

UC Davis

UC Davis Previously Published Works

Title

Ethyl 1-benzyl-1,2,3,3a,4,10b-hexahydropyrrolo[2',3':3,4]pyrrolo[1,2-a]benzimidazole-2-carboxylate

Permalink

<https://escholarship.org/uc/item/6rb1c8np>

Journal

Acta Crystallographica Section E: Crystallographic Communications, 67(5)

ISSN

2056-9890

Authors

Meng, Liping
Fettinger, James C
Kurth, Mark J

Publication Date

2011-05-15

DOI

10.1107/s1600536811014292

Peer reviewed

Ethyl 1-benzyl-1,2,3,3a,4,10b-hexahydro-pyrrolo[2',3':3,4]pyrrolo[1,2-a]-benzimidazole-2-carboxylate

Liping Meng, James C. Fettinger and Mark J. Kurth*

Department of Chemistry, University of California, One Shields Avenue, Davis, CA 95616, USA

Correspondence e-mail: mjkurth@ucdavis.edu

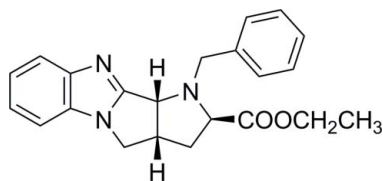
Received 29 March 2011; accepted 15 April 2011

Key indicators: single-crystal X-ray study; $T = 90$ K; mean $\sigma(\text{C}-\text{C}) = 0.002$ Å; R factor = 0.037; wR factor = 0.095; data-to-parameter ratio = 12.5.

The title molecule, $\text{C}_{22}\text{H}_{23}\text{N}_3\text{O}_2$, was obtained *via* an intramolecular cycloaddition of an azomethine ylide and an alkene tethered by a benzimidazole unit. The benzoimidazole unit is essentially planar, with an r.m.s. deviation of 0.0087 Å from the nine constituent atoms. It has a *cis* fusion of the two pyrrolidine rings as well as a *cis* ester appendage. The two pyrrolidine rings rings have envelope conformations. The crystal packing is stabilized by aromatic π - π stacking of parallel benzimidazole ring systems, with a centroid-to-centroid distance of 3.518 (6) Å. Weak intermolecular C—H...O contacts may also play a role in the stability of the packing.

Related literature

Polycyclic nitrogen-containing heterocycles form the basic skeleton of numerous alkaloids and physiologically active compounds, see: Southon & Buckingham (1989). Conformational studies have been reported for related pyrrolidino[3,4-*b*]pyrrolidine-2-carboxylates obtained from intramolecular cycloaddition of azomethine ylides, see: Cheng *et al.* (2001); Meng *et al.* (2007). For related literature on the pharmaceutical properties of benzimidazole and pyrrolidine, see: Gudmundsson *et al.* (2000); Hamilton & Steiner (1997). For related literature on the azomethine ylide cycloaddition in similar systems, Pedrosa *et al.* (2006); Yang *et al.* (2006).



Experimental

Crystal data

$\text{C}_{22}\text{H}_{23}\text{N}_3\text{O}_2$	$V = 1829.00$ (16) Å ³
$M_r = 361.43$	$Z = 4$
Monoclinic, $P2_1/n$	Mo $K\alpha$ radiation
$a = 9.2498$ (5) Å	$\mu = 0.09$ mm ⁻¹
$b = 13.8999$ (7) Å	$T = 90$ K
$c = 14.2258$ (7) Å	$0.39 \times 0.16 \times 0.13$ mm
$\beta = 90.345$ (1)°	

Data collection

Bruker SMART1000 CCD area-detector diffractometer	16147 measured reflections
Absorption correction: numerical (SADABS; Blessing, 1995; Sheldrick, 2007)	4194 independent reflections
$T_{\min} = 0.962$, $T_{\max} = 0.989$	3080 reflections with $I > 2\sigma(I)$
	$R_{\text{int}} = 0.037$

Refinement

$R[F^2 > 2\sigma(F^2)] = 0.037$	336 parameters
$wR(F^2) = 0.095$	All H-atom parameters refined
$S = 1.09$	$\Delta\rho_{\text{max}} = 0.37$ e Å ⁻³
4194 reflections	$\Delta\rho_{\text{min}} = -0.27$ e Å ⁻³

Table 1

Hydrogen-bond geometry (Å, °).

