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Hydrogen-bonded bilayers in 7-benzyl-3-*tert*-butyl-1-phenyl-4,5,6,7-tetrahydro-1*H*-spiro[pyrazolo[3,4-*b*]-pyridine-5,2′-indan]-1′,3′-dione

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In the title compound, $C_{31}H_{29}N_3O_2$, the reduced pyridine ring adopts a conformation intermediate between the envelope and half-chair forms. The aryl rings of the benzyl and phenyl substituents are nearly parallel and overlap, indicative of an intramolecular π–π stacking interaction. A combination of two C—H···O hydrogen bonds and one C—H···N hydrogen bond links the molecules into a bilayer having *tert*-butyl groups on both faces.

Keywords: crystal structure; spiro compounds; hydrogen bonding.

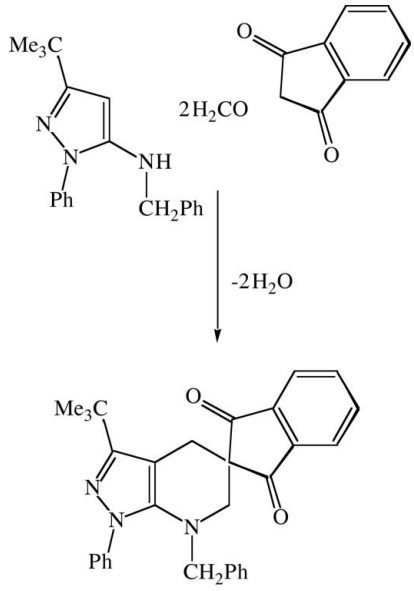
1. Introduction

Compounds with spiro skeletons not only constitute subunits in numerous alkaloids, but are also templates for drug discovery that have been used as scaffolds for combinatorial libraries (Maier & Wuensch, 2002; Shaabani & Bazgir, 2004; Krasnov & Kartsev, 2005; Lang *et al.*, 2005; Kadutskii & Kozlov, 2006; Kuster *et al.*, 2006; Macleod *et al.*, 2006; Nazarenko *et al.*, 2007). The synthesis of spiro compounds can be achieved using conventional methods and procedures based on three-component one-pot reactions (Marti & Carrei, 2003; Rolandsgard *et al.*, 2005; Arya & Dandia, 2007; Rahimizadeh *et al.*, 2007). However, focused microwave irradiation is now emerging as a powerful tool to simplify and improve classic organic reactions, because it often leads to higher yields and cleaner and shorter reaction times, with precise control of the reaction parameters (Kappe, 2004; Martins *et al.*, 2009). We have recently developed a route to spiro compounds through the microwave-assisted reactions between pyrazolo[3,4-*b*]-pyridines, paraformaldehyde and cyclic β-diketones (Quiroga *et al.*, 2010), and we report here the molecular and supramolecular structure of the title compound, (I), as a representative product from this procedure, which was obtained using indan-1,3-dione as the cyclic β-diketone component.

2. Experimental

2.1. Synthesis and crystallization

A mixture of *N*-benzyl-3-*tert*-butyl-1-phenyl-1*H*-pyrazol-5-amine (2 mmol), indan-1,3-dione (2 mmol) and an excess of paraformaldehyde (30 mol%) was subjected to microwave radiation for 25 min at 473 K and a maximum power of 300 W. The mixture was then dissolved in hot ethanol and subsequently allowed to cool to ambient temperature. The resulting solid product was collected by filtration and washed successively with ethanol (5 ml) and hexane (2 × 5 ml) to give pale-yellow crystals of (I) suitable for single-crystal X-ray diffraction (yield 52%, m.p. 458–160 K). MS (EI 70 eV) *m*/*z* (%relative abundance): 475 (M^+, 89), 384 (25), 328 (100); HR–MS, found: 475, 2259; $C_{31}H_{29}N_3O_2$ requires 475, 2260. Analysis found: C 77.3, H 6.2, N 9.3%; $C_{31}H_{29}N_3O_2$ requires: C 78.3, H 6.1, N 8.8%.



(I)

2.2. Refinement

Crystal data, data collection and structure refinement details are summarized in Table 1. All H atoms were located in difference maps but were subsequently treated as riding in geometrically idealized positions, with C—H = 0.95 (aromatic), 0.98 (CH_3) or 0.99 Å (CH_2), 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, or 1.2 for all other H atoms.

3. Results and discussion

The reduced pyridine ring in (I) is markedly nonplanar (Fig. 1), with a ring-puckering amplitude of 0.467 (2) Å; the ring-puckering angles (Cremer & Pople, 1975) calculated for the

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Table 1
Experimental details.

