

# Crystal structure of (1*S*,2*R*)-2-[(3*R*,4*S*)-3-methyl-4-phenyl-1,2,3,4-tetrahydroisoquinolin-2-yl]-1,2-diphenylethanol

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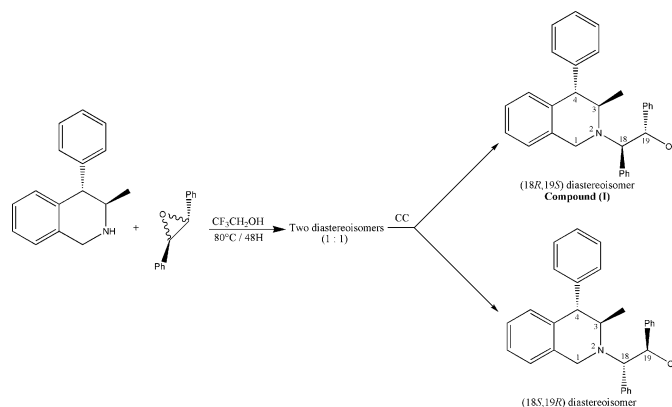
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The synthesis and crystal structure of the title compound, C<sub>30</sub>H<sub>29</sub>NO, are described. This compound is a member of the chiral dihydroisoquinoline-derived family, used as building blocks for functional materials and as source of chirality in asymmetric synthesis, and was isolated as one of two diastereomeric  $\beta$ -amino alcohols, the title molecule being found to be the (*S*,*R*) diastereoisomer. In the crystal, molecules are packed in a herringbone manner parallel to (103) and (10 $\bar{3}$ ) via weak C—H...O and C—H... $\pi$ (ring) interactions. Hirshfeld surface analysis showed that the surface contacts are predominantly H...H interactions (*ca* 75%). The crystal studied was refined as a two-component inversion twin.

## 1. Chemical context

$\beta$ -amino alcohols exhibit a broad spectrum of biological activities and are used as antibacterial and tuberculostatic agents (Yendapally & Lee, 2008). In particular, chiral  $\beta$ -amino alcohols are very important chiral molecules that are used as building blocks and structural motifs in pharmaceutically active molecules and natural products and which serve as the main sources of chirality in asymmetric synthesis (Lee *et al.*, 2003; Malkov *et al.*, 2007; Guo *et al.*, 2017).



Among this family of chiral amino-alcohols is the title compound, (I), which we prepared through the alkylation of tetrahydroisoquinoline by the opening of racemic *trans*-stilbene oxide reaction. Two diastereoisomers were obtained in a 1:1 ratio as determined by <sup>1</sup>H NMR analysis on the crude mixture. These diastereoisomers were separated by column chromatography. The title molecule was found to be the (*S*,*R*) diastereoisomer.

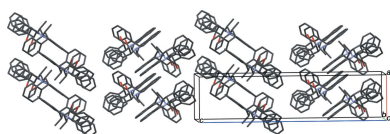


Table 1

Hydrogen-bond geometry (Å, °).

Cg2, Cg3, Cg4 and Cg5 are the centroids of the C5–C10, C12–C17, C20–C25, and C26–C31 rings, respectively.

<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>
O19–H0H···N2	0.86 (3)	2.18 (3)	2.737 (2)	123 (2)
C27–H27···O19	0.93	2.48	2.798 (3)	100
C21–H21···Cg3	0.93	3.14	3.930 (4)	144
C6–H6···O19 <sup>i</sup>	0.93	2.57	3.492 (3)	170
C14–H14···Cg5 <sup>ii</sup>	0.93	2.95	3.770 (4)	147
C16–H16···Cg4 <sup>iii</sup>	0.93	2.92	3.743 (3)	148
C31–H31···Cg2 <sup>iv</sup>	0.93	2.96	3.803 (3)	152

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

## 2. Structural commentary

The structure of (I) was confirmed using single crystal X-ray diffraction. The asymmetric unit of the orthorhombic unit cell comprises a single molecule, shown in Fig. 1. The tetrahydroisoquinoline unit is substituted by a methyl group in position 3, a phenyl substituent in position 4 and a  $\beta$ -alcohol substituent at the N atom. The heterocyclic ring exhibits a half-chair conformation, with atom C3 deviating by 0.706 (3) Å from the plane formed by atoms C1/N2/C4/C9/C10. The substituents in positions 3 and 4 of the heterocyclic ring are in axial positions. The molecular structure of (I) is stabilized by an intramolecular hydrogen bond between the hydroxy O19–H19 group and atom N2, and to a lesser extent, between the aromatic C21–H21 and the phenyl group in position 4 (Table 1). By reference to two unchanging chiral C18 and C19 atoms, the molecule was found to be the (18*R*,19*S*) diastereoisomer resulting from the reaction of tetrahydroisoquinoline and the (*S,S*) *trans*-stilbene oxide enantiomer.

This structure was confirmed through the means of usual 1D and 2D NMR experiments. NMR data show that the *trans* diequatorial arrangement of H3 and H4 is suggested by the coupling constant between H3 and H4 in <sup>1</sup>H NMR ( $J_{3,4}$

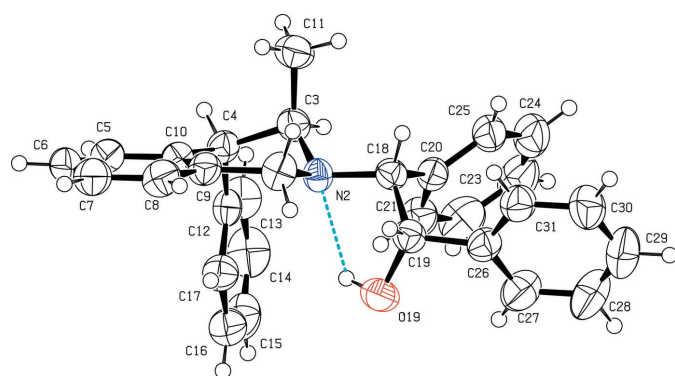


Figure 1

The molecular structure of (I), showing the atom-labelling scheme. Displacement ellipsoids are drawn at the 50% probability level and H atoms are represented as small spheres of arbitrary radius. The dashed cyan line indicates the intramolecular hydrogen bond between the hydroxy group and the secondary amine.