$D-H\cdots A$	$D-H$	$H\cdots A$	$D\cdots A$	$D-H\cdots A$
$\text{C11}-\text{H11B}\cdots\text{O12}^{\text{i}}$	1.005 (15)	2.399 (15)	3.3344 (17)	154.5 (12)
$\text{C18}-\text{H18}\cdots\text{O12}^{\text{ii}}$	0.968 (15)	2.514 (16)	3.3505 (17)	144.6 (12)

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

Data collection: SMART (Bruker, 2002); cell refinement: SAINT (Bruker, 2007); data reduction: SAINT; program(s) used to solve structure: SHELXS97 (Sheldrick, 2008); program(s) used to refine structure: SHELXL97 (Sheldrick, 2008); molecular graphics: XP in SHELXTL/PC (Sheldrick, 2008); software used to prepare material for publication: SHELXL97.

The authors thank the National Science Foundation (grant No. CHE-0910870) and the National Institutes of Health (grant No. GM0891583) for financial support of this work.

Supplementary data and figures for this paper are available from the IUCr electronic archives (Reference: WN2427).

References

- Blessing, R. H. (1995). *Acta Cryst.* **A51**, 33–38.
- Bruker (2002). SMART. Bruker AXS Inc., Madison, Wisconsin, USA.
- Bruker (2007). SAINT. Bruker AXS Inc., Madison, Wisconsin, USA.
- Cheng, Q., Zhang, W., Tagamia, Y. & Oritani, T. (2001). *J. Chem. Soc. Perkin Trans. 1*, pp. 452–456.
- Gudmundsson, K. S., Tidwell, J., Lippa, N., Koszalka, G. W., van Draanen, N., Ptak, R. G., Drach, J. C. & Townsend, L. B. (2000). *J. Med. Chem.* **43**, 2464–2472.
- Hamilton, G. S. & Steiner, J. P. (1997). *Curr. Pharm. Des.* **3**, 405–428.
- Meng, L., Fettinger, C. J. & Kurth, J. M. (2007). *Org. Lett.* **9**, 5055–5058.
- Pedrosa, R., Andres, C., Nieto, J., Perez-Cuadrado, C. & Francisco, I. S. (2006). *Eur. J. Org. Chem.* pp. 3259–3265.
- Sheldrick, G. M. (2007). SADABS. University of Göttingen, Germany.
- Sheldrick, G. M. (2008). *Acta Cryst.* **A64**, 112–122.
- Southon, I. W. & Buckingham, J. (1989). Editors. *Dictionary of Alkaloids*. New York: Chapman & Hall.
- Yang, X., Luo, S., Fang, F., Liu, P., Lu, Y., He, M. & Zhai, H. (2006). *Tetrahedron*, **62**, 2240–2246.

supplementary materials

Acta Cryst. (2011). E67, o1214 [doi:10.1107/S1600536811014292]

Ethyl 1-benzyl-1,2,3,3a,4,10b-hexahydropyrrolo[2',3':3,4]pyrrolo[1,2-*a*]benzimidazole-2-carboxylate

L. Meng, J. C. Fettinger and M. J. Kurth

Comment

Polycyclic nitrogen-containing heterocycles form the basic skeleton of numerous alkaloids and physiologically active compounds (Southon & Buckingham, 1989). The title polycyclic *N*-heterocycle, ethyl 1-benzylpyrrolidino[2',3':3,4]pyrrolidino[1,2-*a*] benzimidazole-2-carboxylate, was obtained *via* an intramolecular azomethine ylide cycloaddition and possesses two medicinally relevant pharmacophores – benzimidazole and pyrrolidine (Gudmundsson *et al.*, 2000; Hamilton & Steiner, 1997)– in one rigid molecule; the title compound may afford important bioactivity.

