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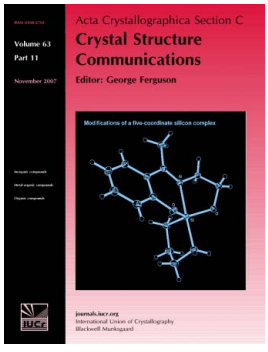

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Hobartine: a tetracyclic indole alkaloid extracted from *Aristotelia chilensis* (maqui)

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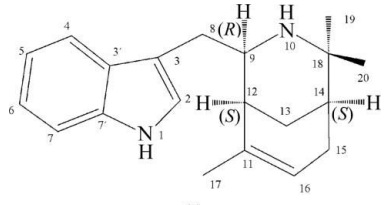
The natural compound hobartine {systematic name: (1*R*)-3-[(1*S*,5*S*)-(4,4,8-trimethylbicyclo[3.3.1]non-7-en-2-yl)methyl]-2,3-dihydro-1*H*-indole}, $C_{20}H_{26}N_2$, (I), is an indole alkaloid isolated from *Aristotelia chilensis* as part of a study of secondary metabolites from Chilean flora. The colourless compound has a tetracyclic structure closely related to the strongly coloured polymorphic structures discussed in Paz *et al.* [*Acta Cryst.* (2013), C**69**, 1509–1512] and Watson *et al.* [*Acta Cryst.* (1989), C**45**, 1322–1324]. The main differences reside in the absence of a keto group in (I) compared with the previous structures, as well as an *endo* double bond in (I) contrasting with the *exo* double bond found in the previous structures. The supramolecular structure of (I) in strongly related to the twofold screw axis, around which isolated chains build up, internally linked by an N—H···N hydrogen bond which is the only significant intermolecular interaction present in the structure.

Keywords: crystal structure; alkaloid; *Aristotelia chilensis*; hobartine; natural products; Chilean flora metabolites; tetracyclic compound; maqui.

1. Introduction

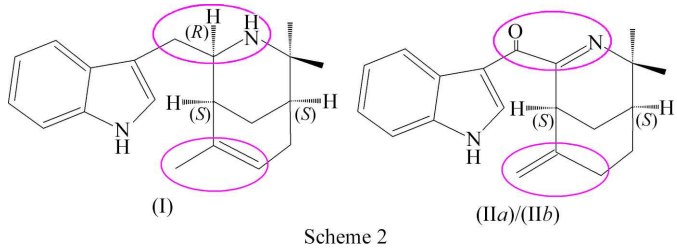
Aristotelia chilensis ([Molina] Stuntz, Elaecarpaceae) is a native Chilean tree commonly known as maqui. It is used particularly as an anti-inflammatory agent against kidney pains, stomach ulcers, diverse digestive ailments (tumors and ulcers), fever and healing injuries (Bhakuni *et al.*, 1976). The fruit is a black berry well known for its high concentration of phenolic compounds. Maqui berries are a healthy fruit with high ORAC (Oxygen Radical Absorbance Capacity) antioxidant properties (Céspedes *et al.*, 2010). Indole alkaloids have been identified from extracts of maqui, examples being aristoteline, aristotelone (Bhakuni *et al.*, 1976), aristotelinine and aristone (Bittner *et al.*, 1978). Continuing our study of naturally occurring products from Chilean flora, we have isolated from *Aristotelia chilensis* the indole alkaloid hobartine, (I).



(I)
Scheme 1

Even if the presence of hobartine in *Aristotelia chilensis* had not been reported, the compound was known to be present in *Aristotelia peduncularis* (Hesse, 1979), and a number of syntheses of the alkaloid have been performed since its discovery (see, for example, Stevens & Kenney, 1983; Darbre *et al.*, 1984; Gribble & Barden, 1985; Galli *et al.*, 2002). All these latter reports gave the absolute configuration shown in Scheme 1, *viz.* 9*R*,12*S*,14*S*.

In addition, the compound is closely related to 8-oxo-9-dehydromakomakine, (II), and of a similar origin (*Aristotelia chilensis)*. Compound (II) was obtained previously in two polymorphic forms with a remarkable colour difference, *viz.* crystals of (II*a*) (Paz *et al.*, 2013) were deep red and those of (II*b*) (Watson *et al.*, 1989) were pale yellow (Scheme 2).



