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Conessine isolated from *Holarrhena floribunda*

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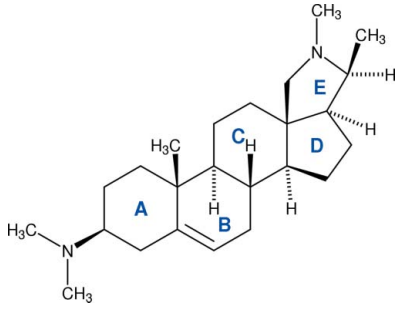
Key indicators: single-crystal X-ray study; T = 173 K; mean σ(C–C) = 0.003 Å; R factor = 0.048; wR factor = 0.119; data-to-parameter ratio = 12.3.

The title compound, $C_{24}H_{40}N_2$, has been isolated from *Holarrhena floribunda* G. Don. (Apocynaceae). The compound has a pentacyclic steroidal nucleus; the ring junctions share the same stereochemistry reported for this class of compounds. Of the three six-membered rings, rings *A* and *C* adopt a chair-like and ring *B* forms a half-chair-like conformation. The cyclopentane ring *D* shows a half-chair conformation and the methylpyrrolidine ring *E* adopts an envelope conformation. The dimethylamino substituent in ring *A* is equatorially oriented.

Related literature

For related literature, see: Allen *et al.* (1987); Berhaut (1971); Biao & Min (2004); Bouillard *et al.* (1987); Chukwurah (1997); Cremer & Pople (1975); Fotie *et al.* (2006); Kumar *et al.* (2007); Leboeuf *et al.* (1969); Tamboura *et al.* (2005); Zirihi *et al.* (2005); Schlittler *et al.* (1949).



Experimental

Crystal data

$C_{24}H_{40}N_2$
M_r = 356.58
Orthorhombic, $P2_12_12_1$
a = 10.4321 (5) Å
b = 10.5977 (5) Å
c = 19.0145 (9) Å
V = 2102.17 (17) Å^3
Z = 4
Mo $K\alpha$ radiation
μ = 0.07 mm^{-1}
T = 173 (2) K
0.45 × 0.19 × 0.11 mm

Data collection

Bruker SMART CCD area-detector diffractometer
Absorption correction: multi-scan (*SADABS*; Sheldrick, 1996)
T_{min} = 0.972, T_{max} = 0.993
14775 measured reflections
2955 independent reflections
2776 reflections with $I > 2\sigma(I)$
R_{int} = 0.034

Refinement

$R[F^2 > 2\sigma(F^2)]$ = 0.048
$wR(F^2)$ = 0.119
S = 1.06
2955 reflections
240 parameters
H-atom parameters constrained
$\Delta\rho_{max}$ = 0.40 e Å^{-3}
$\Delta\rho_{min}$ = −0.18 e Å^{-3}

Data collection: *SMART* (Siemens, 1996); cell refinement: *SAINT* (Siemens, 1996); data reduction: *SAINT*; program(s) used to solve structure: *SHELXTL* (Sheldrick, 1997); program(s) used to refine structure: *SHELXTL*; molecular graphics: *SHELXTL*; software used to prepare material for publication: *SHELXTL*, *PARST* (Nardelli, 1995) and *PLATON* (Spek, 2003).

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Supplementary data and figures for this paper are available from the IUCr electronic archives (Reference: CS2048).

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supplementary materials

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Conessine isolated from *Holarrhena floribunda*