In the structure of the title compound (Fig. 1), the benzimidazole unit is essentially planar, with a root mean square deviation of 0.0087 Å from the nine constituent atoms. The two pyrrolidine rings have envelope forms and are *cis* fused, which is consistent with conventional azomethine ylide cycloadditions in similar systems (Pedrosa *et al.*, 2006; Yang *et al.*, 2006). However, unlike the previously reported analogues obtained from an intramolecular azomethine ylide and alkene cycloaddition tethered by an oxazolidin-2-one (Cheng *et al.*, 2001), the ester appendage in the title structure was unambiguously assigned as *cis* to the angular protons H2A and H10A by X-ray crystallography. The crystal packing (Fig. 2) exhibits π – π stacking of parallel benzimidazole ring systems, with a $Cg1 \cdots Cg2$ distance of 3.518 Å [$Cg1$ and $Cg2$ are the centroids of the C3A–C8A benzene ring in one molecule and the C2B/N2/C3A/C8A/N8 imidazole ring in the other molecule, respectively]. Intermolecular C—H \cdots O contacts may also play a role in the stability of the packing.

Experimental

The title compound was prepared from 1-allyl-1*H*-benzimidazole-2-carbaldehyde, *N*-benzylglycine ethyl ester hydrochloride, and triethylamine according to the procedure reported by Meng *et al.* (2007). Colourless blocks of the title compound were obtained by recrystallization from EtOAc/*n*-hexane 1:1 with slow evaporation at room temperature. These crystals were suitable for X-ray crystallography.

Refinement

H atoms were located directly in a difference Fourier map and then allowed to refine freely throughout the final convergence stage. The final structure was refined to convergence [$\Delta/\sigma \leq 0.001$]. The final difference Fourier map was featureless, indicating that the structure is both correct and complete.

Figures

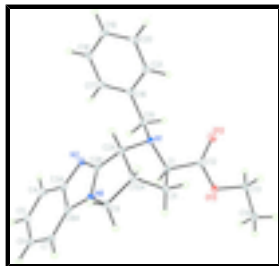


Fig. 1. The molecular structure of the title compound. Ellipsoids are drawn at the 50% probability level. H atoms are represented as small spheres of arbitrary radius.

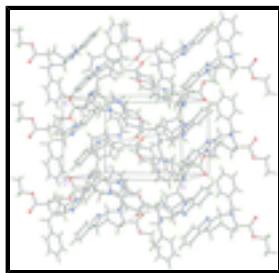


Fig. 2. The crystal packing of the title compound with a view of the C—H...O (dashed lines) and π - π interactions.

ethyl 11-benzyl-1,8,11-triazatetracyclo[7.6.0.0^{2,7}.0^{10,14}]pentadeca- 2(7),3,5,8-tetraene-12-carboxylate

Crystal data

$C_{22}H_{23}N_3O_2$

$M_r = 361.43$

Monoclinic, $P2_1/n$

Hall symbol: -P 2yn

$a = 9.2498$ (5) Å

$b = 13.8999$ (7) Å

$c = 14.2258$ (7) Å

$\beta = 90.345$ (1)°

$V = 1829.00$ (16) Å³

$Z = 4$

$F(000) = 768$

$D_x = 1.313$ Mg m⁻³

Mo $K\alpha$ radiation, $\lambda = 0.71073$ Å

Cell parameters from 7133 reflections

$\theta = 2.6$ – 27.5 °

$\mu = 0.09$ mm⁻¹

$T = 90$ K

Block, colourless

$0.39 \times 0.16 \times 0.13$ mm

Data collection

Bruker SMART1000 CCD area-detector diffractometer

Radiation source: fine-focus sealed tube graphite

ω and φ scans

Absorption correction: numerical (*SADABS*; Blessing, 1995; Sheldrick, 2007)

$T_{\min} = 0.962$, $T_{\max} = 0.989$

16147 measured reflections

4194 independent reflections

3080 reflections with $I > 2\sigma(I)$

$R_{\text{int}} = 0.037$

$\theta_{\text{max}} = 27.5$ °, $\theta_{\text{min}} = 2.1$ °

$h = -12 \rightarrow 12$

$k = -18 \rightarrow 18$

$l = -18 \rightarrow 18$

Refinement

Refinement on F^2	Primary atom site location: structure-invariant direct methods
Least-squares matrix: full	Secondary atom site location: difference Fourier map
$R[F^2 > 2\sigma(F^2)] = 0.037$	Hydrogen site location: inferred from neighbouring sites
$wR(F^2) = 0.095$	All H-atom parameters refined
$S = 1.09$	$w = 1/[\sigma^2(F_o^2) + (0.0417P)^2 + 0.3839P]$
4194 reflections	where $P = (F_o^2 + 2F_c^2)/3$
336 parameters	$(\Delta/\sigma)_{\max} = 0.001$
0 restraints	$\Delta\rho_{\max} = 0.37 \text{ e } \text{\AA}^{-3}$
	$\Delta\rho_{\min} = -0.27 \text{ e } \text{\AA}^{-3}$

