4)
N3	0.22407 (6)	0.76752 (11)	0.32052 (15)	0.0164 (4)
C3a	0.20796 (7)	0.71655 (13)	0.40562 (17)	0.0160 (4)
C4	0.17557 (7)	0.73311 (13)	0.48333 (18)	0.0176 (4)
H4	0.1613	0.7875	0.4860	0.021*
C5	0.16466 (7)	0.66763 (13)	0.55689 (18)	0.0175 (4)
C6	0.18684 (7)	0.58772 (13)	0.55630 (18)	0.0192 (5)
H6	0.1790	0.5446	0.6083	0.023*
C7	0.21981 (7)	0.57093 (13)	0.48158 (18)	0.0183 (5)
H7	0.2355	0.5179	0.4823	0.022*
C7a	0.22872 (7)	0.63584 (13)	0.40526 (17)	0.0164 (4)
N11	0.30521 (6)	0.44808 (11)	0.23533 (15)	0.0185 (4)
H11	0.3002	0.3959	0.2148	0.022*
N12	0.26881 (6)	0.49649 (11)	0.25719 (15)	0.0188 (4)
C13	0.28705 (7)	0.57072 (13)	0.28947 (17)	0.0160 (4)
C14	0.33396 (7)	0.57130 (13)	0.28929 (18)	0.0175 (4)
H14	0.3539	0.6170	0.3099	0.021*
C15	0.34474 (7)	0.49032 (13)	0.25235 (17)	0.0171 (4)
C16	0.38979 (7)	0.45298 (14)	0.22397 (19)	0.0202 (5)
C17	0.39329 (8)	0.35878 (14)	0.2602 (2)	0.0268 (5)
H17A	0.3912	0.3547	0.3423	0.040*
H17B	0.4222	0.3354	0.2393	0.040*
H17C	0.3687	0.3261	0.2223	0.040*
C18	0.39383 (9)	0.46020 (17)	0.0951 (2)	0.0320 (6)
H18A	0.3691	0.4286	0.0560	0.048*
H18B	0.4226	0.4359	0.0748	0.048*
H18C	0.3923	0.5206	0.0727	0.048*
C19	0.42779 (7)	0.50463 (16)	0.2846 (2)	0.0279 (5)
H19A	0.4257	0.5647	0.2606	0.042*
H19B	0.4569	0.4811	0.2653	0.042*
H19C	0.4251	0.5011	0.3665	0.042*
C21	0.27871 (7)	0.74611 (13)	0.17284 (18)	0.0161 (4)
C22	0.28925 (7)	0.68977 (14)	0.08616 (18)	0.0186 (5)
H22	0.2803	0.6314	0.0896	0.022*
C23	0.31252 (7)	0.71816 (14)	-0.00445 (19)	0.0201 (5)
H23	0.3195	0.6799	-0.0633	0.024*
C24	0.32557 (7)	0.80348 (14)	-0.00809 (19)	0.0201 (5)
Cl24	0.35460 (2)	0.84130 (4)	-0.12188 (5)	0.03072 (16)
C25	0.31546 (7)	0.86065 (13)	0.07603 (18)	0.0189 (5)
H25	0.3247	0.9188	0.0723	0.023*

C26	0.29161 (7)	0.83199 (13)	0.16592 (18)	0.0169 (4)
H26	0.2840	0.8711	0.2233	0.020*
C51	0.12816 (7)	0.68442 (14)	0.63483 (18)	0.0189 (5)
O51	0.11099 (5)	0.75352 (10)	0.64901 (14)	0.0246 (4)
O52	0.11534 (5)	0.61234 (9)	0.68670 (13)	0.0225 (4)
C52	0.07993 (8)	0.62233 (15)	0.7656 (2)	0.0264 (5)
H52A	0.0563	0.6616	0.7340	0.032*
H52B	0.0924	0.6463	0.8381	0.032*
C53	0.06049 (8)	0.53415 (15)	0.7840 (2)	0.0283 (5)
H53A	0.0345	0.5399	0.8322	0.034*
H53B	0.0490	0.5112	0.7100	0.034*
C54	0.09297 (8)	0.46972 (16)	0.8382 (2)	0.0277 (5)
H54A	0.1019	0.4889	0.9160	0.033*
H54B	0.1204	0.4678	0.7948	0.033*
C55	0.07286 (8)	0.37921 (15)	0.8432 (2)	0.0261 (5)
H55A	0.0613	0.3626	0.7663	0.031*
H55B	0.0971	0.3385	0.8670	0.031*
C56	0.03485 (8)	0.37089 (15)	0.9238 (2)	0.0262 (5)
H56A	0.0086	0.4043	0.8931	0.031*
H56B	0.0448	0.3962	0.9976	0.031*
C57	0.02003 (8)	0.27838 (15)	0.9425 (2)	0.0264 (5)
H57A	0.0095	0.2533	0.8689	0.032*
H57B	0.0463	0.2446	0.9720	0.032*
C58	-0.01726 (9)	0.27096 (18)	1.0243 (2)	0.0372 (6)
H58A	-0.0447	0.2989	0.9905	0.045*
H58B	-0.0081	0.3022	1.0946	0.045*
C59	-0.02851 (12)	0.1784 (2)	1.0542 (3)	0.0606 (10)
H59A	-0.0365	0.1463	0.9849	0.091*
H59B	-0.0539	0.1778	1.1033	0.091*
H59C	-0.0023	0.1517	1.0938	0.091*