Crystal data	
Chemical formula	$C_{31}H_{29}N_3O_2$
M_r	475.57
Crystal system, space group	Monoclinic, $P2_1/c$
Temperature (K)	120
a, b, c (Å)	16.6917 (18), 5.9748 (4), 24.840 (3)
β (°)	91.841 (10)
V (Å^3)	2476.0 (4)
Z	4
Radiation type	Mo $K\alpha$
μ (mm^{-1})	0.08
Crystal size (mm)	0.34 × 0.27 × 0.22
Data collection	
Diffractometer	Bruker–Nonius KappaCCD area-detector diffractometer
Absorption correction	Multi-scan (*SADABS*; Sheldrick, 2003)
T_{min}, T_{max}	0.973, 0.983
No. of measured, independent and observed [$I > 2\sigma(I)$] reflections	38299, 5679, 3889
R_{int}	0.049
(sin $\theta/\lambda)_{max}$ (Å^{-1})	0.650
Refinement	
$R[F^2 > 2\sigma(F^2)]$, $wR(F^2)$, S	0.046, 0.115, 1.04
No. of reflections	5679
No. of parameters	322
No. of restraints	0
H-atom treatment	H-atom parameters constrained
$\Delta\rho_{max}$, $\Delta\rho_{min}$ (e Å^{-3})	0.23, −0.21

Computer programs: *COLLECT* (Nonius, 1998), *DIRAX/LSQ* (Duisenberg *et al.*, 2000), *EVALCCD* (Duisenberg *et al.*, 2003), *SIR2004* (Burla *et al.*, 2005), *SHELXL97* (Sheldrick, 2008) and *PLATON* (Spek, 2009).

atom sequence N7–C6–C52–C4–C3*A*–C7*A* are θ = 128.9 (2)° and φ = 283.8 (3)°. These values indicate that this ring adopts a conformation intermediate between the half-chair and envelope forms, for which the idealized values (Boeyens, 1978) are θ = 129.2 and 125.3°, respectively, and $\varphi = (60k + 30)°$ and $(60k)°$, respectively, where k represents an integer.

As expected, the mean planes of the two rings which are linked *via* atom C52 are almost orthogonal, with a dihedral angle between the mean planes of 88.1 (3)°. The orientation of the *tert*-butyl group is of some interest as one of the methyl C atoms, atom C34, is close to the plane of the adjacent pyrazole ring but displaced from it by 0.081 (2) Å, as indicated by the value of the N2—C3—C31—C34 torsion angle (Table 2). Both of the other hydrocarbyl substituents, at atoms N1 and N7, are twisted well out of the mean plane of the pyrazolo[3,4-*b*]-pyridine unit, as indicated by the relevant torsion angles (Table 2), but with the result that the two aryl rings (C11–C16 and C71–C76) are themselves very nearly parallel, with a dihedral angle between them of only 9.7 (2)°. The corresponding ring-centroid separation is 3.787 (2) Å and the shortest perpendicular distance from the centroid of one ring to the plane of the other is *ca* 3.41 Å, with a ring-centroid offset of *ca* 1.65 Å. This is indicative of an intramolecular π–π stacking interaction (Fig. 2) and is probably significant in determining the overall orientation of these two substituents. The bond lengths (Table 2) indicate some bond fixation in the pyrazole ring and confirm the reduced nature of the pyridine ring, but otherwise the bond lengths present no features of note.

The supramolecular assembly of (I) is determined by three hydrogen bonds, two of the C—H···O type and one of the C—H···N type (Table 3), but C—H···π(arene) hydrogen bonds and intermolecular π–π stacking interactions are absent. The overall assembly takes the form of a fairly complex bilayer, but the formation of this bilayer is readily analysed in terms of

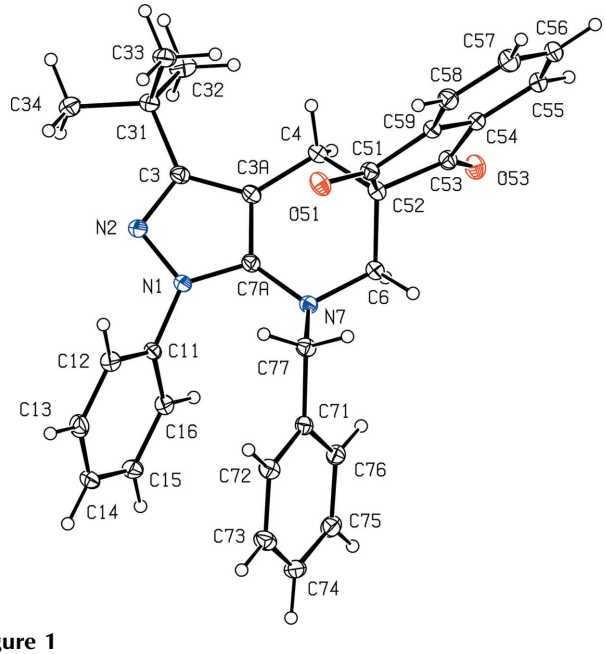

Figure 1
The molecular structure of (I), showing the atom-labelling scheme. Displacement ellipsoids are drawn at the 30% probability level.

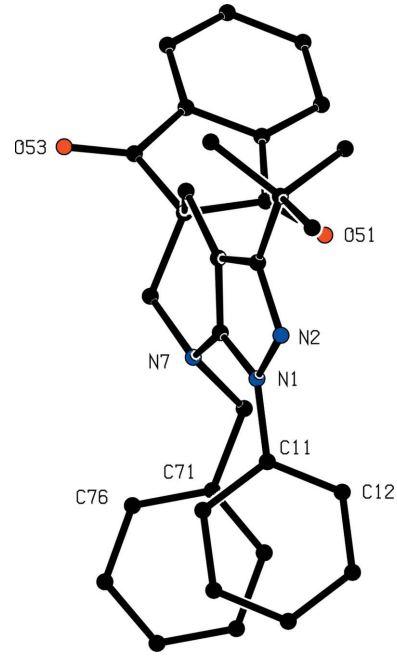

Figure 2
A view of the molecular structure of (I), showing the partial overlap of the C11–C16 and C71–C76 rings, which are nearly parallel. All H atoms have been omitted for the sake of clarity.