Special details

Experimental. A colourless block with approximate orthogonal dimensions $0.39 \times 0.16 \times 0.13 \text{ mm}^3$ was placed and optically centered on the Bruker SMART1000 CCD system at -183°C . The initial unit cell was indexed using a least-squares analysis of a random set of reflections collected from three series of 0.3° wide ω scans, 10 s per frame, and 25 frames per series that were well distributed in reciprocal space. Four ω -scan data frame series were collected [Mo $K\alpha$] with 0.3° wide scans, 30 s per frame and 606, 435, 606, 435 frames collected per series at varying ϕ angles ($\phi = 0^\circ, 90^\circ, 180^\circ, 270^\circ$), respectively.

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. The crystal to detector distance was 4.123 cm, thus providing a complete sphere of data to $2\theta_{\max} = 55.06^\circ$. A total of 23465 reflections were collected and corrected for Lorentz and polarization effects and absorption using Blessing's method (Blessing, 1995) as incorporated into the program *SADABS* with 4390 unique. All crystallographic calculations were performed on a personal computer (PC) with a Pentium 3.20 GHz processor and 1 GB of extended memory. The *SHELXTL* program package was implemented to determine the probable space group and set up the initial files. System symmetry, systematic absences and intensity statistics indicated the centrosymmetric monoclinic non-standard space group $P2_1/n$ (No. 14). The structure was determined by direct methods with the successful location of a majority of the molecule within the asymmetric unit using the program *XS*. The structure was refined with *XL*. The 23465 data collected were merged based upon identical indices yielding 16536 data [$R(\text{int}) = 0.0245$] that were truncated to $2\theta_{\max} = 55.0^\circ$ resulting in 16147 data that were further merged during least-squares refinement to 4194 unique data [$R(\text{int}) = 0.0373$]. A single least-squares difference Fourier cycle was required to locate the remaining non-H atoms. All non-H atoms were refined anisotropically.

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 $F^2 > \sigma(F^2)$ 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 (\AA^2)

x	y	z	$U_{\text{iso}}^*/U_{\text{eq}}$
-----	-----	-----	----------------------------------