(I) (II*a*)/(II*b*)
Scheme 2

In order to ascertain unambiguously the relative position of the double bonds in the structure, as well as to confirm the relative configurations of the asymmetric centres, we analyze herein the thus far unreported crystal structure of hobartine, (I). We shall also discuss similarities and differences with polymorphs (II*a*) and (II*b*).

2. Experimental

2.1. Extraction, purification and crystallization

A. chilensis (maqui) was collected in Concepción, VIII Region of Chile (36° 50′ 01.51″ S 73° 01′ 53.75″ W) in December 2012. Leaves (20 kg) were dried at 313 K, powdered and macerated for 7 d in water acidified with HCl to pH 3. The water layer (50 l) was then separated by filtration, made basic with NaOH to pH 10 and extracted with ethyl acetate (3 × 20 l). The organic layer was concentrated *in vacuo* to obtain a crude alkaloid fraction. The alkaloid extract was chromatographed on aluminium oxide and eluted with a hexane, hexane–ethyl acetate (1:1 *v*/*v*), ethyl acetate and ethyl

Table 1
Experimental details.

Crystal data	
Chemical formula	$C_{20}H_{26}N_2$
M_r	294.43
Crystal system, space group	Monoclinic, $P2_1$
Temperature (K)	294
a, b, c (Å)	9.0358 (5), 9.0395 (4), 11.4988 (7)
β (°)	111.298 (6)
V (Å^3)	875.07 (9)
Z	2
Radiation type	Mo $K\alpha$
μ (mm^{-1})	0.07
Crystal size (mm)	0.30 × 0.18 × 0.18
Data collection	
Diffractometer	Oxford Diffraction Gemini CCD S Ultra diffractometer
Absorption correction	Multi-scan (*CrysAlis PRO*; Oxford Diffraction, 2009)
T_{min}, T_{max}	0.97, 0.99
No. of measured, independent and observed [$I > 2\sigma(I)$] reflections	16112, 3074, 2311
R_{int}	0.075
(sin $\theta/\lambda)_{max}$ (Å^{-1})	0.595
Refinement	
$R[F^2 > 2\sigma(F^2)]$, $wR(F^2)$, S	0.048, 0.140, 0.84
No. of reflections	3074
No. of parameters	210
No. of restraints	3
H-atom treatment	H atoms treated by a mixture of independent and constrained refinement
$\Delta\rho_{max}$, $\Delta\rho_{min}$ (e Å^{-3})	0.09, −0.12

Computer programs: *CrysAlis PRO* (Oxford Diffraction, 2009), *SHELXS97* (Sheldrick, 2008), *XP* in *SHELXTL* (Sheldrick, 2008), *SHELXL2013* (Sheldrick, 2008) and *PLATON* (Spek, 2009).

acetate–methanol (8:2 *v*/*v*) gradient. The preparative chromatography was monitored by thin-layer chromatography (TLC; silica gel) and revealed using UV light and, later, Dragendorff's reagent; those fractions showing similar TLC patterns were pooled and subsequently purified by chromatography using the same procedure to give nine fractions. Fraction 8 (2.1 g) was applied to a Sephadex LH-20 column (EtOAc) and further separated by silica-gel column chromatography (200–300 mesh, EtOAc 100%) affording hobartine, (I) (yield 60 mg). Compound (I) was obtained as a white solid from ethyl acetate and colourless crystals suitable for X-ray diffraction analysis were obtained by recrystallization from methanol.

2.2. Refinement

Crystal data, data collection and structure refinement details are summarized in Table 1. All H atoms were identified in an intermediate difference map and treated differently in the refinement. H atoms on C atoms were idealized and allowed to ride both in coordinates and in displacement parameters, the latter taken as $U_{iso}(H) = xU_{eq}(C)$, with C—H = 0.93 Å and x = 1.2 for aromatic, C—H = 0.97 Å and x = 1.2 for methylene, and C—H = 0.96 Å and x = 1.5 for methyl groups. H atoms attached to N atoms were refined freely. The use of Mo $K\alpha$ radiation for the data collection precluded a trustable determination of the absolute structure from diffraction data alone and the reported configuration was chosen in accordance to that unanimously agreed in synthetic work in the literature, *viz.* C9(*R*), C12(*S*) and C14(*S*).

Table 2
Comparison of selected distances (Å), angles (°) and torsion angles (°) for (I) and polymorphs (II*a*) and (II*b*).