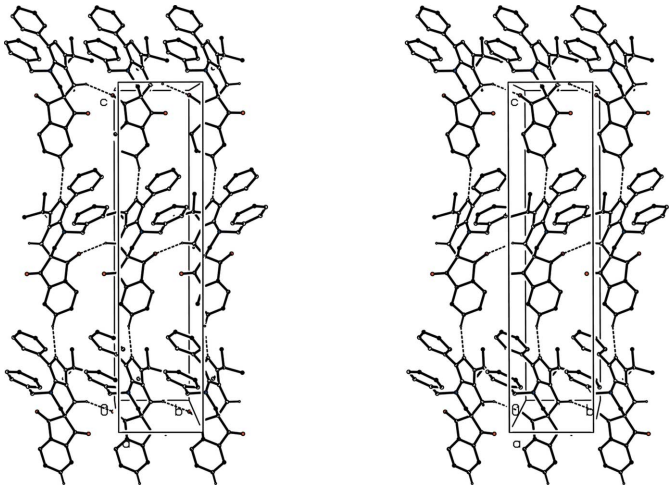

Figure 3
A stereoview of part of the crystal structure of (I), showing the formation of a hydrogen-bonded sheet of $R_4^4(28)$ rings lying parallel to (100). Dashed lines indicate hydrogen bonds. For the sake of clarity, H atoms not involved in the motifs shown have been omitted.

simple substructures (Ferguson *et al.*, 1998*a*,*b*; Gregson *et al.*, 2000). Acting alone, the hydrogen bond having atom O51 as the acceptor (Table 2) links molecules related by translation into a $C(5)$ chain (Bernstein *et al.*, 1995) running parallel to the [010] direction, while the hydrogen bond having atom N2 as the acceptor, when acting alone, links molecules related by the *c*-glide plane at $y = \frac{1}{4}$ into a $C(10)$ chain running parallel to the [001] direction. The combination of these two substructural motifs generates a sheet in the form of a (4,4) net lying parallel to (100) and built from $R_4^4(28)$ rings (Fig. 3). 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 $\frac{1}{2} < x < 1.0$. The final hydrogen bond, having atom O53 as the acceptor, links inversion-related

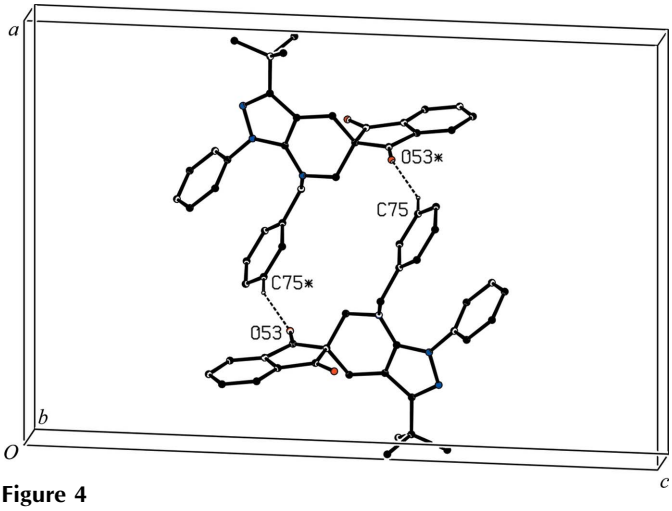

Figure 4
Part of the crystal structure of (I), showing the formation of a centrosymmetric hydrogen-bonded $R_2^2(20)$ ring which links pairs of (100) sheets. Dashed lines indicate hydrogen bonds. For the sake of clarity, H atoms not involved in the motif shown have been omitted. Atoms marked with an asterisk (*) are at the symmetry position $(-x + 1, -y, -z + 1)$.

Table 2
Selected geometric parameters (Å, °).

N1—N2	1.3830 (18)	C3*A*—C4	1.498 (2)
N2—C3	1.334 (2)	C4—C52	1.551 (2)
C3—C3*A*	1.416 (2)	C52—C6	1.552 (2)
C3*A*—C7*A*	1.371 (2)	C6—N7	1.4656 (19)
C7*A*—N1	1.3628 (19)	N7—C7*A*	1.3900 (19)
N2—C3—C31—C32	−135.75 (16)	N2—N1—C11—C12	−65.69 (19)
N2—C3—C31—C33	104.85 (17)	C7*A*—N7—C77—C71	113.17 (15)
N2—C3—C31—C34	−14.0 (2)	N7—C77—C71—C72	−149.38 (14)

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

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
C4—H4*B*···O51^{i}	0.99	2.32	3.145 (2)	141
C56—H56···N2^{ii}	0.95	2.53	3.431 (2)	158
C75—H75···O53^{iii}	0.95	2.46	3.342 (2)	154

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

pairs of molecules in a centrosymmetric $R_2^2(20)$ motif (Table 3 and Fig. 4). The two molecules involved in this ring motif lie in different (100) sheets, so that the effect of this final interaction is to link the sheets in pairs to form a bilayer. The interior of the bilayer contains C—H···O hydrogen bonds, while the *tert*-butyl groups are all on the outer faces. This probably accounts for the absence of any direction-specific interactions between adjacent bilayers.