supplementary materials

C1	0.11370 (13)	0.83406 (9)	0.93388 (9)	0.0171 (3)
H1	0.1841 (15)	0.8014 (10)	0.8905 (10)	0.016 (3)*
N1	-0.03076 (11)	0.79245 (7)	0.92753 (7)	0.0167 (2)
C2A	-0.02373 (14)	0.70281 (9)	0.98214 (9)	0.0168 (3)
H2A	-0.1230 (16)	0.6828 (10)	0.9972 (10)	0.021 (4)*
C2B	0.05845 (13)	0.61970 (9)	0.93939 (9)	0.0164 (3)
N2	0.04725 (11)	0.56851 (8)	0.86159 (7)	0.0188 (2)
C3A	0.15526 (14)	0.49885 (9)	0.87233 (9)	0.0178 (3)
C4	0.19276 (15)	0.42310 (10)	0.81285 (9)	0.0215 (3)
H4	0.1418 (16)	0.4118 (10)	0.7547 (11)	0.024 (4)*
C5	0.30288 (15)	0.36208 (10)	0.84115 (10)	0.0239 (3)
H5	0.3296 (16)	0.3071 (11)	0.8029 (11)	0.024 (4)*
C6	0.37646 (15)	0.37548 (10)	0.92687 (10)	0.0231 (3)
H6	0.4508 (16)	0.3301 (11)	0.9460 (10)	0.025 (4)*
C7	0.34082 (14)	0.44980 (10)	0.98730 (10)	0.0205 (3)
H7	0.3892 (16)	0.4588 (10)	1.0466 (11)	0.023 (4)*
C8A	0.22957 (14)	0.51062 (9)	0.95859 (9)	0.0176 (3)
N8	0.16544 (11)	0.58997 (8)	0.99883 (7)	0.0173 (2)
C9	0.16669 (15)	0.63878 (10)	1.08991 (9)	0.0191 (3)
H9A	0.2688 (16)	0.6555 (10)	1.1086 (10)	0.021 (4)*
H9B	0.1242 (15)	0.5967 (10)	1.1379 (10)	0.022 (4)*
C10A	0.07245 (14)	0.72792 (9)	1.06910 (9)	0.0180 (3)
H10A	0.0137 (14)	0.7435 (9)	1.1239 (10)	0.013 (3)*
C11	0.15928 (15)	0.81681 (10)	1.03687 (9)	0.0193 (3)
H11A	0.2653 (18)	0.8059 (11)	1.0440 (11)	0.029 (4)*
H11B	0.1335 (16)	0.8755 (11)	1.0745 (11)	0.025 (4)*
C12	0.11502 (14)	0.93996 (9)	0.90881 (9)	0.0182 (3)
O12	0.01249 (10)	0.98789 (7)	0.88602 (7)	0.0248 (2)
C13	0.27147 (16)	1.07485 (10)	0.89143 (10)	0.0225 (3)
H13A	0.2190 (16)	1.1145 (11)	0.9382 (11)	0.023 (4)*
H13B	0.2268 (16)	1.0867 (10)	0.8302 (11)	0.022 (4)*
O13	0.25101 (10)	0.97384 (6)	0.91573 (6)	0.0201 (2)
C14	0.43191 (16)	1.09273 (11)	0.89238 (11)	0.0251 (3)
H14A	0.4769 (18)	1.0798 (12)	0.9539 (13)	0.037 (5)*
H14B	0.4516 (18)	1.1615 (13)	0.8784 (11)	0.038 (5)*
H14C	0.4819 (17)	1.0527 (12)	0.8441 (12)	0.035 (4)*
C15	-0.08571 (14)	0.78122 (10)	0.83087 (9)	0.0179 (3)
H15A	-0.0297 (15)	0.7327 (10)	0.7948 (10)	0.018 (4)*
H15B	-0.0739 (15)	0.8460 (11)	0.8007 (10)	0.018 (4)*
C16	-0.24288 (14)	0.75165 (9)	0.82970 (9)	0.0178 (3)
C17	-0.28700 (15)	0.66465 (10)	0.79108 (9)	0.0205 (3)
H17	-0.2161 (17)	0.6209 (11)	0.7651 (11)	0.030 (4)*
C18	-0.43276 (15)	0.63824 (10)	0.79093 (9)	0.0228 (3)
H18	-0.4629 (16)	0.5773 (11)	0.7644 (11)	0.027 (4)*
C19	-0.53434 (15)	0.69891 (11)	0.83067 (9)	0.0232 (3)
H19	-0.6361 (17)	0.6801 (11)	0.8303 (10)	0.024 (4)*
C20	-0.49157 (15)	0.78651 (10)	0.86906 (9)	0.0224 (3)
H20	-0.5630 (16)	0.8300 (11)	0.8959 (10)	0.022 (4)*
C21	-0.34683 (14)	0.81280 (10)	0.86831 (9)	0.0205 (3)