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Comment

Holarrhena floribunda G. Don. (Apocynaceae) is a shrub to medium sized tree, up to 5–15 m in height that grows in central and West African savannah regions. It is commonly used in African folk medicines for the treatment of various ailments such as malaria, dysentery, skin infections and venereal diseases (Berhaut, 1971). Pharmacological investigations of *H. floribunda* revealed antimalarial (Fotie *et al.*, 2006) and antimicrobial (Chukwurah, 1997) activities. Previous phytochemical studies resulted in the isolation of steroidal alkaloids (Leboeuf *et al.*, 1969) and lupeol long-chain fatty acid esters (Fotie *et al.*, 2006). Major compounds found in *Holarrhena floribunda* are steroidal alkaloids of two main chemical families: counanin and pregnen-5. Conessine, holarrhenine, holadienine, holamine, holaphylline, holaphyllamine and kurchicine are well known (Tamboura *et al.*, 2005). Tetracyclic pyrrolidine C, which contains the key BCDE ring system of conessine (I), has four contiguous stereogenic centers, one of which is a quaternary carbon atom. In early reports, the synthesis of racemic steroidal alkaloids from racemic C was reported as an efficient pathway (Biao *et al.*, 2004). No studies have been carried out on the alkaloids biosynthesized in the callus culture. However, previous studies have shown that tissue cultures of *Holarrhena anridysenrerica* produce several steroids and alkaloids, one of which was tentatively identified by thin- layer chromatography (TLC) as conessine (Bouillard *et al.*, 1987). Recently, the antiplasmodial (Zirihi *et al.*, 2005) activity of conessine (I), has been reported against the chloroquine-resistant strain FcB1 of *Plasmodium falciparum*. The antidiarrhoel properties (Kumar *et al.*, 2007) of conessine were also studied. In this paper, we report the absolute structure and relative stereochemistry of title compound (I), isolated from the stem bark of *H. floribunda*.

The bond lengths and angles in the title compound (I) show normal values (Allen *et al.*, 1987) and the pentacyclic steroidal nucleus has a *trans*/*trans*/*cis* conformations for B/C/D rings (Table 1). Among the cylohexane rings, rings A and C adopt chair-like conformation and ring B has half chair-like conformation, with puckering amplitude Q= 0.492 (2)°, θ= 51.4 (2)° and φ= 231.8 (15)° (Cremer & Pople, 1975). The half chair conformation in ring B is attributed to the presence of a double bond between C-5 and C-6 atoms. The cyclopentane ring D shows half chair conformation and a *cis* fused ring E of methylpyrrolidine appeared as an envelop [φ= 25.8 (3)°]. The equatorially oriented dimethylamino substitutent at C-3 is making an angle 77.5 (13)° on the Cremer and Pople plane (Cremer & Pople, 1975). The methyl substituent at C-18 is also attached equatorailly to ring E of the molecule (I) by having an angle 72.9 (3) on Cremer & Pople plane (Cremer & Pople, 1975). The *N*, *N*-dimethyl substitutent at C-3, methyl substituents at C-10 and C-18 are β-oriented in the title compound (I). The sum of the bonds around N1 [337.8°] and N2 [330.1°] are indicative of their sp^3 character.

Experimental

Powdered stem barks of *Holarrhena floribunda* (5.4 kg) were soaked and extracted with MeOH for four days. The combined methanol extracts were dried under vacuum to afford a green gum (224 g). This methanolic extract was percolated with very dilute hydrochloric acid (5%). The liquor was made alkaline with ammonia (pH = 9) and extracted with ethyl acetate. The ethyl acetate extract was subjected to column chromatography, using hexane-ethyl acetate mixture of increasing polarity.

The less polar fraction was further subjected to column chromatography (hexane-ethyl acetate, 70:30) to yield compound (I) as colorless crystals (106 mg).

Refinement

All H atoms in compounds (I) were initially located from the difference map·The C bound H atoms were later placed at calculated positions [C—H=0.96–0.98 A°] with U_{iso} constrained to be $1.5U_{eq}$ of the carrrier atom for the methyl group and $1.2U_{eq}$ for the remaining positions. The Friedel reflections were merged before final refinement because of the absence of anomalous scattering effects.

Figures

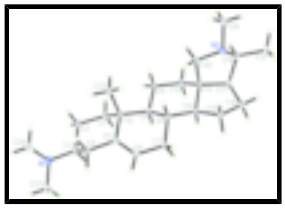


Fig. 1. The structure of the compound (I) showing 50% probability displacement ellipsoids and the atom numbering scheme.