	(I)	(II*a*)	(II*b*)
C3—C8	1.496 (5)	1.441 (3)	1.449 (7)
C9—C12	1.537 (5)	1.503 (4)	1.506 (7)
C9—N10	1.466 (5)	1.264 (3)	1.273 (6)
C11—C16	1.324 (7)	1.496 (7)	1.419 (9)
C11—C17	1.506 (7)	1.327 (7)	1.344 (8)
N10—C9—C12	108.9 (3)	125.5 (3)	126.4 (5)
C9—N10—C18	115.0 (3)	121.8 (3)	120.2 (4)
C3—C8—C9	111.6 (3)	121.63 (18)	118.8 (4)
C11—C16—C15	125.9 (4)	112.1 (4)	116.4 (6)
N10—C9—C8	108.6 (3)	118.2 (2)	117.1 (4)
C12—C11—C16	120.0 (4)	112.5 (3)	115.9 (5)
C9—C12—C11	114.3 (3)	110.2 (2)	108.0 (4)
N10—C18—C14	108.1 (3)	114.0 (2)	115.3 (4)
C3—C8—C9—N10	−74.5 (3)	20.2 (3)	47.8 (6)
N10—C9—C12—C13	61.5 (4)	22.9 (4)	24.9 (7)
C16—C11—C12—C9	91.5 (5)	62.3 (3)	68.8 (6)
C9—C12—C13—C14	−63.1 (4)	−55.2 (3)	−55.5 (6)
C12—C13—C14—C18	61.3 (4)	65.4 (3)	63.6 (6)
C13—C14—C18—N10	−55.0 (4)	−42.4 (3)	−39.7 (6)
C15—C14—C18—N10	67.1 (5)	80.4 (4)	82.5 (6)
C18—N10—C9—C12	−59.6 (4)	0.4 (4)	−0.0 (8)
C9—N10—C18—C14	55.6 (4)	9.5 (4)	7.1 (7)
N10—C9—C12—C11	−60.3 (5)	−97.4 (3)	−94.7 (6)
C13—C14—C15—C16	35.4 (6)	56.2 (4)	53.7 (6)

3. Results and discussion

Fig. 1 shows an ellipsoid plot of hobartine, (I). The molecule is made up of a planar indole system and a bulky azabicycle joined by a central –CH_2– bridge. It is precisely in this bridge where the main differences with the already reported polymorphs of 4,4-dimethyl-8-methylene-3-azabicyclo[3.3.1]non-2-en-2-yl 3-indolyl ketone, denoted (II*a*) (Paz *et al.*, 2013) and (II*b*) (Watson *et al.*, 1989), are apparent, the site in (II*a*)/(II*b*) being sp^2-hybridized and occupied by a ketone group, instead of the sp^3 methylene group seen in (I). The effect extends to

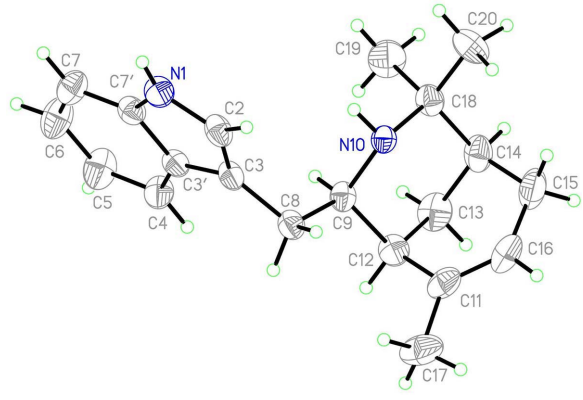


Figure 1
The molecular structure of (I), with ellipsoids drawn at the 30% probability level. H atoms are shown as spheres of arbitrary radii.

Table 3
Relevant distances (Å) in the 3-azabiclycles of (I) and polymorphs (II*a*) and (II*b*), and comparison with corresponding values in the CSD.

The values are from a group of 127 cases with an 'isolated' 3-azabiclycle, *i.e.* not involved in any extra ring.

	(I)	(II*a*)	(II*b*)	CSD range	CSD mean (s.u.)
N10···C16	3.184 (6)	3.288 (7)	3.358 (9)	2.690–3.652	3.235 (142)
C12···C14	2.474 (7)	2.451 (7)	2.461 (9)	2.394–2.544	2.488 (29)
C13···N10	2.862 (6)	2.802 (8)	2.839 (8)	2.695–2.985	2.778 (67)
C13···C16	2.741 (6)	2.913 (7)	2.909 (9)	2.771–3.082	2.963 (58)

the neighbouring C9 atom, also with sp^2-hybridization in (II*a*)/(II*b*), but a chiral sp^3-hybridization in (I). These gross differences are clearly reflected in the distances, angles and torsion angles in the neighbourhood of atom C8, as given in Table 2, where a brief comparison among corresponding data in (I), (II*a*) and (II*b*) is made.