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: FG3298). Services for accessing these data are described at the back of the journal.

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supplementary materials

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Computing details

Data collection: *COLLECT* (Nonius, 1998); 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); molecular graphics: *PLATON* (Spek, 2009); software used to prepare material for publication: *SHELXL97* (Sheldrick, 2008) and *PLATON* (Spek, 2009).

7-Benzyl-3-*tert*-butyl-1-phenyl-4,5,6,7-tetrahydro-1*H*-spiro[pyrazolo[3,4-*b*]pyridine-5,2′-indan]-1′,3′-dione

Crystal data

$C_{31}H_{29}N_3O_2$
$M_r = 475.57$
Monoclinic, $P2_1/c$
Hall symbol: -P 2ybc
$a = 16.6917\ (18)$ Å
$b = 5.9748\ (4)$ Å
$c = 24.840\ (3)$ Å
$\beta = 91.841\ (10)°$
$V = 2476.0\ (4)$ Å^3
$Z = 4$
$F(000) = 1008$
$D_x = 1.276$ Mg m^{-3}
Mo $K\alpha$ radiation, $\lambda = 0.71073$ Å
Cell parameters from 5680 reflections
$\theta = 3.0–27.5°$
$\mu = 0.08$ mm^{-1}
$T = 120$ K
Block, pale yellow
0.34 × 0.27 × 0.22 mm

Data collection

Bruker Nonius KappaCCD area-detector diffractometer
Radiation source: Bruker Nonius FR591 rotating anode
Graphite monochromator
Detector resolution: 9.091 pixels mm^{-1}
φ and ω scans
Absorption correction: multi-scan (*SADABS*; Sheldrick, 2003)
$T_{min} = 0.973$, $T_{max} = 0.983$
38299 measured reflections
5679 independent reflections
3889 reflections with $I > 2\sigma(I)$
$R_{int} = 0.049$
$\theta_{max} = 27.5°$, $\theta_{min} = 3.0°$
$h = -21\rightarrow21$
$k = -7\rightarrow7$
$l = -32\rightarrow32$

Refinement

Refinement on F^2
Least-squares matrix: full
$R[F^2 > 2\sigma(F^2)] = 0.046$
$wR(F^2) = 0.115$
$S = 1.04$
5679 reflections
322 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

$w = 1/[\sigma^2(F_o^2) + (0.0452P)^2 + 1.1191P]$
where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} = 0.001$

$\Delta\rho_{max} = 0.23$ e Å^{-3}
$\Delta\rho_{min} = -0.21$ e Å^{-3}

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

	x	*y*	*z*	U_{iso}*/U_{eq}
N1	0.24247 (8)	0.3603 (2)	0.63330 (5)	0.0228 (3)
N2	0.16935 (8)	0.2808 (2)	0.64967 (5)	0.0250 (3)
C3	0.14271 (9)	0.1498 (3)	0.60944 (6)	0.0224 (3)
C3A	0.19774 (9)	0.1426 (3)	0.56725 (6)	0.0213 (3)
C4	0.19455 (10)	0.0355 (3)	0.51271 (6)	0.0224 (3)
H4A	0.1388	0.0376	0.4978	0.027*
H4B	0.2122	−0.1223	0.5156	0.027*
C52	0.25005 (9)	0.1651 (3)	0.47469 (6)	0.0216 (3)
C6	0.33166 (9)	0.2112 (3)	0.50430 (6)	0.0234 (3)
H6A	0.3579	0.0662	0.5126	0.028*
H6B	0.3665	0.2940	0.4796	0.028*
N7	0.32604 (8)	0.3391 (2)	0.55438 (5)	0.0211 (3)
C7A	0.25948 (9)	0.2808 (3)	0.58353 (6)	0.0208 (3)
C51	0.20610 (9)	0.3730 (3)	0.45367 (6)	0.0225 (3)
O51	0.18240 (7)	0.52709 (19)	0.48063 (4)	0.0293 (3)
C53	0.26266 (10)	0.0272 (3)	0.42381 (6)	0.0236 (4)
O53	0.29945 (7)	−0.1477 (2)	0.42245 (5)	0.0308 (3)
C54	0.22283 (9)	0.1434 (3)	0.37753 (6)	0.0231 (3)
C55	0.21537 (10)	0.0773 (3)	0.32371 (6)	0.0274 (4)
H55	0.2367	−0.0611	0.3120	0.033*
C56	0.17571 (10)	0.2205 (3)	0.28785 (7)	0.0317 (4)
H56	0.1691	0.1791	0.2510	0.038*
C57	0.14545 (11)	0.4244 (3)	0.30528 (7)	0.0336 (4)
H57	0.1189	0.5204	0.2799	0.040*
C58	0.15310 (10)	0.4909 (3)	0.35875 (7)	0.0279 (4)
H58	0.1325	0.6305	0.3703	0.033*
C59	0.19181 (9)	0.3464 (3)	0.39461 (6)	0.0226 (3)
C11	0.29000 (9)	0.4909 (3)	0.67070 (6)	0.0214 (3)
C12	0.26215 (10)	0.6979 (3)	0.68680 (6)	0.0265 (4)
H12	0.2132	0.7554	0.6720	0.032*
C13	0.30642 (11)	0.8207 (3)	0.72471 (7)	0.0309 (4)
H13	0.2877	0.9630	0.7359	0.037*
C14	0.37777 (10)	0.7363 (3)	0.74627 (6)	0.0307 (4)
H14	0.4076	0.8197	0.7726	0.037*
C15	0.40544 (10)	0.5308 (3)	0.72946 (6)	0.0293 (4)
H15	0.4548	0.4741	0.7439	0.035*
C16	0.36168 (10)	0.4066 (3)	0.69159 (6)	0.0249 (4)
H16	0.3807	0.2652	0.6801	0.030*
C31	0.05951 (10)	0.0486 (3)	0.61060 (6)	0.0263 (4)
C32	0.05998 (11)	−0.1994 (3)	0.59411 (8)	0.0341 (4)
H32A	0.0821	−0.2139	0.5582	0.051*
H32B	0.0051	−0.2576	0.5935	0.051*
H32C	0.0931	−0.2847	0.6201	0.051*