conessine

Crystal data

$C_{24}H_{40}N_2$	D_x = 1.127 Mg m^{-3}
M_r = 356.58	Melting point: 398 K
Orthorhombic, $P2_12_12_1$	Mo $K\alpha$ radiation λ = 0.71073 Å
a = 10.4321 (5) Å	Cell parameters from 5789 reflections
b = 10.5977 (5) Å	θ = 2.2–28.3º
c = 19.0145 (9) Å	μ = 0.07 mm^{-1}
V = 2102.17 (17) Å^3	T = 173 (2) K
Z = 4	Block, colorless
F_{000} = 792	0.45 × 0.19 × 0.11 mm

Data collection

Bruker SMART CCD area-detector diffractometer	2955 independent reflections
Radiation source: fine-focus sealed tube	2776 reflections with $I > 2\sigma(I)$
Monochromator: graphite	R_{int} = 0.034
Detector resolution: 8.33 pixels mm^{-1}	θ_{max} = 28.3º
T = 173(2) K	θ_{min} = 2.1º
ω scans	h = −13→13
Absorption correction: multi-scan (SADABS; Sheldrick, 1996)	k = −13→14
T_{min} = 0.972, T_{max} = 0.993	l = −25→18

14775 measured reflections

Refinement

Refinement on F^2

Least-squares matrix: full

$R[F^2 > 2\sigma(F^2)] = 0.048$

$wR(F^2) = 0.119$

$S = 1.06$

2955 reflections

240 parameters

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

$w = 1/[\sigma^2(F_o^2) + (0.0717P)^2 + 0.5901P]$ where $P = (F_o^2 + 2F_c^2)/3$

$(\Delta/\sigma)_{max} < 0.001$

$\Delta\rho_{max} = 0.40$ e Å^{-3}

$\Delta\rho_{min} = -0.18$ e Å^{-3}

Extinction correction: none

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.

Refinement. Refinement of F^2 against ALL reflections. The weighted *R*-factor *wR* and goodness of fit S are based on F^2, conventional *R*-factors *R* are based on F, with F set to zero for negative F^2. The threshold expression of $F^2 > 2$sigma(F^2) is used only for calculating *R*-factors(gt) *etc*. and is not relevant to the choice of reflections for refinement. *R*-factors based on F^2 are statistically about twice as large as those based on F, and R– factors based on ALL data will be even larger.

Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (Å^2)

	x	*y*	*z*	U_{iso}*/U_{eq}
N1	0.33771 (18)	0.85002 (16)	0.75323 (9)	0.0165 (4)
N2	0.30144 (17)	1.59443 (16)	0.37967 (9)	0.0146 (4)
C1	0.4697 (2)	1.12294 (19)	0.64348 (12)	0.0163 (4)
H1A	0.5446	1.1282	0.6134	0.020*
H1B	0.4834	1.1795	0.6829	0.020*
C2	0.4587 (2)	0.98782 (19)	0.67155 (11)	0.0169 (4)
H2A	0.4518	0.9294	0.6324	0.020*
H2B	0.5353	0.9666	0.6980	0.020*
C3	0.3417 (2)	0.97494 (19)	0.71873 (10)	0.0149 (4)
H3A	0.3506	1.0379	0.7561	0.018*
C4	0.22080 (19)	1.01018 (19)	0.67649 (10)	0.0138 (4)
H4A	0.2079	0.9485	0.6395	0.017*
H4B	0.1468	1.0073	0.7073	0.017*
C5	0.23053 (19)	1.14076 (18)	0.64399 (10)	0.0118 (4)
C6	0.13639 (18)	1.22437 (18)	0.65267 (10)	0.0122 (4)