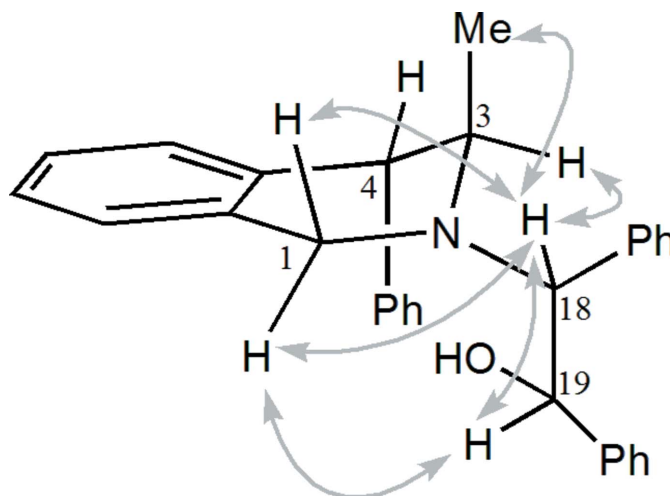


Figure 2

Selected NOESY correlations observed for compound (I).

~0 Hz), so the substituents C3-methyl and C4-phenyl are in an axial disposition. The absolute configurations of carbon atoms C18 and C19 were deduced from the NOESY maps to be *R* and *S*, respectively (Fig. 2).

## 3. Supramolecular features

In the crystal, molecules of (I) pack with no classical hydrogen bonds: the potential donor hydroxyl group is involved in an intramolecular interaction with the N atom. However, the oxygen atom acts as an acceptor in the short contact C6–H6···O19 ( $-x, \frac{1}{2} + y, \frac{1}{2} - z$ ) with an O19···H distance of 2.57 Å, which is of the same order of magnitude of the H···O van der Waals distance (2.60 Å), whereas C–H···O contacts are frequently reported with H···O separations shorter than 2.4 Å (Taylor & Kennard, 1982). The N atom does not play a role in the packing as it is buried inside the structure. Nevertheless, these directed C–H···O interactions make an

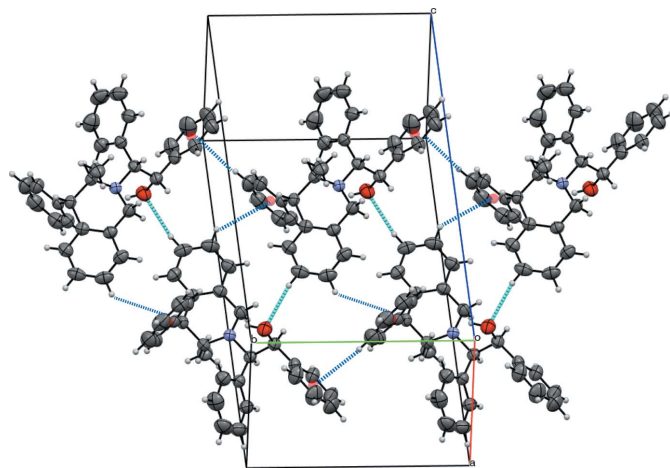
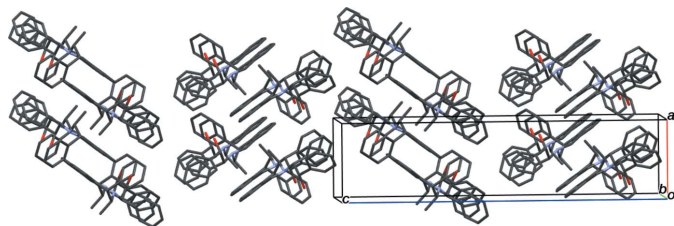


Figure 3

The ribbon structure of (I) formed along the *b*-axis direction via C–H···O interactions (cyan dashed lines) and C–H··· $\pi$  interactions (blue dashed lines). The red spheres indicate the centroids of the phenyl rings.



**Figure 4**  
Crystal packing of compound (I) viewed down the  $b$ -axis direction. Ribbons stack in a herringbone arrangement with the phenyl groups at the column interface.

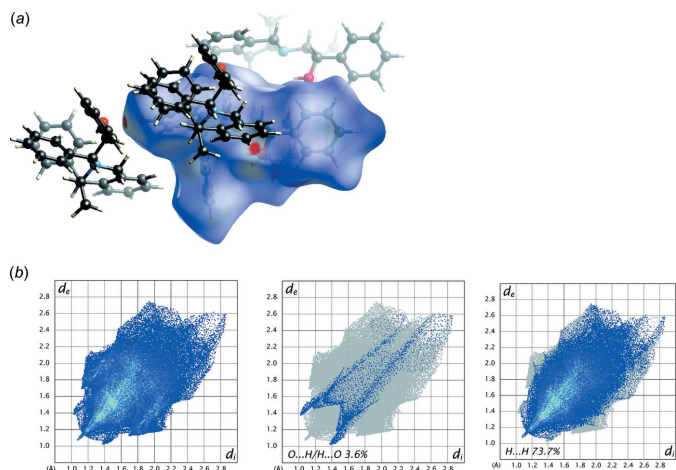
important contribution to the packing: zigzagging along the [010] direction, they pair molecules in ribbons, placing the isoquinoline moieties parallel to the (103) plane on both sides but without overlapping. The ribbon cohesion is reinforced by  $C-H \cdots \pi$  interactions involving the phenyl group in position 4 and those attached to the  $\beta$ -alcohol part and which flank the ribbon, as shown in Fig. 3. They stack in the [100] direction as columns arranged in a herringbone manner but avoiding  $\pi$ - $\pi$ -stacking (Fig. 4).