C33	0.00517 (10)	0.1790 (3)	0.57030 (7)	0.0305 (4)
H33A	0.0039	0.3372	0.5807	0.046*
H33B	−0.0492	0.1174	0.5705	0.046*
H33C	0.0262	0.1653	0.5341	0.046*
C34	0.02508 (11)	0.0698 (4)	0.66680 (7)	0.0421 (5)
H34A	0.0573	−0.0200	0.6925	0.063*
H34B	−0.0304	0.0159	0.6659	0.063*
H34C	0.0263	0.2271	0.6780	0.063*
C77	0.34898 (10)	0.5767 (3)	0.55292 (6)	0.0230 (3)
H77A	0.3066	0.6665	0.5697	0.028*
H77B	0.3520	0.6244	0.5149	0.028*
C71	0.42857 (9)	0.6264 (3)	0.58165 (6)	0.0215 (3)
C72	0.44048 (10)	0.8345 (3)	0.60595 (6)	0.0251 (4)
H72	0.3995	0.9447	0.6034	0.030*
C73	0.51192 (10)	0.8816 (3)	0.63387 (7)	0.0293 (4)
H73	0.5196	1.0241	0.6502	0.035*
C74	0.57188 (10)	0.7225 (3)	0.63803 (7)	0.0302 (4)
H74	0.6201	0.7541	0.6580	0.036*
C75	0.56146 (10)	0.5170 (3)	0.61303 (7)	0.0295 (4)
H75	0.6030	0.4082	0.6152	0.035*
C76	0.49021 (10)	0.4696 (3)	0.58466 (6)	0.0251 (4)
H76	0.4836	0.3290	0.5672	0.030*

Atomic displacement parameters (Å²)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
N1	0.0218 (7)	0.0290 (8)	0.0176 (6)	−0.0061 (6)	0.0002 (5)	−0.0029 (6)
N2	0.0224 (7)	0.0319 (8)	0.0206 (7)	−0.0057 (6)	−0.0001 (5)	−0.0005 (6)
C3	0.0230 (8)	0.0242 (8)	0.0197 (8)	−0.0012 (7)	−0.0033 (6)	0.0013 (7)
C3A	0.0240 (8)	0.0207 (8)	0.0192 (7)	0.0004 (7)	−0.0023 (6)	0.0002 (6)
C4	0.0250 (8)	0.0215 (8)	0.0204 (8)	−0.0007 (7)	−0.0028 (6)	−0.0013 (6)
C52	0.0251 (8)	0.0206 (8)	0.0191 (7)	0.0006 (7)	0.0000 (6)	−0.0017 (6)
C6	0.0240 (8)	0.0262 (9)	0.0200 (8)	−0.0012 (7)	0.0000 (6)	−0.0017 (7)
N7	0.0224 (7)	0.0217 (7)	0.0192 (6)	−0.0030 (6)	0.0004 (5)	−0.0013 (5)
C7A	0.0223 (8)	0.0218 (8)	0.0181 (7)	−0.0003 (7)	−0.0011 (6)	0.0004 (6)
C51	0.0234 (8)	0.0230 (9)	0.0210 (8)	−0.0029 (7)	−0.0001 (6)	−0.0014 (7)
O51	0.0394 (7)	0.0232 (6)	0.0252 (6)	0.0039 (5)	−0.0011 (5)	−0.0052 (5)
C53	0.0247 (8)	0.0227 (9)	0.0233 (8)	−0.0015 (7)	0.0025 (6)	−0.0034 (7)
O53	0.0361 (7)	0.0264 (7)	0.0301 (6)	0.0052 (6)	0.0036 (5)	−0.0042 (5)
C54	0.0204 (8)	0.0285 (9)	0.0204 (8)	−0.0038 (7)	0.0021 (6)	−0.0025 (7)
C55	0.0255 (9)	0.0347 (10)	0.0222 (8)	−0.0043 (8)	0.0034 (7)	−0.0065 (7)
C56	0.0280 (9)	0.0483 (12)	0.0189 (8)	−0.0058 (8)	0.0009 (7)	−0.0025 (8)
C57	0.0325 (10)	0.0453 (12)	0.0226 (8)	−0.0004 (9)	−0.0027 (7)	0.0086 (8)
C58	0.0282 (9)	0.0300 (9)	0.0254 (8)	0.0007 (8)	0.0002 (7)	0.0016 (7)
C59	0.0206 (8)	0.0277 (9)	0.0194 (7)	−0.0026 (7)	0.0007 (6)	−0.0013 (7)
C11	0.0228 (8)	0.0256 (9)	0.0159 (7)	−0.0059 (7)	0.0003 (6)	−0.0015 (6)
C12	0.0248 (8)	0.0288 (9)	0.0259 (8)	0.0000 (7)	0.0005 (7)	−0.0005 (7)
C13	0.0370 (10)	0.0274 (9)	0.0288 (9)	−0.0055 (8)	0.0081 (7)	−0.0074 (7)
C14	0.0306 (9)	0.0392 (11)	0.0222 (8)	−0.0132 (8)	0.0003 (7)	−0.0075 (8)
C15	0.0232 (8)	0.0414 (11)	0.0230 (8)	−0.0019 (8)	−0.0036 (7)	0.0011 (8)