H6A	0.0674	1.2007	0.6807	0.015*
C7	0.13313 (19)	1.35374 (18)	0.62063 (10)	0.0129 (4)
H7A	0.1442	1.4160	0.6575	0.016*
H7B	0.0497	1.3674	0.5995	0.016*
C8	0.23672 (18)	1.37331 (17)	0.56477 (9)	0.0105 (4)
H8A	0.2098	1.3321	0.5210	0.013*
C9	0.36390 (18)	1.31410 (17)	0.58981 (10)	0.0109 (4)
H9A	0.3820	1.3510	0.6360	0.013*
C10	0.35160 (19)	1.16911 (17)	0.60156 (10)	0.0119 (4)
C11	0.47783 (19)	1.35004 (18)	0.54206 (11)	0.0148 (4)
H11A	0.5564	1.3192	0.5632	0.018*
H11B	0.4678	1.3083	0.4970	0.018*
C12	0.49036 (19)	1.49317 (19)	0.52965 (11)	0.0155 (4)
H12A	0.5080	1.5356	0.5738	0.019*
H12B	0.5608	1.5098	0.4977	0.019*
C13	0.36558 (19)	1.54292 (17)	0.49836 (10)	0.0115 (4)
C14	0.25743 (18)	1.51380 (18)	0.55081 (10)	0.0109 (4)
H14A	0.2845	1.5504	0.5958	0.013*
C15	0.14650 (19)	1.59521 (18)	0.52506 (11)	0.0140 (4)
H15A	0.0811	1.6044	0.5609	0.017*
H15B	0.1081	1.5605	0.4828	0.017*
C16	0.2138 (2)	1.72121 (18)	0.51012 (10)	0.0155 (4)
H16A	0.2158	1.7729	0.5522	0.019*
H16B	0.1690	1.7671	0.4735	0.019*
C17	0.3527 (2)	1.68821 (17)	0.48602 (10)	0.0128 (4)
H17A	0.4168	1.7355	0.5129	0.015*
C18	0.37303 (19)	1.70307 (19)	0.40682 (10)	0.0138 (4)
H18A	0.4642	1.6907	0.3965	0.017*
C19	0.3209 (2)	1.5710 (2)	0.30505 (11)	0.0195 (4)
H19A	0.2854	1.6395	0.2783	0.029*
H19B	0.2792	1.4938	0.2920	0.029*
H19C	0.4110	1.5644	0.2955	0.029*
C20	0.3438 (2)	1.48859 (18)	0.42341 (10)	0.0148 (4)
H20A	0.4227	1.4530	0.4051	0.018*
H20B	0.2790	1.4230	0.4244	0.018*
C21	0.3299 (2)	1.82678 (19)	0.37369 (11)	0.0194 (4)
H21A	0.3655	1.8339	0.3273	0.029*
H21B	0.3589	1.8961	0.4020	0.029*
H21C	0.2380	1.8284	0.3708	0.029*
C22	0.3436 (2)	1.09705 (18)	0.53084 (10)	0.0159 (4)
H22A	0.3255	1.0097	0.5397	0.024*
H22B	0.4239	1.1042	0.5064	0.024*
H22C	0.2765	1.1326	0.5025	0.024*
C23	0.2463 (2)	0.8454 (2)	0.81097 (12)	0.0235 (5)
H23A	0.2558	0.7671	0.8359	0.035*
H23B	0.1607	0.8515	0.7927	0.035*
H23C	0.2619	0.9144	0.8425	0.035*
C24	0.3179 (2)	0.7438 (2)	0.70574 (12)	0.0231 (5)
H24A	0.3292	0.6662	0.7310	0.035*