In this regard, it is worth noting that the most relevant difference between the (highly coloured) polymorphic forms (II*a*) and (II*b*) was found to be the torsion angle between the indolyl ketone system and the planar portion of the heterocyclic six-membered ring [C3—C8—C9—N10 = −47.8 (6)° in (II*a*) *versus* −20.2 (3)° in (II*b*)]. The responsibility for the colour variation was precisely ascribed to this difference in the degree of electronic conjugation it would give rise to. The fact that (I) presents no conjugation whatsoever in this bridging section [C3—C8—C9—N10 = −74.3 (3)°] and that its crystals are colourless seems to support this idea put forward in Paz *et al.* (2013).

Regarding the geometries of the two well-defined groups, *viz.* the rigid indole and the more flexible 3-azabicycle, the former does not show, as expected, any relevant difference departing from standard uncertainties. Sensible differences are found, however, in the latter and they mainly involve the single- (s) or double-bond (d) character of C9—N10, C11—C16 and C11—C17, whose sequence is 's–d–s' in (I) and 'd–s–d' in polymorphs (II*a*) and (II*b*), as well as the already mentioned sp^3/sp^2 character of atom C9 (Scheme 1). These differences lead to the misfit schematically shown in Fig. 2, where the three nuclei have been superimposed by forcing the least-squares fit of those atoms not involved in the single/double bonding issue, *viz.* C12, C13, C14, C15 and C18.

In order to assess in a more quantitative way the real significance of these differences in the overall geometry of the 'cage', four representative distances are represented in Table 3. Summarizing, they tell us that the eight-membered group in (I) is more 'closed' (first entry) and that the 'apical' C13 atom is sensibly leaned toward C16. Even if these differences may seem important, they appear small compared with the spread of values found in similar 3-azabicycles in the literature (Table 3), which confirms that the group is rather flexible irrespective of its closed structure.

Regarding the supramolecular structure in (I), there is only one significant intermolecular interaction, involving the indole N1—H1N group as donor and heterocyclic atom N10^{i} as acceptor (Table 4); on the other hand, atom H10N is not involved in any hydrogen bond, as no further acceptor is available in the structure.

The N—H···N hydrogen bond connects neighbouring molecules into a *C*(7) chain structure (Bernstein *et al.*, 1995)

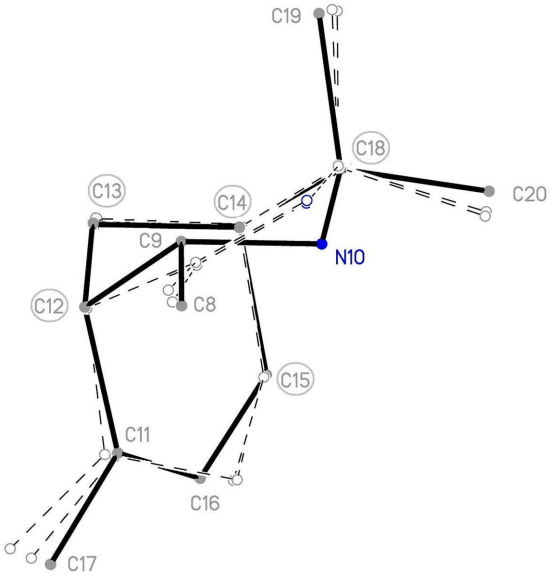


Figure 2
Least-squares superposition of the azabicycles in (I), (II*a*) and (II*b*), highlighting the differences between them. The atoms used in the fit (circled) are C12, C13, C14, C15 and C18.