#### 4. Database survey

A search of the Cambridge Structural Database, CSD (Version 5.40; *ConQuest* 1.21; Groom *et al.*, 2016) found 495 structures of tetrahydroisoquinoline derivatives. Limiting the search to compounds with tri-substitutions on positions C3, C4 and the secondary amine N reduces the number of structures to seven: ADAGOC (Gzella *et al.*, 2006), JIPKEZ (White *et al.*, 2007), TIBPIE (Ben Ali *et al.*, 2007), VAHJOG (Davies *et al.*, 2016), XOSDUE (Gzella *et al.*, 2002), YEKKIK (Shi *et al.*, 2012) and ZIFSUE (Guo *et al.*, 2013). Except for the racemic VAHJOG, they all crystallize in the same  $P2_12_12_1$  space group. The structures of ZIFSUE, TIBPIE, VAHJOG, JIPKEZ and (I) superimpose well over the heterobicycle with the same conformation, unlike ADAGOC and XOSDUE which have a different half-chair configuration. The amino alcohol TIBPIE is obviously the closest related structure, differing in the N substitution of a cyclohexane carrying the hydroxyl group which is involved in the intramolecular hydrogen bond.

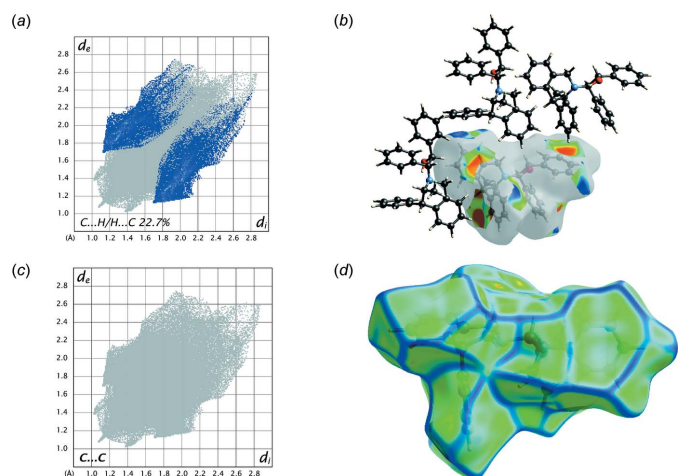
#### 5. Hirshfeld surface analysis

The intermolecular interactions were quantified using Hirshfeld surface analysis and the associated two-dimensional fingerprint plots using *CrystalExplorer17.5* (Turner *et al.*, 2017). The electrostatic potentials were calculated using *TONTO*, integrated within *CrystalExplorer*. The analysis of intermolecular interactions through the mapping of  $d_{\text{norm}}$  presented in Fig. 5 compares the contact distances  $d_i$  and  $d_e$  from the Hirshfeld surface to the nearest atom inside and outside, respectively, with their respective van der Waals radii. The blue, white and red colour conventions recognize the interatomic contacts as longer, at van der Waals separations and short interatomic contacts. The  $C-H \cdots O$  contacts are



**Figure 5**  
(a) View of the three-dimensional Hirshfeld surface mapped over  $d_{\text{norm}}$ , over the range  $-0.1345$  and  $+1.8231$  arbitrary units, (b) the full two-dimensional fingerprint plot for (I) and the two-dimensional fingerprint plots for the  $O \cdots H/H \cdots O$  interactions and the  $H \cdots H$  interactions

identified in the  $d_{\text{norm}}$ -mapped surface as two red spots showing the interaction between the neighbouring molecules (Fig. 5a). The overall two-dimensional fingerprint plot derived from the Hirshfeld surface is a useful method to summarize the frequency of each combination of  $d_e$  and  $d_i$  across the surface of the studied molecule, encompassing all intermolecular contacts (Fig. 5b). The delineated fingerprint plots (Fig. 5b and 6a,c) focus on specific interactions, providing information about the major and minor percentage contribution of interatomic contacts in the compound. The  $H \cdots H$  interactions account for the three quarters of the total (73.7%) with an evident sting at about  $d_i = d_e = 1.1 \text{ \AA}$  (Fig. 5b). The  $C \cdots H/H \cdots C$  plot, which refers to the  $C-H \cdots \pi$  interactions previously described (22.7%), shows two broad symmetrical wings at about  $d_i + d_e = 2.8 \text{ \AA}$  (Fig. 6a). These interactions are



**Figure 6**  
(a) The Hirshfeld surface mapped over the shape-index property, (b) the two-dimensional fingerprint plot for the  $H \cdots C/C \cdots H$  interactions, (c) the Hirshfeld surface mapped over curviness and (d) the two-dimensional fingerprint plot for the  $C \cdots C$  interactions in the title compound.