H24B	0.3788	0.7480	0.6680	0.035*
H24C	0.2326	0.7473	0.6869	0.035*

Atomic displacement parameters (Å^2)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
N1	0.0241 (9)	0.0107 (8)	0.0146 (7)	0.0005 (7)	−0.0013 (7)	0.0028 (6)
N2	0.0175 (8)	0.0135 (8)	0.0128 (7)	−0.0010 (7)	0.0006 (7)	0.0000 (6)
C1	0.0122 (9)	0.0128 (9)	0.0238 (10)	0.0003 (7)	−0.0027 (8)	0.0044 (8)
C2	0.0142 (9)	0.0121 (9)	0.0243 (10)	0.0019 (8)	−0.0020 (8)	0.0046 (8)
C3	0.0191 (10)	0.0097 (8)	0.0159 (8)	−0.0008 (8)	−0.0016 (8)	0.0012 (7)
C4	0.0130 (9)	0.0120 (9)	0.0164 (9)	−0.0017 (7)	0.0002 (7)	0.0008 (7)
C5	0.0125 (8)	0.0117 (8)	0.0111 (8)	−0.0021 (7)	−0.0010 (7)	−0.0006 (7)
C6	0.0114 (8)	0.0143 (9)	0.0110 (8)	−0.0009 (7)	0.0005 (7)	0.0016 (7)
C7	0.0131 (9)	0.0108 (8)	0.0148 (8)	0.0026 (7)	0.0004 (7)	0.0026 (7)
C8	0.0116 (8)	0.0099 (8)	0.0099 (8)	0.0006 (7)	0.0001 (7)	−0.0005 (6)
C9	0.0123 (8)	0.0073 (8)	0.0129 (8)	−0.0007 (7)	−0.0016 (7)	−0.0005 (7)
C10	0.0123 (8)	0.0090 (8)	0.0142 (8)	−0.0001 (7)	−0.0002 (7)	−0.0002 (7)
C11	0.0100 (8)	0.0114 (9)	0.0230 (10)	0.0016 (7)	0.0037 (7)	0.0041 (8)
C12	0.0138 (9)	0.0107 (9)	0.0219 (10)	−0.0020 (7)	−0.0002 (8)	0.0041 (8)
C13	0.0128 (9)	0.0074 (8)	0.0142 (8)	−0.0006 (7)	0.0008 (7)	0.0013 (7)
C14	0.0126 (8)	0.0086 (8)	0.0114 (8)	0.0011 (7)	−0.0007 (7)	−0.0014 (7)
C15	0.0137 (9)	0.0118 (8)	0.0164 (8)	0.0035 (8)	0.0017 (8)	0.0004 (7)
C16	0.0195 (10)	0.0106 (9)	0.0166 (9)	0.0033 (8)	0.0003 (8)	0.0009 (7)
C17	0.0152 (9)	0.0070 (8)	0.0161 (9)	0.0005 (7)	−0.0031 (7)	0.0007 (7)
C18	0.0134 (9)	0.0117 (9)	0.0162 (9)	0.0001 (7)	−0.0014 (7)	0.0028 (7)
C19	0.0200 (10)	0.0234 (11)	0.0151 (9)	−0.0023 (8)	−0.0002 (8)	0.0000 (8)
C20	0.0171 (9)	0.0105 (8)	0.0168 (9)	−0.0005 (8)	0.0040 (8)	−0.0010 (7)
C21	0.0223 (10)	0.0156 (10)	0.0203 (10)	0.0001 (8)	−0.0054 (8)	0.0051 (8)
C22	0.0206 (10)	0.0117 (8)	0.0154 (9)	0.0007 (8)	0.0046 (8)	−0.0009 (7)
C23	0.0305 (12)	0.0182 (10)	0.0218 (10)	0.0016 (9)	0.0044 (9)	0.0080 (8)
C24	0.0345 (12)	0.0121 (9)	0.0227 (10)	−0.0017 (9)	−0.0021 (9)	0.0030 (8)

Geometric parameters (Å, °)