H21 -0.3146 (16) 0.8746 (11) 0.8952 (10) 0.022 (4)*

Atomic displacement parameters (Å²)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
C1	0.0135 (6)	0.0187 (6)	0.0189 (6)	0.0002 (5)	0.0018 (5)	-0.0014 (5)
N1	0.0149 (5)	0.0182 (6)	0.0170 (5)	-0.0009 (4)	-0.0002 (4)	0.0011 (4)
C2A	0.0146 (6)	0.0196 (7)	0.0161 (6)	-0.0012 (5)	0.0012 (5)	0.0005 (5)
C2B	0.0145 (6)	0.0186 (6)	0.0162 (6)	-0.0027 (5)	0.0009 (5)	0.0025 (5)
N2	0.0194 (6)	0.0191 (6)	0.0180 (5)	0.0006 (4)	0.0011 (4)	0.0000 (4)
C3A	0.0165 (6)	0.0193 (6)	0.0177 (6)	-0.0013 (5)	0.0030 (5)	0.0042 (5)
C4	0.0244 (7)	0.0236 (7)	0.0164 (7)	-0.0002 (6)	0.0044 (5)	0.0006 (5)
C5	0.0251 (7)	0.0226 (7)	0.0242 (7)	0.0017 (6)	0.0096 (6)	0.0001 (6)
C6	0.0172 (7)	0.0221 (7)	0.0300 (8)	0.0013 (6)	0.0049 (6)	0.0053 (6)
C7	0.0159 (7)	0.0225 (7)	0.0230 (7)	-0.0026 (5)	0.0004 (5)	0.0050 (5)
C8A	0.0173 (6)	0.0179 (6)	0.0177 (6)	-0.0027 (5)	0.0028 (5)	0.0026 (5)
N8	0.0170 (6)	0.0184 (5)	0.0165 (5)	-0.0004 (4)	-0.0005 (4)	0.0013 (4)
C9	0.0207 (7)	0.0208 (7)	0.0157 (6)	-0.0023 (5)	-0.0014 (5)	-0.0002 (5)
C10A	0.0179 (6)	0.0216 (7)	0.0146 (6)	-0.0013 (5)	0.0022 (5)	-0.0014 (5)
C11	0.0194 (7)	0.0182 (7)	0.0204 (7)	-0.0005 (5)	-0.0029 (5)	0.0004 (5)
C12	0.0187 (7)	0.0213 (7)	0.0146 (6)	0.0013 (5)	0.0022 (5)	-0.0021 (5)
O12	0.0232 (5)	0.0226 (5)	0.0284 (5)	0.0044 (4)	-0.0022 (4)	0.0015 (4)
C13	0.0289 (8)	0.0154 (7)	0.0233 (7)	-0.0024 (6)	-0.0026 (6)	0.0023 (5)
O13	0.0207 (5)	0.0161 (5)	0.0235 (5)	-0.0020 (4)	0.0003 (4)	0.0015 (4)
C14	0.0297 (8)	0.0199 (7)	0.0257 (8)	-0.0066 (6)	-0.0002 (6)	0.0008 (6)
C15	0.0159 (6)	0.0221 (7)	0.0156 (6)	0.0008 (5)	0.0010 (5)	0.0000 (5)
C16	0.0173 (7)	0.0229 (7)	0.0130 (6)	0.0012 (5)	-0.0013 (5)	0.0031 (5)
C17	0.0201 (7)	0.0248 (7)	0.0164 (6)	0.0032 (6)	-0.0009 (5)	0.0009 (5)
C18	0.0242 (7)	0.0247 (7)	0.0193 (7)	-0.0027 (6)	-0.0052 (5)	0.0014 (6)
C19	0.0165 (7)	0.0322 (8)	0.0209 (7)	-0.0019 (6)	-0.0033 (5)	0.0043 (6)
C20	0.0171 (7)	0.0305 (8)	0.0195 (7)	0.0047 (6)	-0.0005 (5)	0.0010 (6)
C21	0.0206 (7)	0.0232 (7)	0.0177 (6)	0.0010 (6)	-0.0011 (5)	-0.0008 (5)

Geometric parameters (Å, °)

C1—N1	1.4582 (16)	C10A—C11	1.5448 (18)
C1—C12	1.5147 (18)	C10A—H10A	0.977 (14)
C1—C11	1.5409 (18)	C11—H11A	0.997 (16)
C1—H1	1.008 (14)	C11—H11B	1.005 (15)
N1—C2A	1.4696 (16)	C12—O12	1.2019 (16)
N1—C15	1.4714 (16)	C12—O13	1.3462 (15)
C2A—C2B	1.5126 (18)	C13—O13	1.4584 (16)
C2A—C10A	1.5590 (17)	C13—C14	1.505 (2)
C2A—H2A	0.984 (15)	C13—H13A	0.993 (15)
C2B—N2	1.3193 (16)	C13—H13B	0.976 (15)
C2B—N8	1.3620 (16)	C14—H14A	0.983 (18)
N2—C3A	1.3990 (17)	C14—H14B	0.994 (18)
C3A—C4	1.3959 (18)	C14—H14C	0.999 (17)
C3A—C8A	1.4125 (18)	C15—C16	1.5108 (18)