**Table 2**  
Experimental details.

Crystal data	
Chemical formula	C <sub>30</sub> H <sub>29</sub> NO
<i>M<sub>r</sub></i>	419.54
Crystal system, space group	Orthorhombic, <i>P</i> 2 <sub>1</sub> 2 <sub>1</sub> 2 <sub>1</sub>
Temperature (K)	293
<i>a</i> , <i>b</i> , <i>c</i> (Å)	7.3009 (8), 11.0552 (11), 30.006 (3)
<i>V</i> (Å <sup>3</sup> )	2421.8 (4)
<i>Z</i>	4
Radiation type	Mo <i>K</i> α
<i>μ</i> (mm <sup>-1</sup> )	0.07
Crystal size (mm)	0.59 × 0.45 × 0.35
Data collection	
Diffractometer	Nonius KappaCCD area detector
Absorption correction	Multi-scan ( <i>CrysAlis PRO</i> ; Rigaku OD, 2019)
<i>T<sub>min</sub></i> , <i>T<sub>max</sub></i>	0.844, 1.000
No. of measured, independent and observed [ <i>I</i> > 2σ( <i>I</i> )] reflections	21751, 4427, 3948
<i>R<sub>int</sub></i>	0.027
(sin θ/λ) <sub>max</sub> (Å <sup>-1</sup> )	0.602
Refinement	
<i>R</i> [ <i>F</i> <sup>2</sup> > 2σ( <i>F</i> <sup>2</sup> )], <i>wR</i> ( <i>F</i> <sup>2</sup> ), <i>S</i>	0.038, 0.083, 1.07
No. of reflections	4425
No. of parameters	295
H-atom treatment	H atoms treated by a mixture of independent and constrained refinement
Δρ <sub>max</sub> , Δρ <sub>min</sub> (e Å <sup>-3</sup> )	0.11, -0.11
Absolute structure	Refined as an inversion twin.

Computer programs: *DENZO* (Otwinowski & Minor, 1997); *COLLECT* (Hooft, 1998), *CrysAlis PRO* (Rigaku OD, 2019), *SHELXT2014/5* (Sheldrick, 2015a), *SHELXL2018/3* (Sheldrick, 2015b).

observed as red regions on the shape-index surface (Fig. 6*b*). The absence of C···C contacts, highlighted by the Hirshfeld surface with high curvedness delineated by dark-blue edges, confirms that no π–π stacking interactions take place in the crystal packing (Fig. 6*c,d*). The third marginal contribution is O···H/H···O (3.6%) with a pair of sharp spikes at about *d<sub>i</sub>* + *d<sub>e</sub>* = 2.4 Å, symmetrically disposed with respect to the diagonal, indicating the presence of intermolecular C–H···O interactions, which play a role in ordering the molecules inside the crystal.

## 6. Synthesis and crystallization

The title β-amino alcohol was obtained by mixing racemic *trans*-stilbene oxide (5.1g, 26mmol) with (3*R*,4*S*)-3-methyl-4-phenyl-1,2,3,4-tetrahydroisoquinoline (3g, 13mmol), which was prepared according to the method of Bohé *et al.* (1999).

The mixture was heated at 353.15 K for 48 h in CF<sub>3</sub>CH<sub>2</sub>OH (65 ml), the reaction being monitored by TLC. Two diastereoisomers were obtained in a 1:1 ratio. These diastereoisomers were separated by column chromatography. Only the title compound (white solid) was successfully recrystallized. Crystals were grown by placing this diastereoisomer in a minimum

amount of hot heptane. [α]<sub>D</sub><sup>25</sup> = -23.6 (*c* 1, CHCl<sub>3</sub>), m.p. 425 K.

## 7. Refinement

Crystal data, data collection and structure refinement details are summarized in Table 2. H atoms were placed in calculated positions (C–H = 0.93–0.98 Å) and refined as riding with *U*<sub>iso</sub>(H) = 1.2*U*<sub>eq</sub>(C). The crystal studied was refined as a two-component inversion twin.

## Acknowledgements

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## supporting information

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## Crystal structure of (1*S*,2*R*)-2-[(3*R*,4*S*)-3-methyl-4-phenyl-1,2,3,4-tetrahydroisoquinolin-2-yl]-1,2-diphenylethanol

Karim Ben Ali and Pascal Retailleau

### Computing details

Data collection: *DENZO* (Otwinowski & Minor, 1997); *COLLECT* (Hooft, 1998); cell refinement: *CrysAlis PRO* (Rigaku OD, 2019); data reduction: *CrysAlis PRO* (Rigaku OD, 2019); program(s) used to solve structure: *SHELXT2014/5* (Sheldrick, 2015a); program(s) used to refine structure: *SHELXL2018/3* (Sheldrick, 2015b); software used to prepare material for publication: *SHELXL2018/3* (Sheldrick, 2015b).

### (1*S*,2*R*)-2-[(3*R*,4*S*)-3-Methyl-4-phenyl-1,2,3,4-tetrahydroisoquinolin-2-yl]-1,2-diphenylethanol

#### Crystal data

C<sub>30</sub>H<sub>29</sub>NO

*M<sub>r</sub>* = 419.54

Orthorhombic, *P*2<sub>1</sub>2<sub>1</sub>2<sub>1</sub>

*a* = 7.3009 (8) Å

*b* = 11.0552 (11) Å

*c* = 30.006 (3) Å

*V* = 2421.8 (4) Å<sup>3</sup>

*Z* = 4

*F*(000) = 896

*D<sub>x</sub>* = 1.151 Mg m<sup>-3</sup>

Mo *K*α radiation, λ = 0.71073 Å

Cell parameters from 6302 reflections

θ = 2.0–24.2°

μ = 0.07 mm<sup>-1</sup>

*T* = 293 K

Prism, colorless

0.59 × 0.45 × 0.35 mm

#### Data collection

Nonius KappaCCD area detector  
diffractometer

Radiation source: 1.5kW sealed tube

Graphite monochromator

ω and φ scans

Absorption correction: multi-scan  
(*CrysAlisPro*; Rigaku OD, 2019)