C16	0.0251 (8)	0.0277 (9)	0.0219 (8)	0.0002 (7)	0.0010 (6)	−0.0011 (7)
C31	0.0234 (8)	0.0324 (10)	0.0231 (8)	−0.0045 (7)	−0.0013 (6)	−0.0015 (7)
C32	0.0277 (9)	0.0314 (10)	0.0429 (11)	−0.0055 (8)	−0.0042 (8)	0.0045 (8)
C33	0.0246 (9)	0.0322 (10)	0.0342 (9)	0.0006 (8)	−0.0054 (7)	−0.0068 (8)
C34	0.0289 (10)	0.0693 (15)	0.0283 (9)	−0.0172 (10)	0.0029 (7)	−0.0027 (9)
C77	0.0253 (8)	0.0222 (8)	0.0213 (8)	−0.0014 (7)	−0.0022 (6)	0.0023 (7)
C71	0.0239 (8)	0.0238 (8)	0.0167 (7)	−0.0035 (7)	0.0012 (6)	0.0032 (6)
C72	0.0289 (9)	0.0226 (9)	0.0235 (8)	−0.0020 (7)	−0.0020 (7)	0.0027 (7)
C73	0.0338 (10)	0.0271 (9)	0.0267 (9)	−0.0093 (8)	−0.0029 (7)	−0.0001 (7)
C74	0.0235 (9)	0.0405 (11)	0.0266 (9)	−0.0082 (8)	−0.0020 (7)	0.0025 (8)
C75	0.0234 (9)	0.0369 (10)	0.0284 (9)	0.0017 (8)	0.0025 (7)	0.0034 (8)
C76	0.0248 (8)	0.0256 (9)	0.0250 (8)	−0.0015 (7)	0.0033 (7)	−0.0012 (7)

Geometric parameters (Å, º)

N1—N2	1.3830 (18)	C12—C13	1.388 (2)
N1—C11	1.433 (2)	C12—H12	0.9500
N2—C3	1.334 (2)	C13—C14	1.385 (2)
C3—C3A	1.416 (2)	C13—H13	0.9500
C3—C31	1.516 (2)	C14—C15	1.381 (3)
C3A—C7A	1.371 (2)	C14—H14	0.9500
C7A—N1	1.3628 (19)	C15—C16	1.387 (2)
C3A—C4	1.498 (2)	C15—H15	0.9500
C4—C52	1.551 (2)	C16—H16	0.9500
C4—H4A	0.9900	C31—C34	1.532 (2)
C4—H4B	0.9900	C31—C32	1.537 (2)
C52—C51	1.526 (2)	C31—C33	1.541 (2)
C52—C53	1.529 (2)	C32—H32A	0.9800
C52—C6	1.552 (2)	C32—H32B	0.9800
C6—N7	1.4656 (19)	C32—H32C	0.9800
C6—H6A	0.9900	C33—H33A	0.9800
C6—H6B	0.9900	C33—H33B	0.9800
N7—C7A	1.3900 (19)	C33—H33C	0.9800
N7—C77	1.471 (2)	C34—H34A	0.9800
C51—O51	1.2124 (19)	C34—H34B	0.9800
C51—C59	1.487 (2)	C34—H34C	0.9800
C53—O53	1.2135 (19)	C77—C71	1.517 (2)
C53—C54	1.482 (2)	C77—H77A	0.9900
C54—C59	1.391 (2)	C77—H77B	0.9900
C54—C55	1.396 (2)	C71—C76	1.392 (2)
C55—C56	1.388 (2)	C71—C72	1.393 (2)
C55—H55	0.9500	C72—C73	1.389 (2)
C56—C57	1.393 (3)	C72—H72	0.9500
C56—H56	0.9500	C73—C74	1.382 (3)
C57—C58	1.388 (2)	C73—H73	0.9500
C57—H57	0.9500	C74—C75	1.385 (3)
C58—C59	1.386 (2)	C74—H74	0.9500
C58—H58	0.9500	C75—C76	1.392 (2)
C11—C16	1.384 (2)	C75—H75	0.9500
C11—C12	1.385 (2)	C76—H76	0.9500