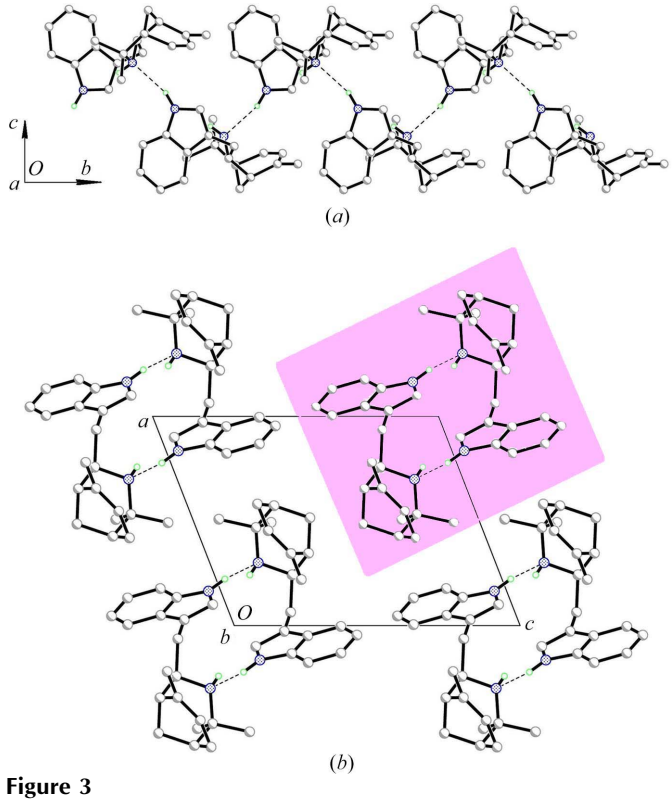


Figure 3
Packing views of (I), showing (*a*) the [010] hydrogen-bonded chain, with the hydrogen bonds drawn as broken lines, and (*b*) a view along *b*, showing the weakly interacting chains in projection (one of them is highlighted). The broken lines indicate the intra-chain hydrogen bonds.

Table 4
Hydrogen-bond geometry (Å, °).

D—H···A	D—H	H···A	D···A	D—H···A
N1—H1N···N10^{i}	0.85 (4)	2.30 (4)	3.116 (5)	160 (5)

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

running along *b* and built up around the twofold screw axis (Fig. 3*a*). Incidentally, this pattern is frequently found in compounds crystallizing in the few enantiomeric space groups with screw axes; as a matter of fact, it has also been found in polymorphs (II*a*) and (II*b*), even cosidering the different space groups ($P2_12_12_1$ *versus* $P2_1$) and different synthons (N—H···N *versus* N—H···O) involved in the interaction.

These [010] chains are almost non-interacting, with no link connecting them except for diffuse dispersion forces. This is observable in Fig. 3(*b*) (where chains are viewed side-by-side) and quantitatively assessed by the rather low packing index of 63.8 (Kitaigorodsky, 1973), calculated using *PLATON* (Spek, 2009). As a comparison, packing indices for structures (II*a*) and (II*b*) are about 4–5% larger, *viz.* 66.3 for (II*a*) and 67.3 for (II*b*).

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supporting information

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Computing details

Data collection: *CrysAlis PRO* (Oxford Diffraction, 2009); cell refinement: *CrysAlis PRO* (Oxford Diffraction, 2009); data reduction: *CrysAlis PRO* (Oxford Diffraction, 2009); program(s) used to solve structure: *SHELXS97* (Sheldrick, 2008); program(s) used to refine structure: *SHELXL2013* (Sheldrick, 2008); molecular graphics: *XP* in *SHELXTL* (Sheldrick, 2008); software used to prepare material for publication: *SHELXL2013* (Sheldrick, 2008) and *PLATON* (Spek, 2009).

(1*R*)-3-[(1*S*,5*S*)-(4,4,8-Trimethylbicyclo[3.3.1]non-7-en-2-yl)methyl]-2,3-dihydro-1*H*-indole

Crystal data

$C_{20}H_{26}N_2$
$M_r = 294.43$
Monoclinic, $P2_1$
$a = 9.0358\ (5)$ Å
$b = 9.0395\ (4)$ Å
$c = 11.4988\ (7)$ Å
$\beta = 111.298\ (6)°$
$V = 875.07\ (9)$ Å^3
$Z = 2$
$F(000) = 320$
$D_x = 1.117$ Mg m^{-3}
Mo $K\alpha$ radiation, $\lambda = 0.71073$ Å
Cell parameters from 2433 reflections
$\theta = 4.0–23.0°$
$\mu = 0.07$ mm^{-1}
$T = 294$ K
Blocks, colourless
0.30 × 0.18 × 0.18 mm

Data collection

Oxford Diffraction Gemini CCD S Ultra diffractometer
ω scans, thick slices
Absorption correction: multi-scan (*CrysAlis PRO*; Oxford Diffraction, 2009)
$T_{min} = 0.97$, $T_{max} = 0.99$
16112 measured reflections
3074 independent reflections
2311 reflections with $I > 2\sigma(I)$
$R_{int} = 0.075$
$\theta_{max} = 25.0°$, $\theta_{min} = 3.8°$
$h = -10\rightarrow10$
$k = -10\rightarrow10$
$l = -13\rightarrow13$