supplementary materials

C4—C5	1.383 (2)	C15—H15A	0.994 (14)
C4—H4	0.963 (16)	C15—H15B	1.004 (15)
C5—C6	1.405 (2)	C16—C17	1.3885 (19)
C5—H5	0.971 (15)	C16—C21	1.3982 (18)
C6—C7	1.385 (2)	C17—C18	1.3973 (19)
C6—H6	0.971 (16)	C17—H17	0.969 (16)
C7—C8A	1.3912 (18)	C18—C19	1.386 (2)
C7—H7	0.961 (15)	C18—H18	0.967 (16)
C8A—N8	1.3785 (16)	C19—C20	1.391 (2)
N8—C9	1.4625 (16)	C19—H19	0.977 (15)
C9—C10A	1.5425 (18)	C20—C21	1.3879 (19)
C9—H9A	1.006 (15)	C20—H20	0.975 (15)
C9—H9B	0.983 (15)	C21—H21	0.986 (15)
N1—C1—C12	112.30 (10)	C9—C10A—H10A	110.0 (8)
N1—C1—C11	104.04 (10)	C11—C10A—H10A	110.6 (8)
C12—C1—C11	111.87 (11)	C2A—C10A—H10A	111.4 (8)
N1—C1—H1	112.2 (8)	C1—C11—C10A	105.48 (10)
C12—C1—H1	106.7 (8)	C1—C11—H11A	112.6 (9)
C11—C1—H1	109.7 (8)	C10A—C11—H11A	111.2 (9)
C1—N1—C2A	105.42 (10)	C1—C11—H11B	108.4 (9)
C1—N1—C15	114.29 (10)	C10A—C11—H11B	111.5 (9)
C2A—N1—C15	114.70 (10)	H11A—C11—H11B	107.8 (12)
N1—C2A—C2B	117.12 (10)	O12—C12—O13	124.14 (12)
N1—C2A—C10A	104.65 (10)	O12—C12—C1	126.49 (12)
C2B—C2A—C10A	101.79 (10)	O13—C12—C1	109.37 (11)
N1—C2A—H2A	108.5 (8)	O13—C13—C14	106.64 (11)
C2B—C2A—H2A	110.1 (9)	O13—C13—H13A	108.1 (9)
C10A—C2A—H2A	114.8 (8)	C14—C13—H13A	112.9 (9)
N2—C2B—N8	114.23 (11)	O13—C13—H13B	108.6 (9)
N2—C2B—C2A	135.40 (12)	C14—C13—H13B	113.1 (9)
N8—C2B—C2A	110.31 (11)	H13A—C13—H13B	107.4 (12)
C2B—N2—C3A	103.25 (11)	C12—O13—C13	116.23 (10)
C4—C3A—N2	129.48 (12)	C13—C14—H14A	112.9 (10)
C4—C3A—C8A	119.52 (12)	C13—C14—H14B	109.8 (10)
N2—C3A—C8A	110.99 (11)	H14A—C14—H14B	106.1 (14)
C5—C4—C3A	118.11 (13)	C13—C14—H14C	111.3 (10)
C5—C4—H4	120.4 (9)	H14A—C14—H14C	108.3 (14)
C3A—C4—H4	121.5 (9)	H14B—C14—H14C	108.2 (13)
C4—C5—C6	121.55 (13)	N1—C15—C16	111.48 (10)
C4—C5—H5	120.6 (9)	N1—C15—H15A	112.1 (8)
C6—C5—H5	117.8 (9)	C16—C15—H15A	108.3 (8)
C7—C6—C5	121.44 (13)	N1—C15—H15B	105.5 (8)
C7—C6—H6	118.8 (9)	C16—C15—H15B	110.3 (8)
C5—C6—H6	119.7 (9)	H15A—C15—H15B	109.2 (11)
C6—C7—C8A	116.70 (13)	C17—C16—C21	118.93 (12)
C6—C7—H7	122.1 (9)	C17—C16—C15	121.45 (12)
C8A—C7—H7	121.2 (9)	C21—C16—C15	119.62 (12)
N8—C8A—C7	133.13 (12)	C16—C17—C18	120.71 (13)
N8—C8A—C3A	104.19 (11)	C16—C17—H17	119.9 (9)