C7A—N1—N2	111.00 (12)	C11—C12—H12	120.3
C7A—N1—C11	130.59 (13)	C13—C12—H12	120.3
N2—N1—C11	118.16 (12)	C14—C13—C12	120.15 (16)
C3—N2—N1	104.91 (12)	C14—C13—H13	119.9
N2—C3—C3A	111.32 (14)	C12—C13—H13	119.9
N2—C3—C31	120.21 (14)	C15—C14—C13	119.90 (16)
C3A—C3—C31	128.20 (14)	C15—C14—H14	120.0
C7A—C3A—C3	105.22 (13)	C13—C14—H14	120.0
C7A—C3A—C4	121.91 (14)	C14—C15—C16	120.43 (16)
C3—C3A—C4	132.64 (14)	C14—C15—H15	119.8
C3A—C4—C52	109.45 (13)	C16—C15—H15	119.8
C3A—C4—H4A	109.8	C11—C16—C15	119.33 (16)
C52—C4—H4A	109.8	C11—C16—H16	120.3
C3A—C4—H4B	109.8	C15—C16—H16	120.3
C52—C4—H4B	109.8	C3—C31—C34	110.80 (13)
H4A—C4—H4B	108.2	C3—C31—C32	111.51 (14)
C51—C52—C53	103.48 (12)	C34—C31—C32	109.14 (15)
C51—C52—C4	108.94 (13)	C3—C31—C33	107.86 (14)
C53—C52—C4	109.59 (13)	C34—C31—C33	108.67 (15)
C51—C52—C6	115.01 (13)	C32—C31—C33	108.80 (14)
C53—C52—C6	110.21 (13)	C31—C32—H32A	109.5
C4—C52—C6	109.42 (12)	C31—C32—H32B	109.5
N7—C6—C52	114.57 (13)	H32A—C32—H32B	109.5
N7—C6—H6A	108.6	C31—C32—H32C	109.5
C52—C6—H6A	108.6	H32A—C32—H32C	109.5
N7—C6—H6B	108.6	H32B—C32—H32C	109.5
C52—C6—H6B	108.6	C31—C33—H33A	109.5
H6A—C6—H6B	107.6	C31—C33—H33B	109.5
C7A—N7—C6	112.68 (12)	H33A—C33—H33B	109.5
C7A—N7—C77	117.90 (13)	C31—C33—H33C	109.5
C6—N7—C77	117.28 (12)	H33A—C33—H33C	109.5
N1—C7A—C3A	107.52 (13)	H33B—C33—H33C	109.5
N1—C7A—N7	125.35 (14)	C31—C34—H34A	109.5
C3A—C7A—N7	127.08 (14)	C31—C34—H34B	109.5
O51—C51—C59	125.52 (15)	H34A—C34—H34B	109.5
O51—C51—C52	126.22 (14)	C31—C34—H34C	109.5
C59—C51—C52	108.12 (13)	H34A—C34—H34C	109.5
O53—C53—C54	126.63 (15)	H34B—C34—H34C	109.5
O53—C53—C52	124.78 (15)	N7—C77—C71	113.70 (13)
C54—C53—C52	108.58 (13)	N7—C77—H77A	108.8
C59—C54—C55	121.08 (15)	C71—C77—H77A	108.8
C59—C54—C53	109.52 (13)	N7—C77—H77B	108.8
C55—C54—C53	129.39 (16)	C71—C77—H77B	108.8
C56—C55—C54	117.81 (16)	H77A—C77—H77B	107.7
C56—C55—H55	121.1	C76—C71—C72	118.84 (15)
C54—C55—H55	121.1	C76—C71—C77	121.88 (15)
C55—C56—C57	120.65 (16)	C72—C71—C77	119.28 (14)
C55—C56—H56	119.7	C73—C72—C71	120.36 (16)

C57—C56—H56	119.7	C73—C72—H72	119.8
C58—C57—C56	121.63 (16)	C71—C72—H72	119.8
C58—C57—H57	119.2	C74—C73—C72	120.39 (16)
C56—C57—H57	119.2	C74—C73—H73	119.8
C59—C58—C57	117.61 (17)	C72—C73—H73	119.8
C59—C58—H58	121.2	C73—C74—C75	119.77 (16)
C57—C58—H58	121.2	C73—C74—H74	120.1
C58—C59—C54	121.20 (15)	C75—C74—H74	120.1
C58—C59—C51	128.65 (15)	C74—C75—C76	120.03 (16)
C54—C59—C51	110.15 (14)	C74—C75—H75	120.0
C16—C11—C12	120.72 (15)	C76—C75—H75	120.0
C16—C11—N1	119.94 (15)	C71—C76—C75	120.56 (16)
C12—C11—N1	119.30 (14)	C71—C76—H76	119.7
C11—C12—C13	119.45 (16)	C75—C76—H76	119.7