*T<sub>min</sub>* = 0.844, *T<sub>max</sub>* = 1.000

21751 measured reflections

4427 independent reflections

3948 reflections with *I* > 2σ(*I*)

*R<sub>int</sub>* = 0.027

θ<sub>max</sub> = 25.4°, θ<sub>min</sub> = 2.7°

*h* = −8→8

*k* = −13→13

*l* = −36→36

#### Refinement

Refinement on *F*<sup>2</sup>

Least-squares matrix: full

*R*[*F*<sup>2</sup> > 2σ(*F*<sup>2</sup>)] = 0.038

*wR*(*F*<sup>2</sup>) = 0.083

*S* = 1.07

4425 reflections

295 parameters

0 restraints

Primary atom site location: dual

Secondary atom site location: difference Fourier  
map

Hydrogen site location: mixed

H atoms treated by a mixture of independent  
and constrained refinement

*w* = 1/[σ<sup>2</sup>(*F<sub>o</sub>*<sup>2</sup>) + (0.0304*P*)<sup>2</sup> + 0.3321*P*]

where *P* = (*F<sub>o</sub>*<sup>2</sup> + 2*F<sub>c</sub>*<sup>2</sup>)/3

(Δ/σ)<sub>max</sub> < 0.001

Δρ<sub>max</sub> = 0.11 e Å<sup>-3</sup>

Δρ<sub>min</sub> = −0.11 e Å<sup>-3</sup>

Extinction correction: SHELXL-2018/3

(Sheldrick 2015b),

*F<sub>c</sub>*\* = *kF<sub>c</sub>*[1 + 0.001 × *F<sub>c</sub>*<sup>2</sup>λ<sup>3</sup>/sin(2θ)]<sup>-1/4</sup>

Extinction coefficient: 0.0139 (11)

Absolute structure: Refined as an inversion  
twin.*Special details*

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

**Refinement.** Refined as a 2-component inversion twin.

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

	<i>x</i>	<i>y</i>	<i>z</i>	$U_{\text{iso}}^*/U_{\text{eq}}$
C1	0.3286 (4)	−0.0015 (2)	0.21766 (7)	0.0459 (6)
H1A	0.428447	−0.038350	0.234113	0.053*
H1B	0.243483	−0.065133	0.209524	0.053*
N2	0.4019 (2)	0.05352 (14)	0.17689 (6)	0.0355 (4)
C3	0.5027 (3)	0.16552 (19)	0.18741 (7)	0.0400 (5)
H3	0.556815	0.195001	0.159563	0.046*
C4	0.3616 (3)	0.26023 (18)	0.20271 (7)	0.0379 (5)
H4	0.430488	0.329448	0.214349	0.044*
C5	0.1547 (3)	0.2891 (2)	0.26931 (7)	0.0471 (6)
H5	0.162708	0.372208	0.264993	0.054*
C6	0.0507 (3)	0.2447 (3)	0.30407 (8)	0.0553 (7)
H6	−0.009196	0.297836	0.323159	0.064*
C7	0.0357 (4)	0.1222 (3)	0.31050 (8)	0.0576 (7)
H7	−0.035474	0.092057	0.333677	0.066*
C8	0.1265 (3)	0.0443 (2)	0.28246 (8)	0.0518 (6)
H8	0.116921	−0.038604	0.287084	0.060*
C9	0.2328 (3)	0.0871 (2)	0.24723 (7)	0.0405 (5)
C10	0.2479 (3)	0.2114 (2)	0.24055 (7)	0.0383 (5)
C11	0.6589 (3)	0.1502 (2)	0.22101 (9)	0.0567 (7)
H11A	0.726198	0.224575	0.223262	0.068*
H11B	0.739191	0.086877	0.211187	0.068*
H11C	0.609065	0.129700	0.249634	0.068*
C12	0.2492 (3)	0.30571 (18)	0.16372 (7)	0.0400 (5)
C13	0.3195 (4)	0.3956 (2)	0.13673 (8)	0.0570 (7)
H13	0.431991	0.430129	0.143737	0.066*
C14	0.2254 (5)	0.4350 (3)	0.09946 (9)	0.0707 (9)
H14	0.275393	0.495164	0.081543	0.081*
C15	0.0593 (5)	0.3858 (3)	0.08888 (9)	0.0699 (9)
H15	−0.003927	0.412441	0.063832	0.080*
C16	−0.0138 (4)	0.2967 (3)	0.11542 (9)	0.0623 (7)
H16	−0.126869	0.262995	0.108399	0.072*
C17	0.0809 (3)	0.2573 (2)	0.15257 (8)	0.0488 (6)
H17	0.030362	0.197119	0.170385	0.056*
C18	0.5032 (3)	−0.03477 (18)	0.14947 (7)	0.0367 (5)
H18	0.600714	−0.070012	0.167776	0.042*
C19	0.3684 (3)	−0.13740 (19)	0.13610 (8)	0.0416 (5)