Atomic displacement parameters (Å²)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
N1	0.0180 (9)	0.0123 (8)	0.0187 (9)	-0.0007 (7)	0.0018 (7)	-0.0002 (7)
C2	0.0169 (10)	0.0110 (10)	0.0176 (11)	-0.0017 (8)	-0.0020 (8)	0.0009 (8)
N3	0.0174 (9)	0.0133 (8)	0.0184 (9)	-0.0008 (7)	0.0009 (7)	0.0018 (7)
C3a	0.0188 (11)	0.0123 (10)	0.0166 (11)	-0.0014 (8)	-0.0014 (8)	0.0000 (8)
C4	0.0182 (11)	0.0135 (10)	0.0208 (11)	-0.0012 (8)	-0.0016 (9)	-0.0006 (9)
C5	0.0186 (11)	0.0170 (10)	0.0166 (11)	-0.0036 (9)	-0.0014 (8)	-0.0011 (9)
C6	0.0237 (12)	0.0147 (10)	0.0190 (11)	-0.0052 (9)	0.0001 (9)	0.0027 (9)
C7	0.0220 (11)	0.0127 (10)	0.0200 (11)	0.0002 (9)	-0.0012 (9)	0.0007 (9)
C7a	0.0173 (10)	0.0155 (10)	0.0164 (11)	-0.0017 (8)	0.0007 (8)	-0.0014 (8)
N11	0.0203 (9)	0.0113 (8)	0.0242 (10)	-0.0006 (7)	0.0033 (7)	-0.0037 (7)
N12	0.0204 (9)	0.0142 (9)	0.0220 (10)	-0.0002 (7)	0.0020 (7)	-0.0005 (7)
C13	0.0212 (11)	0.0116 (10)	0.0152 (11)	0.0008 (8)	-0.0003 (8)	0.0011 (8)
C14	0.0186 (11)	0.0146 (10)	0.0192 (11)	-0.0024 (9)	0.0011 (9)	-0.0006 (9)
C15	0.0203 (11)	0.0161 (10)	0.0149 (11)	-0.0026 (9)	0.0014 (8)	0.0017 (9)
C16	0.0208 (11)	0.0182 (11)	0.0222 (12)	0.0009 (9)	0.0071 (9)	0.0002 (9)
C17	0.0252 (12)	0.0213 (12)	0.0344 (14)	0.0061 (10)	0.0079 (10)	0.0012 (10)