C7—C8A—C3A	122.68 (12)	C18—C17—H17	119.3 (9)
C2B—N8—C8A	107.32 (10)	C19—C18—C17	119.74 (13)
C2B—N8—C9	114.28 (11)	C19—C18—H18	119.8 (9)
C8A—N8—C9	137.56 (11)	C17—C18—H18	120.4 (9)
N8—C9—C10A	101.61 (10)	C18—C19—C20	120.07 (13)
N8—C9—H9A	110.0 (8)	C18—C19—H19	119.4 (9)
C10A—C9—H9A	113.2 (8)	C20—C19—H19	120.6 (9)
N8—C9—H9B	109.8 (9)	C21—C20—C19	119.96 (13)
C10A—C9—H9B	112.6 (9)	C21—C20—H20	119.7 (9)
H9A—C9—H9B	109.4 (12)	C19—C20—H20	120.3 (9)
C9—C10A—C11	113.90 (11)	C20—C21—C16	120.58 (13)
C9—C10A—C2A	106.95 (10)	C20—C21—H21	121.1 (9)
C11—C10A—C2A	103.81 (10)	C16—C21—H21	118.4 (9)

Hydrogen-bond geometry (Å, °)

<i>D</i> —H \cdots <i>A</i>	<i>D</i> —H	H \cdots <i>A</i>	<i>D</i> \cdots <i>A</i>	<i>D</i> —H \cdots <i>A</i>
C11—H11B \cdots O12 ⁱ	1.005 (15)	2.399 (15)	3.3344 (17)	154.5 (12)
C18—H18 \cdots O12 ⁱⁱ	0.968 (15)	2.514 (16)	3.3505 (17)	144.6 (12)

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

Fig. 1

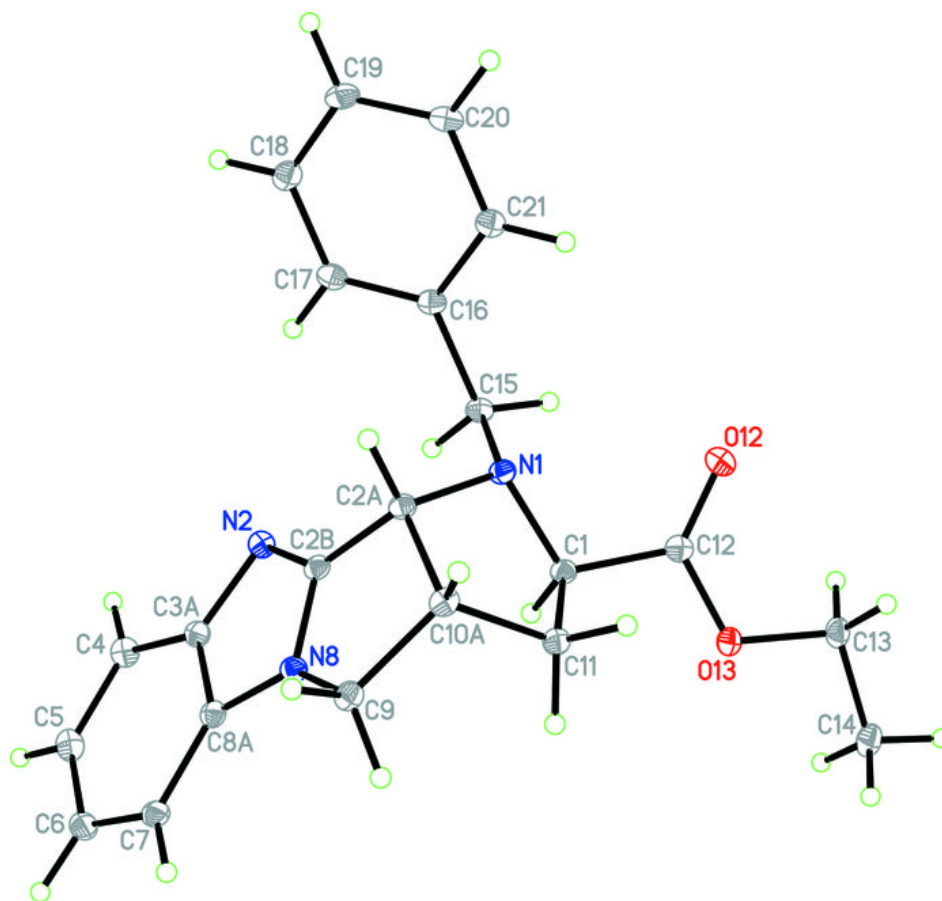


Fig. 2