Refinement

Refinement on F^2
Least-squares matrix: full
$R[F^2 > 2\sigma(F^2)] = 0.048$
$wR(F^2) = 0.140$
$S = 0.84$
3074 reflections
210 parameters
3 restraints
Hydrogen site location: mixed
H atoms treated by a mixture of independent and constrained refinement
$w = 1/[\sigma^2(F_o^2) + (0.096P)^2]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} < 0.001$
$\Delta\rho_{max} = 0.09$ e Å^{-3}
$\Delta\rho_{min} = -0.12$ e Å^{-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 (Å²)

	x	*y*	*z*	U_{iso}*/U_{eq}
N1	−0.1645 (4)	0.1938 (4)	0.0433 (3)	0.0584 (9)
H1N	−0.218 (5)	0.149 (5)	−0.024 (3)	0.081 (14)*
C2	−0.1002 (4)	0.3316 (5)	0.0468 (3)	0.0550 (10)
H2	−0.1051	0.3858	−0.0232	0.066*
C3	−0.0281 (4)	0.3788 (4)	0.1670 (3)	0.0477 (8)
C3′	−0.0489 (4)	0.2617 (4)	0.2435 (3)	0.0462 (8)
C4	−0.0043 (5)	0.2434 (5)	0.3719 (3)	0.0600 (10)
H4	0.0526	0.3167	0.4266	0.072*
C5	−0.0457 (6)	0.1150 (5)	0.4162 (4)	0.0780 (14)
H5	−0.0153	0.1012	0.5018	0.094*
C6	−0.1319 (6)	0.0059 (5)	0.3354 (4)	0.0788 (14)
H6	−0.1602	−0.0789	0.3682	0.095*
C7	−0.1769 (5)	0.0196 (5)	0.2082 (4)	0.0668 (11)
H7	−0.2337	−0.0547	0.1546	0.080*
C7′	−0.1347 (4)	0.1479 (4)	0.1630 (3)	0.0493 (9)
C8	0.0641 (4)	0.5175 (4)	0.2155 (3)	0.0510 (9)
H8A	0.0298	0.5607	0.2787	0.061*
H8B	0.0423	0.5882	0.1479	0.061*
C9	0.2427 (4)	0.4876 (4)	0.2715 (3)	0.0475 (8)
H9	0.2581	0.3957	0.3197	0.057*
N10	0.3007 (3)	0.4620 (3)	0.1696 (3)	0.0436 (7)
H10N	0.244 (3)	0.392 (3)	0.125 (3)	0.042 (9)*
C11	0.3442 (5)	0.7536 (5)	0.2969 (4)	0.0663 (11)
C12	0.3460 (5)	0.6071 (5)	0.3587 (3)	0.0573 (10)
H12	0.3084	0.6219	0.4277	0.069*
C13	0.5150 (5)	0.5482 (5)	0.4117 (4)	0.0713 (12)
H13A	0.5176	0.4550	0.4543	0.086*
H13B	0.5833	0.6180	0.4712	0.086*
C14	0.5731 (5)	0.5257 (5)	0.3028 (4)	0.0653 (11)
H14	0.6814	0.4861	0.3371	0.078*
C15	0.5809 (6)	0.6782 (6)	0.2469 (5)	0.0865 (14)
H15A	0.6831	0.7226	0.2933	0.104*
H15B	0.5741	0.6654	0.1614	0.104*
C16	0.4536 (6)	0.7811 (5)	0.2483 (5)	0.0801 (14)
H16	0.4504	0.8733	0.2117	0.096*
C17	0.2200 (6)	0.8645 (6)	0.2973 (5)	0.0888 (16)
H17A	0.2421	0.9580	0.2675	0.133*
H17B	0.2216	0.8758	0.3807	0.133*
H17C	0.1172	0.8304	0.2438	0.133*

C18	0.4688 (4)	0.4119 (4)	0.2096 (3)	0.0540 (10)
C19	0.4934 (6)	0.2569 (5)	0.2697 (5)	0.0861 (15)
H19A	0.4283	0.1865	0.2107	0.129*
H19B	0.4644	0.2586	0.3422	0.129*
H19C	0.6030	0.2290	0.2938	0.129*
C20	0.5081 (6)	0.4008 (6)	0.0911 (4)	0.0790 (14)
H20A	0.4782	0.4910	0.0444	0.119*
H20B	0.4506	0.3196	0.0411	0.119*
H20C	0.6200	0.3847	0.1136	0.119*