C18	0.0393 (14)	0.0329 (14)	0.0249 (13)	0.0033 (12)	0.0124 (11)	-0.0006 (11)
C19	0.0209 (12)	0.0295 (13)	0.0339 (14)	-0.0002 (10)	0.0071 (10)	-0.0025 (11)
C21	0.0148 (10)	0.0163 (10)	0.0169 (11)	0.0017 (8)	-0.0009 (8)	0.0026 (8)
C22	0.0210 (11)	0.0145 (10)	0.0197 (11)	0.0007 (9)	-0.0022 (9)	0.0021 (9)
C23	0.0228 (12)	0.0187 (11)	0.0187 (11)	0.0023 (9)	0.0007 (9)	-0.0020 (9)
C24	0.0150 (11)	0.0243 (11)	0.0212 (12)	0.0009 (9)	0.0043 (9)	0.0056 (9)
Cl24	0.0378 (3)	0.0283 (3)	0.0275 (3)	-0.0043 (3)	0.0143 (3)	0.0025 (3)
C25	0.0179 (11)	0.0144 (10)	0.0242 (12)	-0.0004 (9)	-0.0008 (9)	0.0016 (9)
C26	0.0178 (11)	0.0145 (10)	0.0183 (11)	0.0014 (8)	-0.0012 (8)	-0.0011 (9)
C51	0.0178 (11)	0.0201 (11)	0.0185 (12)	-0.0049 (9)	-0.0027 (9)	-0.0016 (9)
O51	0.0239 (8)	0.0176 (8)	0.0329 (10)	-0.0012 (7)	0.0076 (7)	-0.0019 (7)
O52	0.0230 (8)	0.0189 (8)	0.0266 (9)	-0.0018 (6)	0.0097 (7)	0.0029 (7)
C52	0.0215 (12)	0.0278 (12)	0.0308 (13)	-0.0007 (10)	0.0104 (10)	0.0017 (10)
C53	0.0210 (12)	0.0304 (13)	0.0341 (14)	-0.0039 (10)	0.0070 (10)	0.0039 (11)
C54	0.0190 (12)	0.0351 (14)	0.0292 (13)	-0.0022 (10)	0.0033 (10)	0.0038 (11)
C55	0.0262 (12)	0.0249 (12)	0.0277 (13)	0.0014 (10)	0.0072 (10)	0.0028 (10)
C56	0.0263 (12)	0.0238 (12)	0.0293 (13)	0.0012 (10)	0.0075 (10)	0.0037 (10)
C57	0.0283 (13)	0.0251 (12)	0.0256 (13)	-0.0042 (10)	0.0009 (10)	0.0022 (10)
C58	0.0361 (15)	0.0404 (16)	0.0357 (15)	-0.0085 (12)	0.0065 (12)	0.0063 (13)
C59	0.071 (2)	0.054 (2)	0.058 (2)	-0.0285 (18)	0.0091 (18)	0.0178 (17)

Geometric parameters (Å, °)

N1—C2	1.381 (3)	C21—C22	1.401 (3)
N1—C13	1.424 (3)	C22—C23	1.383 (3)
C2—N3	1.324 (3)	C22—H22	0.9500
C2—C21	1.472 (3)	C23—C24	1.388 (3)
N3—C3a	1.391 (3)	C23—H23	0.9500
C3a—C4	1.394 (3)	C24—C25	1.383 (3)
C3a—C7a	1.403 (3)	C24—Cl24	1.745 (2)
C7a—N1	1.386 (3)	C25—C26	1.387 (3)
C4—C5	1.393 (3)	C25—H25	0.9500
C4—H4	0.9500	C26—H26	0.9500
C5—C6	1.411 (3)	C51—O51	1.209 (3)
C5—C51	1.488 (3)	C51—O52	1.347 (3)
C6—C7	1.383 (3)	O52—C52	1.457 (3)
C6—H6	0.9500	C52—C53	1.513 (3)
C7—C7a	1.393 (3)	C52—H52A	0.9900
C7—H7	0.9500	C52—H52B	0.9900
N11—N12	1.358 (2)	C53—C54	1.513 (3)
N11—H11	0.8601	C53—H53A	0.9900
N12—C13	1.326 (3)	C53—H53B	0.9900
C13—C14	1.397 (3)	C54—C55	1.536 (3)
C14—C15	1.381 (3)	C54—H54A	0.9900
C15—N11	1.354 (3)	C54—H54B	0.9900
C14—H14	0.9500	C55—C56	1.526 (3)
C15—C16	1.517 (3)	C55—H55A	0.9900
C16—C17	1.533 (3)	C55—H55B	0.9900
C16—C19	1.534 (3)	C56—C57	1.529 (3)
C16—C18	1.542 (3)	C56—H56A	0.9900