H19	0.338016	-0.182861	0.163143	0.048*
O19	0.2046 (2)	-0.08765 (16)	0.11933 (6)	0.0560 (5)
HOH	0.198 (4)	-0.016 (3)	0.1307 (9)	0.067*
C20	0.5896 (3)	0.02111 (19)	0.10855 (7)	0.0394 (5)
C21	0.4942 (4)	0.0997 (2)	0.08094 (8)	0.0553 (7)
H21	0.377223	0.125320	0.088719	0.064*
C22	0.5742 (5)	0.1398 (3)	0.04165 (9)	0.0730 (8)
H22	0.510686	0.192712	0.023154	0.084*
C23	0.7467 (5)	0.1018 (3)	0.02999 (10)	0.0778 (10)
H23	0.798359	0.127746	0.003312	0.089*
C24	0.8428 (4)	0.0263 (3)	0.05729 (10)	0.0685 (8)
H24	0.960600	0.001927	0.049589	0.079*
C25	0.7644 (3)	-0.0137 (2)	0.09627 (8)	0.0502 (6)
H25	0.830335	-0.065258	0.114775	0.058*
C26	0.4523 (3)	-0.22470 (19)	0.10333 (7)	0.0434 (5)
C27	0.4150 (4)	-0.2197 (2)	0.05843 (9)	0.0648 (8)
H27	0.330932	-0.163529	0.047712	0.075*
C28	0.5013 (5)	-0.2974 (3)	0.02915 (9)	0.0816 (10)
H28	0.474735	-0.293390	-0.001130	0.094*
C29	0.6252 (5)	-0.3798 (3)	0.04431 (11)	0.0786 (9)
H29	0.684240	-0.431168	0.024431	0.090*
C30	0.6622 (4)	-0.3865 (2)	0.08887 (11)	0.0693 (8)
H30	0.746120	-0.442975	0.099374	0.080*
C31	0.5752 (4)	-0.3097 (2)	0.11835 (9)	0.0533 (6)
H31	0.599963	-0.315488	0.148673	0.061*

Atomic displacement parameters ( $\text{\AA}^2$ )

	$U^{11}$	$U^{22}$	$U^{33}$	$U^{12}$	$U^{13}$	$U^{23}$
C1	0.0562 (15)	0.0388 (12)	0.0426 (13)	-0.0048 (11)	0.0068 (11)	0.0038 (10)
N2	0.0361 (10)	0.0336 (8)	0.0369 (9)	-0.0008 (8)	0.0058 (8)	0.0001 (7)
C3	0.0384 (12)	0.0391 (11)	0.0426 (12)	-0.0037 (10)	0.0039 (10)	-0.0003 (9)
C4	0.0419 (13)	0.0322 (10)	0.0395 (12)	-0.0059 (10)	0.0006 (10)	-0.0037 (9)
C5	0.0441 (13)	0.0536 (14)	0.0437 (13)	0.0038 (11)	-0.0043 (11)	-0.0078 (11)
C6	0.0421 (14)	0.0826 (19)	0.0413 (13)	0.0074 (14)	0.0005 (11)	-0.0127 (13)
C7	0.0482 (15)	0.0850 (19)	0.0395 (13)	-0.0076 (14)	0.0064 (12)	0.0015 (13)
C8	0.0552 (15)	0.0596 (14)	0.0406 (13)	-0.0126 (13)	0.0031 (12)	0.0036 (11)
C9	0.0423 (13)	0.0472 (12)	0.0320 (11)	-0.0030 (11)	0.0010 (10)	0.0002 (9)
C10	0.0364 (12)	0.0442 (12)	0.0342 (11)	0.0002 (10)	-0.0019 (10)	-0.0030 (9)
C11	0.0433 (14)	0.0589 (15)	0.0680 (17)	-0.0014 (12)	-0.0081 (13)	-0.0064 (13)
C12	0.0494 (14)	0.0319 (10)	0.0387 (12)	0.0043 (11)	0.0068 (10)	-0.0036 (9)
C13	0.0653 (17)	0.0470 (13)	0.0586 (16)	-0.0024 (13)	0.0074 (14)	0.0085 (12)
C14	0.093 (2)	0.0637 (17)	0.0558 (17)	0.0100 (18)	0.0123 (17)	0.0203 (14)
C15	0.091 (2)	0.0766 (19)	0.0426 (15)	0.0331 (19)	-0.0020 (15)	0.0037 (14)
C16	0.0589 (16)	0.0737 (17)	0.0544 (16)	0.0111 (15)	-0.0078 (14)	-0.0108 (14)
C17	0.0526 (15)	0.0485 (13)	0.0452 (13)	0.0024 (12)	-0.0009 (11)	0.0013 (11)
C18	0.0336 (11)	0.0391 (11)	0.0375 (11)	0.0034 (10)	-0.0016 (10)	0.0010 (9)
C19	0.0396 (12)	0.0390 (11)	0.0463 (13)	0.0003 (10)	-0.0006 (10)	-0.0009 (10)

O19	0.0414 (9)	0.0551 (10)	0.0715 (12)	0.0037 (8)	-0.0092 (9)	-0.0069 (9)
C20	0.0415 (13)	0.0403 (11)	0.0364 (12)	-0.0010 (10)	0.0015 (10)	-0.0042 (9)
C21	0.0617 (17)	0.0595 (14)	0.0448 (14)	0.0047 (14)	0.0015 (12)	0.0049 (12)
C22	0.097 (2)	0.0752 (19)	0.0467 (15)	-0.0039 (19)	-0.0026 (17)	0.0129 (14)
C23	0.095 (3)	0.091 (2)	0.0469 (16)	-0.024 (2)	0.0244 (17)	-0.0042 (16)
C24	0.0622 (18)	0.082 (2)	0.0616 (18)	-0.0138 (17)	0.0209 (15)	-0.0176 (16)
C25	0.0452 (14)	0.0532 (14)	0.0522 (15)	-0.0035 (12)	0.0073 (11)	-0.0090 (11)
C26	0.0456 (14)	0.0384 (11)	0.0461 (13)	-0.0055 (11)	-0.0012 (11)	-0.0046 (10)
C27	0.086 (2)	0.0577 (15)	0.0507 (16)	0.0103 (16)	-0.0131 (15)	-0.0060 (12)
C28	0.122 (3)	0.076 (2)	0.0477 (16)	0.007 (2)	-0.0009 (18)	-0.0158 (15)
C29	0.095 (2)	0.0622 (18)	0.078 (2)	0.0071 (19)	0.0216 (19)	-0.0239 (16)
C30	0.069 (2)	0.0568 (16)	0.082 (2)	0.0137 (15)	0.0011 (17)	-0.0151 (15)
C31	0.0581 (16)	0.0453 (12)	0.0563 (15)	0.0058 (12)	-0.0049 (13)	-0.0066 (11)