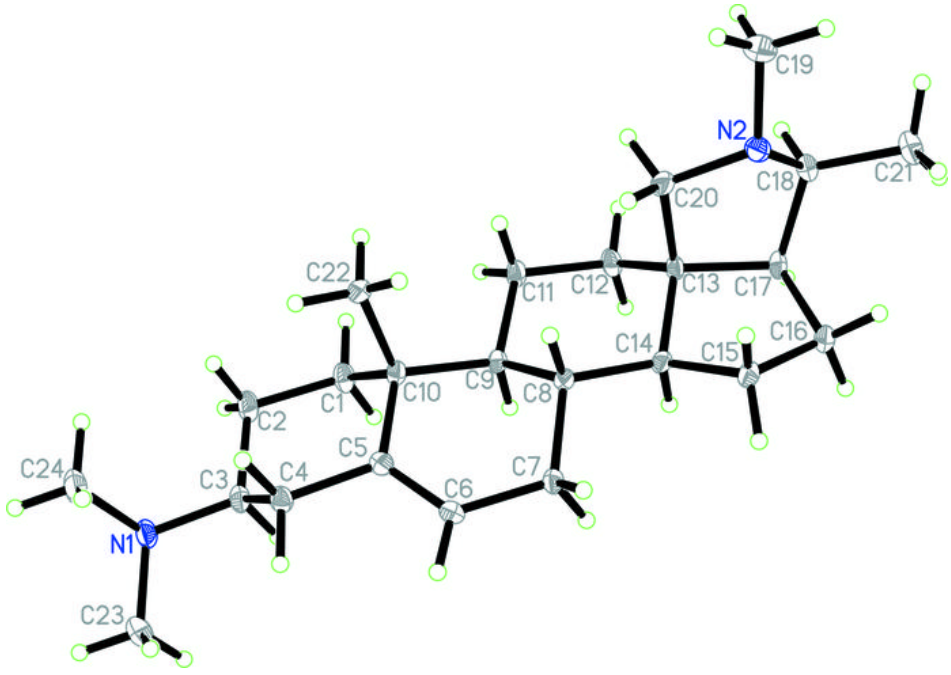
N1—C23	1.455 (3)	C12—C13	1.525 (3)
N1—C24	1.458 (3)	C12—H12A	0.9700
N1—C3	1.478 (2)	C12—H12B	0.9700
N2—C19	1.455 (3)	C13—C14	1.537 (3)
N2—C20	1.465 (3)	C13—C20	1.554 (3)
N2—C18	1.466 (3)	C13—C17	1.563 (3)
C1—C2	1.533 (3)	C14—C15	1.524 (3)
C1—C10	1.547 (3)	C14—H14A	0.9800
C1—H1A	0.9700	C15—C16	1.535 (3)
C1—H1B	0.9700	C15—H15A	0.9700
C2—C3	1.521 (3)	C15—H15B	0.9700
C2—H2A	0.9700	C16—C17	1.559 (3)
C2—H2B	0.9700	C16—H16A	0.9700
C3—C4	1.541 (3)	C16—H16B	0.9700

C3—H3A	0.9800	C17—C18	1.529 (3)
C4—C5	1.519 (3)	C17—H17A	0.9800
C4—H4A	0.9700	C18—C21	1.523 (3)
C4—H4B	0.9700	C18—H18A	0.9800
C5—C6	1.333 (3)	C19—H19A	0.9600
C5—C10	1.529 (3)	C19—H19B	0.9600
C6—C7	1.501 (3)	C19—H19C	0.9600
C6—H6A	0.9300	C20—H20A	0.9700
C7—C8	1.529 (3)	C20—H20B	0.9700
C7—H7A	0.9700	C21—H21A	0.9600
C7—H7B	0.9700	C21—H21B	0.9600
C8—C14	1.528 (3)	C21—H21C	0.9600
C8—C9	1.543 (3)	C22—H22A	0.9600
C8—H8A	0.9800	C22—H22B	0.9600
C9—C11	1.543 (3)	C22—H22C	0.9600
C9—C10	1.558 (3)	C23—H23A	0.9600
C9—H9A	0.9800	C23—H23B	0.9600
C10—C22	1.549 (3)	C23—H23C	0.9600
C11—C12	1.541 (3)	C24—H24A	0.9600
C11—H11A	0.9700	C24—H24B	0.9600
C11—H11B	0.9700	C24—H24C	0.9600
C23—N1—C24	110.38 (18)	C12—C13—C14	107.69 (15)
C23—N1—C3	112.55 (17)	C12—C13—C20	110.76 (16)
C24—N1—C3	114.87 (16)	C14—C13—C20	114.42 (16)
C19—N2—C20	112.41 (16)	C12—C13—C17	118.20 (16)
C19—N2—C18	113.96 (17)	C14—C13—C17	103.40 (15)
C20—N2—C18	104.34 (15)	C20—C13—C17	102.40 (15)
C2—C1—C10	114.53 (17)	C15—C14—C8	120.00 (16)
C2—C1—H1A	108.6	C15—C14—C13	103.61 (15)
C10—C1—H1A	108.6	C8—C14—C13	114.35 (15)
C2—C1—H1B	108.6	C15—C14—H14A	106.0
C10—C1—H1B	108.6	C8—C14—H14A	106.0
H1A—C1—H1B	107.6	C13—C14—H14A	106.0
C3—C2—C1	110.45 (17)	C14—C15—C16	101.81 (16)
C3—C2—H2A	109.6	C14—C15—H15A	111.4
C1—C2—H2A	109.6	C16—C15—H15A	111.4
C3—C2—H2B	109.6	C14—C15—H15B	111.4
C1—C2—H2B	109.6	C16—C15—H15B	111.4
H2A—C2—H2B	108.1	H15A—C15—H15B	109.3
N1—C3—C2	111.37 (17)	C15—C16—C17	106.51 (15)
N1—C3—C4	115.19 (17)	C15—C16—H16A	110.4
C2—C3—C4	109.12 (16)	C17—C16—H16A	110.4
N1—C3—H3A	106.9	C15—C16—H16B	110.4
C2—C3—H3A	106.9	C17—C16—H16B	110.4
C4—C3—H3A	106.9	H16A—C16—H16B	108.6
C5—C4—C3	112.22 (16)	C18—C17—C16	113.29 (16)
C5—C4—H4A	109.2	C18—C17—C13	103.72 (15)
C3—C4—H4A	109.2	C16—C17—C13	104.89 (16)
C5—C4—H4B	109.2	C18—C17—H17A	111.5