C17—H17A	0.9800	C56—H56B	0.9900
C17—H17B	0.9800	C57—C58	1.519 (3)
C17—H17C	0.9800	C57—H57A	0.9900
C18—H18A	0.9800	C57—H57B	0.9900
C18—H18B	0.9800	C58—C59	1.529 (4)
C18—H18C	0.9800	C58—H58A	0.9900
C19—H19A	0.9800	C58—H58B	0.9900
C19—H19B	0.9800	C59—H59A	0.9800
C19—H19C	0.9800	C59—H59B	0.9800
C21—C26	1.397 (3)	C59—H59C	0.9800
C2—N1—C7a	106.69 (17)	C23—C22—H22	119.6
C2—N1—C13	128.55 (17)	C21—C22—H22	119.6
C7a—N1—C13	124.75 (17)	C22—C23—C24	119.0 (2)
N3—C2—N1	112.47 (18)	C22—C23—H23	120.5
N3—C2—C21	124.71 (18)	C24—C23—H23	120.5
N1—C2—C21	122.82 (18)	C25—C24—C23	121.5 (2)
C2—N3—C3a	105.35 (17)	C25—C24—C124	118.43 (17)
N3—C3a—C4	130.73 (19)	C23—C24—C124	120.01 (17)
N3—C3a—C7a	109.94 (18)	C24—C25—C26	119.1 (2)
C4—C3a—C7a	119.31 (19)	C24—C25—H25	120.4
C5—C4—C3a	118.14 (19)	C26—C25—H25	120.4
C5—C4—H4	120.9	C25—C26—C21	120.6 (2)
C3a—C4—H4	120.9	C25—C26—H26	119.7
C4—C5—C6	121.3 (2)	C21—C26—H26	119.7
C4—C5—C51	117.60 (19)	O51—C51—O52	123.2 (2)
C6—C5—C51	121.12 (19)	O51—C51—C5	124.9 (2)
C7—C6—C5	121.3 (2)	O52—C51—C5	111.82 (18)
C7—C6—H6	119.3	C51—O52—C52	115.94 (17)
C5—C6—H6	119.3	O52—C52—C53	106.96 (19)
C6—C7—C7a	116.47 (19)	O52—C52—H52A	110.3
C6—C7—H7	121.8	C53—C52—H52A	110.3
C7a—C7—H7	121.8	O52—C52—H52B	110.3
N1—C7a—C7	131.05 (19)	C53—C52—H52B	110.3
N1—C7a—C3a	105.55 (17)	H52A—C52—H52B	108.6
C7—C7a—C3a	123.40 (19)	C54—C53—C52	115.1 (2)
C15—N11—N12	113.41 (17)	C54—C53—H53A	108.5
C15—N11—H11	129.7	C52—C53—H53A	108.5
N12—N11—H11	116.9	C54—C53—H53B	108.5
C13—N12—N11	102.86 (16)	C52—C53—H53B	108.5
N12—C13—C14	113.48 (18)	H53A—C53—H53B	107.5
N12—C13—N1	118.29 (18)	C53—C54—C55	112.70 (19)
C14—C13—N1	128.23 (18)	C53—C54—H54A	109.1
C15—C14—C13	104.17 (18)	C55—C54—H54A	109.1
C15—C14—H14	127.9	C53—C54—H54B	109.1
C13—C14—H14	127.9	C55—C54—H54B	109.1
N11—C15—C14	106.08 (18)	H54A—C54—H54B	107.8
N11—C15—C16	123.49 (18)	C56—C55—C54	114.0 (2)
C14—C15—C16	130.22 (19)	C56—C55—H55A	108.8