*Geometric parameters (Å, °)*

C1—N2	1.467 (3)	C16—C17	1.382 (3)
C1—C9	1.496 (3)	C16—H16	0.9300
C1—H1A	0.9700	C17—H17	0.9300
C1—H1B	0.9700	C18—C20	1.512 (3)
N2—C3	1.475 (3)	C18—C19	1.555 (3)
N2—C18	1.475 (3)	C18—H18	0.9800
C3—C11	1.531 (3)	C19—O19	1.409 (3)
C3—C4	1.539 (3)	C19—C26	1.508 (3)
C3—H3	0.9800	C19—H19	0.9800
C4—C10	1.507 (3)	O19—HOH	0.86 (3)
C4—C12	1.515 (3)	C20—C25	1.383 (3)
C4—H4	0.9800	C20—C21	1.388 (3)
C5—C6	1.380 (3)	C21—C22	1.389 (4)
C5—C10	1.395 (3)	C21—H21	0.9300
C5—H5	0.9300	C22—C23	1.373 (4)
C6—C7	1.372 (4)	C22—H22	0.9300
C6—H6	0.9300	C23—C24	1.364 (4)
C7—C8	1.374 (4)	C23—H23	0.9300
C7—H7	0.9300	C24—C25	1.375 (4)
C8—C9	1.394 (3)	C24—H24	0.9300
C8—H8	0.9300	C25—H25	0.9300
C9—C10	1.393 (3)	C26—C31	1.375 (3)
C11—H11A	0.9600	C26—C27	1.376 (3)
C11—H11B	0.9600	C27—C28	1.381 (4)
C11—H11C	0.9600	C27—H27	0.9300
C12—C13	1.380 (3)	C28—C29	1.362 (4)
C12—C17	1.381 (3)	C28—H28	0.9300
C13—C14	1.383 (4)	C29—C30	1.366 (4)
C13—H13	0.9300	C29—H29	0.9300
C14—C15	1.367 (4)	C30—C31	1.381 (4)
C14—H14	0.9300	C30—H30	0.9300
C15—C16	1.374 (4)	C31—H31	0.9300



C15—H15	0.9300		
N2—C1—C9	113.18 (17)	C16—C15—H15	120.2
N2—C1—H1A	108.9	C15—C16—C17	119.9 (3)
C9—C1—H1A	108.9	C15—C16—H16	120.0
N2—C1—H1B	108.9	C17—C16—H16	120.0
C9—C1—H1B	108.9	C12—C17—C16	121.2 (2)
H1A—C1—H1B	107.8	C12—C17—H17	119.4
C1—N2—C3	110.59 (16)	C16—C17—H17	119.4
C1—N2—C18	111.93 (16)	N2—C18—C20	113.06 (16)
C3—N2—C18	115.13 (16)	N2—C18—C19	108.02 (16)
N2—C3—C11	114.83 (18)	C20—C18—C19	110.66 (17)
N2—C3—C4	107.52 (17)	N2—C18—H18	108.3
C11—C3—C4	112.15 (18)	C20—C18—H18	108.3
N2—C3—H3	107.3	C19—C18—H18	108.3
C11—C3—H3	107.3	O19—C19—C26	111.22 (19)
C4—C3—H3	107.3	O19—C19—C18	110.15 (17)
C10—C4—C12	113.71 (18)	C26—C19—C18	112.22 (18)
C10—C4—C3	110.49 (17)	O19—C19—H19	107.7
C12—C4—C3	110.99 (17)	C26—C19—H19	107.7
C10—C4—H4	107.1	C18—C19—H19	107.7
C12—C4—H4	107.1	C19—O19—HOH	105 (2)
C3—C4—H4	107.1	C25—C20—C21	118.6 (2)
C6—C5—C10	121.1 (2)	C25—C20—C18	119.2 (2)
C6—C5—H5	119.4	C21—C20—C18	122.1 (2)
C10—C5—H5	119.4	C20—C21—C22	119.7 (3)
C7—C6—C5	120.1 (2)	C20—C21—H21	120.1
C7—C6—H6	120.0	C22—C21—H21	120.1
C5—C6—H6	120.0	C23—C22—C21	120.3 (3)
C6—C7—C8	119.6 (2)	C23—C22—H22	119.9
C6—C7—H7	120.2	C21—C22—H22	119.9
C8—C7—H7	120.2	C24—C23—C22	120.4 (3)
C7—C8—C9	121.3 (2)	C24—C23—H23	119.8
C7—C8—H8	119.3	C22—C23—H23	119.8
C9—C8—H8	119.3	C23—C24—C25	119.5 (3)
C10—C9—C8	119.2 (2)	C23—C24—H24	120.2
C10—C9—C1	121.60 (19)	C25—C24—H24	120.2
C8—C9—C1	119.2 (2)	C24—C25—C20	121.4 (3)
C9—C10—C5	118.7 (2)	C24—C25—H25	119.3
C9—C10—C4	120.36 (19)	C20—C25—H25	119.3
C5—C10—C4	121.0 (2)	C31—C26—C27	118.6 (2)
C3—C11—H11A	109.5	C31—C26—C19	119.3 (2)
C3—C11—H11B	109.5	C27—C26—C19	122.2 (2)
H11A—C11—H11B	109.5	C26—C27—C28	120.5 (3)
C3—C11—H11C	109.5	C26—C27—H27	119.8
H11A—C11—H11C	109.5	C28—C27—H27	119.8
H11B—C11—H11C	109.5	C29—C28—C27	120.4 (3)
C13—C12—C17	117.9 (2)	C29—C28—H28	119.8