Atomic displacement parameters (Å²)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
N1	0.052 (2)	0.076 (2)	0.0448 (19)	−0.0122 (18)	0.0153 (15)	−0.0148 (16)
C2	0.044 (2)	0.082 (3)	0.0404 (19)	−0.005 (2)	0.0173 (16)	−0.0005 (18)
C3	0.0378 (18)	0.064 (2)	0.0435 (19)	−0.0044 (17)	0.0175 (15)	−0.0035 (17)
C3′	0.0389 (18)	0.059 (2)	0.0409 (17)	−0.0005 (17)	0.0150 (15)	−0.0061 (17)
C4	0.063 (2)	0.072 (3)	0.0435 (19)	−0.016 (2)	0.0179 (18)	−0.0069 (19)
C5	0.089 (3)	0.088 (3)	0.050 (2)	−0.019 (3)	0.017 (2)	0.012 (2)
C6	0.085 (3)	0.074 (3)	0.065 (3)	−0.020 (3)	0.013 (2)	0.015 (2)
C7	0.060 (3)	0.060 (2)	0.070 (3)	−0.011 (2)	0.011 (2)	−0.004 (2)
C7′	0.0378 (18)	0.063 (2)	0.045 (2)	0.0005 (17)	0.0130 (15)	−0.0043 (17)
C8	0.048 (2)	0.061 (2)	0.0477 (19)	−0.0044 (18)	0.0214 (16)	−0.0017 (16)
C9	0.047 (2)	0.053 (2)	0.0408 (17)	−0.0055 (16)	0.0144 (15)	0.0033 (16)
N10	0.0363 (16)	0.0463 (16)	0.0457 (16)	−0.0041 (13)	0.0119 (12)	−0.0030 (13)
C11	0.065 (3)	0.057 (2)	0.061 (2)	−0.014 (2)	0.005 (2)	−0.018 (2)
C12	0.053 (2)	0.075 (3)	0.0383 (19)	−0.008 (2)	0.0098 (17)	−0.0087 (18)
C13	0.059 (3)	0.089 (3)	0.048 (2)	−0.006 (2)	−0.0032 (19)	0.001 (2)
C14	0.038 (2)	0.074 (3)	0.073 (3)	−0.0051 (19)	0.0080 (19)	0.007 (2)
C15	0.071 (3)	0.074 (3)	0.115 (4)	−0.028 (3)	0.034 (3)	0.002 (3)
C16	0.078 (3)	0.055 (3)	0.095 (3)	−0.023 (2)	0.018 (3)	0.001 (2)
C17	0.089 (4)	0.077 (3)	0.081 (3)	0.006 (3)	0.007 (3)	−0.029 (3)
C18	0.044 (2)	0.056 (2)	0.060 (2)	0.0070 (17)	0.0173 (18)	0.0102 (18)
C19	0.078 (3)	0.065 (3)	0.111 (4)	0.022 (3)	0.030 (3)	0.023 (3)
C20	0.059 (3)	0.100 (4)	0.085 (3)	0.020 (3)	0.035 (2)	0.003 (3)

Geometric parameters (Å, º)

N1—C7′	1.367 (5)	C11—C12	1.500 (6)
N1—C2	1.369 (5)	C11—C17	1.506 (7)
N1—H1N	0.855 (14)	C12—C13	1.520 (6)
C2—C3	1.365 (5)	C12—H12	0.9800
C2—H2	0.9300	C13—C14	1.537 (6)
C3—C3′	1.431 (5)	C13—H13A	0.9700
C3—C8	1.496 (5)	C13—H13B	0.9700
C3′—C4	1.392 (5)	C14—C15	1.533 (6)
C3′—C7′	1.413 (5)	C14—C18	1.536 (5)
C4—C5	1.372 (6)	C14—H14	0.9800