C7A—N1—N2—C3	0.73 (17)	C59—C54—C55—C56	−0.3 (2)
C11—N1—N2—C3	−174.20 (14)	C53—C54—C55—C56	−179.00 (16)
N1—N2—C3—C3A	0.22 (18)	C54—C55—C56—C57	0.8 (2)
N1—N2—C3—C31	−174.25 (14)	C55—C56—C57—C58	−0.5 (3)
N2—C3—C3A—C7A	−1.06 (18)	C56—C57—C58—C59	−0.3 (3)
C31—C3—C3A—C7A	172.86 (16)	C57—C58—C59—C54	0.8 (2)
N2—C3—C3A—C4	−175.40 (16)	C57—C58—C59—C51	−178.19 (16)
C31—C3—C3A—C4	−1.5 (3)	C55—C54—C59—C58	−0.6 (2)
C7A—C3A—C4—C52	−19.4 (2)	C53—C54—C59—C58	178.40 (15)
C3—C3A—C4—C52	154.13 (17)	C55—C54—C59—C51	178.61 (14)
C3A—C4—C52—C51	−80.74 (15)	C53—C54—C59—C51	−2.42 (18)
C3A—C4—C52—C53	166.70 (13)	O51—C51—C59—C58	3.1 (3)
C3A—C4—C52—C6	45.76 (17)	C52—C51—C59—C58	178.98 (16)
C51—C52—C6—N7	64.66 (17)	O51—C51—C59—C54	−176.01 (16)
C53—C52—C6—N7	−178.87 (13)	C52—C51—C59—C54	−0.13 (17)
C4—C52—C6—N7	−58.31 (17)	C7A—N1—C11—C16	−61.5 (2)
C52—C6—N7—C7A	37.90 (18)	N2—N1—C11—C16	112.29 (17)
C52—C6—N7—C77	−103.91 (16)	C7A—N1—C11—C12	120.54 (19)
N2—N1—C7A—C3A	−1.41 (18)	C16—C11—C12—C13	−0.6 (2)
C11—N1—C7A—C3A	172.71 (15)	N1—C11—C12—C13	177.32 (14)
N2—N1—C7A—N7	176.11 (14)	C11—C12—C13—C14	−0.1 (2)
C11—N1—C7A—N7	−9.8 (3)	C12—C13—C14—C15	0.9 (3)
C3—C3A—C7A—N1	1.45 (17)	C13—C14—C15—C16	−0.9 (3)
C4—C3A—C7A—N1	176.55 (14)	C12—C11—C16—C15	0.6 (2)
C3—C3A—C7A—N7	−176.01 (15)	N1—C11—C16—C15	−177.31 (14)
C4—C3A—C7A—N7	−0.9 (3)	C14—C15—C16—C11	0.1 (2)
C6—N7—C7A—N1	174.92 (15)	N2—C3—C31—C32	−135.75 (16)
C77—N7—C7A—N1	−43.5 (2)	C3A—C3—C31—C32	50.8 (2)
C6—N7—C7A—C3A	−8.1 (2)	N2—C3—C31—C33	104.85 (17)
C77—N7—C7A—C3A	133.50 (17)	N2—C3—C31—C34	−14.0 (2)
C53—C52—C51—O51	178.31 (15)	C3A—C3—C31—C34	172.58 (17)
C4—C52—C51—O51	61.8 (2)	C3A—C3—C31—C33	−68.6 (2)
C6—C52—C51—O51	−61.4 (2)	N2—N1—C11—C12	−65.69 (19)
C53—C52—C51—C59	2.47 (16)	C7A—N7—C77—C71	113.17 (15)

C4—C52—C51—C59	−114.06 (14)	C6—N7—C77—C71	−107.03 (15)
C6—C52—C51—C59	122.71 (14)	N7—C77—C71—C76	30.4 (2)
C51—C52—C53—O53	176.06 (15)	N7—C77—C71—C72	−149.38 (14)
C4—C52—C53—O53	−67.9 (2)	C76—C71—C72—C73	−1.7 (2)
C6—C52—C53—O53	52.6 (2)	C77—C71—C72—C73	178.07 (15)
C51—C52—C53—C54	−3.88 (16)	C71—C72—C73—C74	−0.2 (2)
C4—C52—C53—C54	112.20 (14)	C72—C73—C74—C75	1.7 (3)
C6—C52—C53—C54	−127.34 (14)	C73—C74—C75—C76	−1.2 (2)
O53—C53—C54—C59	−175.90 (16)	C72—C71—C76—C75	2.2 (2)
C52—C53—C54—C59	4.04 (18)	C77—C71—C76—C75	−177.57 (15)
O53—C53—C54—C55	3.0 (3)	C74—C75—C76—C71	−0.8 (2)
C52—C53—C54—C55	−177.10 (16)		

Hydrogen-bond geometry (Å, º)

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
C4—H4*B*···O51^{i}	0.99	2.32	3.145 (2)	141
C56—H56···N2^{ii}	0.95	2.53	3.431 (2)	158
C75—H75···O53^{iii}	0.95	2.46	3.342 (2)	154

Symmetry codes: (i) *x*, *y*−1, *z*; (ii) *x*, −*y*+1/2, *z*−1/2; (iii) −*x*+1, −*y*, −*z*+1.