C13—C12—C4	119.3 (2)	C27—C28—H28	119.8
C17—C12—C4	122.7 (2)	C28—C29—C30	119.7 (3)
C12—C13—C14	121.1 (3)	C28—C29—H29	120.2
C12—C13—H13	119.5	C30—C29—H29	120.2
C14—C13—H13	119.5	C29—C30—C31	120.2 (3)
C15—C14—C13	120.2 (3)	C29—C30—H30	119.9
C15—C14—H14	119.9	C31—C30—H30	119.9
C13—C14—H14	119.9	C26—C31—C30	120.7 (3)
C14—C15—C16	119.7 (3)	C26—C31—H31	119.7
C14—C15—H15	120.2	C30—C31—H31	119.7
C9—C1—N2—C3	47.4 (2)	C13—C12—C17—C16	0.5 (3)
C9—C1—N2—C18	177.26 (19)	C4—C12—C17—C16	-176.6 (2)
C1—N2—C3—C11	56.3 (2)	C15—C16—C17—C12	-0.1 (4)
C18—N2—C3—C11	-71.7 (2)	C1—N2—C18—C20	-176.66 (18)
C1—N2—C3—C4	-69.2 (2)	C3—N2—C18—C20	-49.2 (2)
C18—N2—C3—C4	162.68 (16)	C1—N2—C18—C19	60.5 (2)
N2—C3—C4—C10	54.4 (2)	C3—N2—C18—C19	-172.04 (17)
C11—C3—C4—C10	-72.8 (2)	N2—C18—C19—O19	48.5 (2)
N2—C3—C4—C12	-72.7 (2)	C20—C18—C19—O19	-75.7 (2)
C11—C3—C4—C12	160.16 (19)	N2—C18—C19—C26	173.03 (17)
C10—C5—C6—C7	-0.8 (4)	C20—C18—C19—C26	48.8 (2)
C5—C6—C7—C8	0.8 (4)	N2—C18—C20—C25	138.8 (2)
C6—C7—C8—C9	-0.6 (4)	C19—C18—C20—C25	-99.9 (2)
C7—C8—C9—C10	0.4 (4)	N2—C18—C20—C21	-46.1 (3)
C7—C8—C9—C1	-179.9 (2)	C19—C18—C20—C21	75.2 (2)
N2—C1—C9—C10	-12.7 (3)	C25—C20—C21—C22	1.0 (4)
N2—C1—C9—C8	167.7 (2)	C18—C20—C21—C22	-174.2 (2)
C8—C9—C10—C5	-0.4 (3)	C20—C21—C22—C23	0.2 (4)
C1—C9—C10—C5	179.9 (2)	C21—C22—C23—C24	-1.4 (5)
C8—C9—C10—C4	-179.9 (2)	C22—C23—C24—C25	1.3 (4)
C1—C9—C10—C4	0.4 (3)	C23—C24—C25—C20	-0.1 (4)
C6—C5—C10—C9	0.6 (3)	C21—C20—C25—C24	-1.1 (3)
C6—C5—C10—C4	-179.8 (2)	C18—C20—C25—C24	174.2 (2)
C12—C4—C10—C9	104.1 (2)	O19—C19—C26—C31	-159.3 (2)
C3—C4—C10—C9	-21.5 (3)	C18—C19—C26—C31	76.8 (3)
C12—C4—C10—C5	-75.4 (2)	O19—C19—C26—C27	23.1 (3)
C3—C4—C10—C5	159.02 (19)	C18—C19—C26—C27	-100.8 (3)
C10—C4—C12—C13	152.5 (2)	C31—C26—C27—C28	-0.9 (4)
C3—C4—C12—C13	-82.2 (2)	C19—C26—C27—C28	176.8 (3)
C10—C4—C12—C17	-30.5 (3)	C26—C27—C28—C29	-0.2 (5)
C3—C4—C12—C17	94.8 (2)	C27—C28—C29—C30	0.9 (5)
C17—C12—C13—C14	-0.7 (4)	C28—C29—C30—C31	-0.4 (5)
C4—C12—C13—C14	176.5 (2)	C27—C26—C31—C30	1.4 (4)
C12—C13—C14—C15	0.5 (4)	C19—C26—C31—C30	-176.4 (2)
C13—C14—C15—C16	-0.1 (4)	C29—C30—C31—C26	-0.8 (4)
C14—C15—C16—C17	-0.1 (4)		

*Hydrogen-bond geometry (Å, °)*

*Cg*2, *Cg*3, *Cg*4 and *Cg*5 are the centroids of the C5–C10, C12–C17, C20–C25, and C26–C31 rings, respectively.

<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>
O19—HOH···N2	0.86 (3)	2.18 (3)	2.737 (2)	123 (2)
C27—H27···O19	0.93	2.48	2.798 (3)	100
C21—H21··· <i>Cg</i> 3	0.93	3.14	3.930 (4)	144
C6—H6···O19 <sup>i</sup>	0.93	2.57	3.492 (3)	170
C14—H14··· <i>Cg</i> 5 <sup>ii</sup>	0.93	2.95	3.770 (4)	147
C16—H16··· <i>Cg</i> 4 <sup>iii</sup>	0.93	2.92	3.743 (3)	148
C31—H31··· <i>Cg</i> 2 <sup>iv</sup>	0.93	2.96	3.803 (3)	152

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