C4—H4	0.9300	C15—C16	1.483 (7)
C5—C6	1.384 (6)	C15—H15A	0.9700
C5—H5	0.9300	C15—H15B	0.9700
C6—C7	1.374 (6)	C16—H16	0.9300
C6—H6	0.9300	C17—H17A	0.9600
C7—C7′	1.380 (6)	C17—H17B	0.9600
C7—H7	0.9300	C17—H17C	0.9600
C8—C9	1.529 (5)	C18—C20	1.531 (6)
C8—H8A	0.9700	C18—C19	1.543 (6)
C8—H8B	0.9700	C19—H19A	0.9600
C9—N10	1.466 (4)	C19—H19B	0.9600
C9—C12	1.537 (5)	C19—H19C	0.9600
C9—H9	0.9800	C20—H20A	0.9600
N10—C18	1.488 (5)	C20—H20B	0.9600
N10—H10N	0.855 (14)	C20—H20C	0.9600
C11—C16	1.324 (7)		

C7′—N1—C2	108.7 (3)	C11—C12—H12	108.4
C7′—N1—H1N	128 (3)	C13—C12—H12	108.4
C2—N1—H1N	124 (3)	C9—C12—H12	108.4
C3—C2—N1	110.9 (3)	C12—C13—C14	108.0 (3)
C3—C2—H2	124.6	C12—C13—H13A	110.1
N1—C2—H2	124.6	C14—C13—H13A	110.1
C2—C3—C3′	105.6 (3)	C12—C13—H13B	110.1
C2—C3—C8	129.5 (3)	C14—C13—H13B	110.1
C3′—C3—C8	124.8 (3)	H13A—C13—H13B	108.4
C4—C3′—C7′	119.2 (3)	C15—C14—C18	114.8 (4)
C4—C3′—C3	133.4 (3)	C15—C14—C13	107.7 (4)
C7′—C3′—C3	107.4 (3)	C18—C14—C13	110.6 (3)
C5—C4—C3′	118.8 (3)	C15—C14—H14	107.8
C5—C4—H4	120.6	C18—C14—H14	107.8
C3′—C4—H4	120.6	C13—C14—H14	107.8
C4—C5—C6	121.1 (4)	C16—C15—C14	114.0 (4)
C4—C5—H5	119.5	C16—C15—H15A	108.8
C6—C5—H5	119.5	C14—C15—H15A	108.8
C7—C6—C5	121.8 (4)	C16—C15—H15B	108.8
C7—C6—H6	119.1	C14—C15—H15B	108.8
C5—C6—H6	119.1	H15A—C15—H15B	107.7
C6—C7—C7′	117.5 (4)	C11—C16—C15	126.0 (4)
C6—C7—H7	121.2	C11—C16—H16	117.0
C7′—C7—H7	121.2	C15—C16—H16	117.0
N1—C7′—C7	130.9 (3)	C11—C17—H17A	109.5
N1—C7′—C3′	107.4 (3)	C11—C17—H17B	109.5
C7—C7′—C3′	121.7 (3)	H17A—C17—H17B	109.5
C3—C8—C9	111.6 (3)	C11—C17—H17C	109.5
C3—C8—H8A	109.3	H17A—C17—H17C	109.5
C9—C8—H8A	109.3	H17B—C17—H17C	109.5
C3—C8—H8B	109.3	N10—C18—C20	106.6 (3)

C9—C8—H8B	109.3	N10—C18—C14	108.1 (3)
H8A—C8—H8B	108.0	C20—C18—C14	112.5 (3)
N10—C9—C8	108.7 (3)	N10—C18—C19	112.3 (3)
N10—C9—C12	108.9 (3)	C20—C18—C19	107.3 (4)
C8—C9—C12	116.7 (3)	C14—C18—C19	110.1 (3)
N10—C9—H9	107.4	C18—C19—H19A	109.5
C8—C9—H9	107.4	C18—C19—H19B	109.5
C12—C9—H9	107.4	H19A—C19—H19B	109.5
C9—N10—C18	115.0 (3)	C18—C19—H19C	109.5
C9—N10—H10N	106 (2)	H19A—C19—H19C	109.5
C18—N10—H10N	107 (2)	H19B—C19—H19C	109.5
C16—C11—C12	119.0 (4)	C18—C20—H20A	109.5
C16—C11—C17	123.2 (5)	C18—C20—H20B	109.5
C12—C11—C17	117.8 (4)	H20A—C20—H20B	109.5
C11—C12—C13	109.6 (4)	C18—C20—H20C	109.5
C11—C12—C9	114.3 (3)	H20A—C20—H20C	109.5
C13—C12—C9	107.4 (3)	H20B—C20—H20C	109.5

Hydrogen-bond geometry (Å, º)

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
N1—H1*N*···N10^{i}	0.85 (4)	2.30 (4)	3.116 (5)	160 (5)

Symmetry code: (i) −*x*, *y*−1/2, −*z*.