C3—C4—H4B	109.2	C16—C17—H17A	111.5
H4A—C4—H4B	107.9	C13—C17—H17A	111.5
C6—C5—C4	120.40 (18)	N2—C18—C21	112.33 (16)
C6—C5—C10	122.92 (18)	N2—C18—C17	101.25 (15)
C4—C5—C10	116.68 (16)	C21—C18—C17	117.07 (17)
C5—C6—C7	125.01 (18)	N2—C18—H18A	108.6
C5—C6—H6A	117.5	C21—C18—H18A	108.6
C7—C6—H6A	117.5	C17—C18—H18A	108.6
C6—C7—C8	112.94 (16)	N2—C19—H19A	109.5
C6—C7—H7A	109.0	N2—C19—H19B	109.5
C8—C7—H7A	109.0	H19A—C19—H19B	109.5
C6—C7—H7B	109.0	N2—C19—H19C	109.5
C8—C7—H7B	109.0	H19A—C19—H19C	109.5
H7A—C7—H7B	107.8	H19B—C19—H19C	109.5
C14—C8—C7	110.66 (15)	N2—C20—C13	106.33 (15)
C14—C8—C9	109.17 (15)	N2—C20—H20A	110.5
C7—C8—C9	109.76 (15)	C13—C20—H20A	110.5
C14—C8—H8A	109.1	N2—C20—H20B	110.5
C7—C8—H8A	109.1	C13—C20—H20B	110.5
C9—C8—H8A	109.1	H20A—C20—H20B	108.7
C8—C9—C11	112.35 (15)	C18—C21—H21A	109.5
C8—C9—C10	111.99 (16)	C18—C21—H21B	109.5
C11—C9—C10	113.03 (16)	H21A—C21—H21B	109.5
C8—C9—H9A	106.3	C18—C21—H21C	109.5
C11—C9—H9A	106.3	H21A—C21—H21C	109.5
C10—C9—H9A	106.3	H21B—C21—H21C	109.5
C5—C10—C1	108.91 (15)	C10—C22—H22A	109.5
C5—C10—C22	108.48 (15)	C10—C22—H22B	109.5
C1—C10—C22	109.53 (16)	H22A—C22—H22B	109.5
C5—C10—C9	109.73 (16)	C10—C22—H22C	109.5
C1—C10—C9	108.67 (16)	H22A—C22—H22C	109.5
C22—C10—C9	111.49 (15)	H22B—C22—H22C	109.5
C12—C11—C9	113.48 (16)	N1—C23—H23A	109.5
C12—C11—H11A	108.9	N1—C23—H23B	109.5
C9—C11—H11A	108.9	H23A—C23—H23B	109.5
C12—C11—H11B	108.9	N1—C23—H23C	109.5
C9—C11—H11B	108.9	H23A—C23—H23C	109.5
H11A—C11—H11B	107.7	H23B—C23—H23C	109.5
C13—C12—C11	109.12 (16)	N1—C24—H24A	109.5
C13—C12—H12A	109.9	N1—C24—H24B	109.5
C11—C12—H12A	109.9	H24A—C24—H24B	109.5
C13—C12—H12B	109.9	N1—C24—H24C	109.5
C11—C12—H12B	109.9	H24A—C24—H24C	109.5
H12A—C12—H12B	108.3	H24B—C24—H24C	109.5
C10—C1—C2—C3	−58.0 (2)	C11—C12—C13—C14	59.3 (2)
C23—N1—C3—C2	165.95 (18)	C11—C12—C13—C20	−66.5 (2)
C24—N1—C3—C2	−66.6 (2)	C11—C12—C13—C17	175.91 (17)
C23—N1—C3—C4	−69.1 (2)	C7—C8—C14—C15	−59.3 (2)
C24—N1—C3—C4	58.3 (2)	C9—C8—C14—C15	179.75 (16)