C15—C16—C17	110.67 (17)	C54—C55—H55A	108.8
C15—C16—C19	109.41 (18)	C56—C55—H55B	108.8
C17—C16—C19	109.62 (19)	C54—C55—H55B	108.8
C15—C16—C18	108.11 (18)	H55A—C55—H55B	107.6
C17—C16—C18	109.84 (19)	C55—C56—C57	113.6 (2)
C19—C16—C18	109.15 (19)	C55—C56—H56A	108.8
C16—C17—H17A	109.5	C57—C56—H56A	108.8
C16—C17—H17B	109.5	C55—C56—H56B	108.8
H17A—C17—H17B	109.5	C57—C56—H56B	108.8
C16—C17—H17C	109.5	H56A—C56—H56B	107.7
H17A—C17—H17C	109.5	C58—C57—C56	113.1 (2)
H17B—C17—H17C	109.5	C58—C57—H57A	109.0
C16—C18—H18A	109.5	C56—C57—H57A	109.0
C16—C18—H18B	109.5	C58—C57—H57B	109.0
H18A—C18—H18B	109.5	C56—C57—H57B	109.0
C16—C18—H18C	109.5	H57A—C57—H57B	107.8
H18A—C18—H18C	109.5	C57—C58—C59	113.4 (2)
H18B—C18—H18C	109.5	C57—C58—H58A	108.9
C16—C19—H19A	109.5	C59—C58—H58A	108.9
C16—C19—H19B	109.5	C57—C58—H58B	108.9
H19A—C19—H19B	109.5	C59—C58—H58B	108.9
C16—C19—H19C	109.5	H58A—C58—H58B	107.7
H19A—C19—H19C	109.5	C58—C59—H59A	109.5
H19B—C19—H19C	109.5	C58—C59—H59B	109.5
C26—C21—C22	119.02 (19)	H59A—C59—H59B	109.5
C26—C21—C2	118.38 (19)	C58—C59—H59C	109.5
C22—C21—C2	122.58 (19)	H59A—C59—H59C	109.5
C23—C22—C21	120.7 (2)	H59B—C59—H59C	109.5
C7a—N1—C2—N3	0.7 (2)	C13—C14—C15—N11	-0.9 (2)
C13—N1—C2—N3	-177.69 (19)	N1—C2—C21—C22	35.2 (3)
C7a—N1—C2—C21	-179.10 (18)	N1—C2—C21—C26	-146.5 (2)
C13—N1—C2—C21	2.5 (3)	N3—C2—C21—C22	-144.6 (2)
N1—C2—N3—C3a	-0.6 (2)	N3—C2—C21—C26	33.7 (3)
C21—C2—N3—C3a	179.14 (19)	C13—C14—C15—C16	173.9 (2)
C2—N3—C3a—C4	-177.9 (2)	N11—C15—C16—C17	-42.5 (3)
C2—N3—C3a—C7a	0.3 (2)	C14—C15—C16—C17	143.4 (2)
N3—C3a—C4—C5	177.2 (2)	N11—C15—C16—C19	-163.4 (2)
C7a—C3a—C4—C5	-0.9 (3)	N11—C15—C16—C18	77.8 (3)
C3a—C4—C5—C6	2.4 (3)	C14—C15—C16—C18	-96.2 (3)
C3a—C4—C5—C51	-176.51 (19)	C14—C15—C16—C19	22.5 (3)
C4—C5—C6—C7	-0.9 (3)	C26—C21—C22—C23	0.8 (3)
C51—C5—C6—C7	177.96 (19)	C2—C21—C22—C23	179.03 (19)
C5—C6—C7—C7a	-2.0 (3)	C21—C22—C23—C24	0.3 (3)
C2—N1—C7a—C7	-179.7 (2)	C22—C23—C24—C25	-0.7 (3)
C13—N1—C7a—C7	-1.2 (3)	C22—C23—C24—C124	-179.52 (16)
C2—N1—C7a—C3a	-0.4 (2)	C23—C24—C25—C26	-0.2 (3)
C13—N1—C7a—C3a	178.03 (18)	C124—C24—C25—C26	178.72 (16)
C6—C7—C7a—N1	-177.3 (2)	C24—C25—C26—C21	1.3 (3)

C6—C7—C7a—C3a	3.6 (3)	C22—C21—C26—C25	-1.6 (3)
N3—C3a—C7a—N1	0.1 (2)	C2—C21—C26—C25	-179.93 (18)
C4—C3a—C7a—N1	178.55 (18)	C4—C5—C51—O51	-9.4 (3)
N3—C3a—C7a—C7	179.37 (19)	C6—C5—C51—O51	171.6 (2)
C4—C3a—C7a—C7	-2.1 (3)	C4—C5—C51—O52	168.98 (18)
C15—N11—N12—C13	-0.5 (2)	C6—C5—C51—O52	-10.0 (3)
N11—N12—C13—C14	-0.2 (2)	O51—C51—O52—C52	-2.1 (3)
N11—N12—C13—N1	179.17 (17)	C5—C51—O52—C52	179.49 (18)
C2—N1—C13—N12	-120.5 (2)	C51—O52—C52—C53	161.93 (19)
C2—N1—C13—C14	58.7 (3)	O52—C52—C53—C54	63.2 (3)
C7a—N1—C13—N12	61.4 (3)	C52—C53—C54—C55	-173.9 (2)
C7a—N1—C13—C14	-119.4 (2)	C53—C54—C55—C56	-68.1 (3)
N12—C13—C14—C15	0.7 (2)	C54—C55—C56—C57	-170.9 (2)
N1—C13—C14—C15	-178.6 (2)	C55—C56—C57—C58	179.0 (2)
N12—N11—C15—C14	0.9 (2)	C56—C57—C58—C59	-173.3 (2)
N12—N11—C15—C16	-174.38 (18)		

Hydrogen-bond geometry (Å, °)

Cg1 is the centroid of the N11/N12/C13—C15 ring.

<i>D—H...A</i>	<i>D—H</i>	<i>H...A</i>	<i>D...A</i>	<i>D—H...A</i>
N11—H11...N3 ⁱ	0.86	2.16	3.011 (2)	169
C14—H14...O51 ⁱⁱ	0.95	2.31	3.249 (3)	168
C26—H26...N12 ⁱⁱⁱ	0.95	2.53	3.292 (3)	137
C22—H22...Cg1	0.95	2.84	3.472 (3)	125

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