C1—C2—C3—N1	−173.11 (16)	C7—C8—C14—C13	176.63 (15)
C1—C2—C3—C4	58.6 (2)	C9—C8—C14—C13	55.7 (2)
N1—C3—C4—C5	178.69 (15)	C12—C13—C14—C15	165.73 (15)
C2—C3—C4—C5	−55.2 (2)	C20—C13—C14—C15	−70.66 (19)
C3—C4—C5—C6	−129.52 (19)	C17—C13—C14—C15	39.87 (18)
C3—C4—C5—C10	50.8 (2)	C12—C13—C14—C8	−61.9 (2)
C4—C5—C6—C7	−177.33 (17)	C20—C13—C14—C8	61.7 (2)
C10—C5—C6—C7	2.4 (3)	C17—C13—C14—C8	172.26 (15)
C5—C6—C7—C8	11.1 (3)	C8—C14—C15—C16	−173.52 (16)
C6—C7—C8—C14	−162.15 (16)	C13—C14—C15—C16	−44.50 (18)
C6—C7—C8—C9	−41.6 (2)	C14—C15—C16—C17	31.96 (19)
C14—C8—C9—C11	−48.7 (2)	C15—C16—C17—C18	104.67 (18)
C7—C8—C9—C11	−170.16 (15)	C15—C16—C17—C13	−7.77 (19)
C14—C8—C9—C10	−177.18 (15)	C12—C13—C17—C18	102.76 (19)
C7—C8—C9—C10	61.4 (2)	C14—C13—C17—C18	−138.40 (16)
C6—C5—C10—C1	134.57 (19)	C20—C13—C17—C18	−19.2 (2)
C4—C5—C10—C1	−45.7 (2)	C12—C13—C17—C16	−138.15 (18)
C6—C5—C10—C22	−106.3 (2)	C14—C13—C17—C16	−19.32 (18)
C4—C5—C10—C22	73.4 (2)	C20—C13—C17—C16	99.87 (17)
C6—C5—C10—C9	15.7 (2)	C19—N2—C18—C21	64.1 (2)
C4—C5—C10—C9	−164.58 (16)	C20—N2—C18—C21	−172.98 (17)
C2—C1—C10—C5	49.1 (2)	C19—N2—C18—C17	−170.26 (17)
C2—C1—C10—C22	−69.4 (2)	C20—N2—C18—C17	−47.29 (18)
C2—C1—C10—C9	168.55 (17)	C16—C17—C18—N2	−72.50 (19)
C8—C9—C10—C5	−47.1 (2)	C13—C17—C18—N2	40.64 (19)
C11—C9—C10—C5	−175.22 (15)	C16—C17—C18—C21	50.0 (2)
C8—C9—C10—C1	−166.09 (15)	C13—C17—C18—C21	163.11 (17)
C11—C9—C10—C1	65.8 (2)	C19—N2—C20—C13	159.37 (17)
C8—C9—C10—C22	73.1 (2)	C18—N2—C20—C13	35.4 (2)
C11—C9—C10—C22	−55.0 (2)	C12—C13—C20—N2	−135.88 (16)
C8—C9—C11—C12	51.7 (2)	C14—C13—C20—N2	102.18 (18)
C10—C9—C11—C12	179.59 (17)	C17—C13—C20—N2	−9.0 (2)
C9—C11—C12—C13	−56.9 (2)		

Fig. 1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