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Carbamazepine furfural hemisolvate

Andrea Johnston,[a] Alastair J. Florence[a]* and Alan R. Kennedy[b]

[a]Department of Pharmaceutical Sciences, University of Strathclyde, 27 Taylor Street, Glasgow G4 0NR, Scotland, and [b]WestCHEM, Department of Pure and Applied Chemistry, University of Strathclyde, 295 Cathedral Street, Glasgow G1 1XL, Scotland

Correspondence e-mail: alastair.florence@strath.ac.uk

Key indicators

Single-crystal synchrotron study
T = 120 K
Mean σ(C–C) = 0.002 Å
R factor = 0.056
wR factor = 0.151
Data-to-parameter ratio = 19.2

For details of how these key indicators were automatically derived from the article, see http://journals.iucr.org/e.

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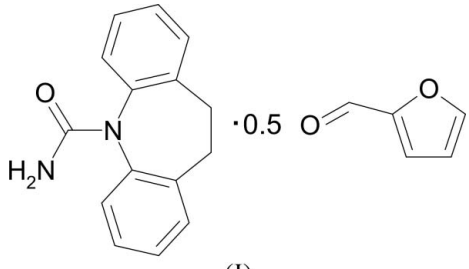
In the title compound, $C_{15}H_{12}N_2O\cdot0.5C_5H_4O_2$, carbamazepine molecules retain the $R_2^2(8)$ N—H···O hydrogen-bonded dimer arrangement observed in the crystal structures of each of the four known anhydrous polymorphs. The furfural molecule is located between adjacent carbamazepine dimers and is hydrogen bonded to only one of the *anti*-oriented NH groups available on the dimer.

Comment

The antiepileptic compound carbamazepine (CBZ) is known to crystallize in at least four anhydrous polymorphic forms (Grzesiak *et al.*, 2003) and the crystal structures of several solvates and co-crystals have also been reported (Fleischman *et al.*, 2003). The title compound, (I), was produced during an automated parallel crystallization polymorph screen on CBZ. The sample was identified as a novel form using multisample X-ray powder diffraction analysis of all recrystallized samples (Florence *et al.*, 2003). Subsequent manual recrystallization from a saturated furfural solution by slow evaporation at 278 K yielded samples of the carbamazepine furfural hemisolvate suitable for synchrotron-based single-crystal X-ray analysis (Cernik *et al.*, 1997).



(I)

The asymmetric unit of (I) contains two molecules of CBZ and one of furfural (Fig. 1). Pairs of CBZ molecules are connected by two N—H···O hydrogen bonds (contacts 1 and 2, Fig. 2) to form the $R_2^2(8)$ dimer motif. This motif is observed in all of the known polymorphs and the majority of CBZ solvate crystal structures (Fleischman *et al.*, 2003). In all other CBZ solvate crystal structures, each of the NH donor groups is involved in hydrogen-bonding interactions; the *syn*-oriented NH group of CBZ forms the dimer motif and the *anti*-oriented NH donors connect to molecules of solvent. In (I), however, only one of the *anti*-oriented NH groups is utilized in a hydrogen bond between CBZ and solvent (contact 3, Fig. 2). The structure also contains four C—H···O interactions: contacts 4, 6 and 7 connect CBZ and furfural molecules, and contact 5 connects molecules of CBZ. The molecules pack

such that the polar groups (furfural and CBZ carboxamide moiety) and hydrophobic azepine rings are segregated into alternating polar and non-polar layers in the *ac* plane, which are stacked in the direction of the *b* axis.

Experimental

A single-crystal sample of the title compound was recrystallized from a furfural solution of carbamazepine (used as supplied from Sigma–Aldrich) by slow evaporation at 278 K.

Crystal data

$C_{15}H_{12}N_2O\cdot0.5C_5H_4O_2$
$M_r = 284.31$
Monoclinic, $P2_1/n$
$a = 5.1815\ (4)$ Å
$b = 26.0450\ (19)$ Å
$c = 20.5735\ (15)$ Å
$\beta = 91.302\ (2)^\circ$
$V = 2775.7\ (4)$ Å^3
$Z = 8$
$D_x = 1.361$ Mg m^{-3}
Synchrotron radiation, $\lambda = 0.6902$ Å
Cell parameters from 4821 reflections
$\theta = 2.5$–29.5°
$\mu = 0.11$ mm^{-1}
$T = 120\ (2)$ K
Plate, brown
$0.04 \times 0.04 \times 0.01$ mm

Data collection

Bruker SMART APEX2 CCD diffractometer
Fine-slice ω scans
Absorption correction: none
28844 measured reflections
8144 independent reflections
5329 reflections with $I > 2\sigma(I)$
$R_{int} = 0.053$
$\theta_{max} = 29.5^\circ$
$h = -7 \rightarrow 7$
$k = -37 \rightarrow 35$
$l = -29 \rightarrow 28$

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.057$
$wR(F^2) = 0.151$
$S = 1.01$
8144 reflections
424 parameters
H atoms treated by a mixture of independent and constrained refinement
$w = 1/[\sigma^2(F_o^2) + (0.0702P)^2 + 0.8667P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} < 0.001$
$\Delta\rho_{max} = 0.30$ e Å^{-3}
$\Delta\rho_{min} = -0.25$ e Å^{-3}

Table 1
Hydrogen-bonding geometry (Å, °).

D—H···A	D—H	H···A	D···A	D—H···A
N2—H1N···O1A^{i}	0.91 (2)	1.91 (2)	2.817 (2)	175 (2)
N2A—H3N···O1^{ii}	0.93 (2)	1.95 (2)	2.876 (2)	175 (2)
N2A—H4N···O3	0.89 (2)	2.13 (2)	2.961 (2)	156 (2)
C3A—H3A···O3^{i}	0.95	2.45	3.250 (2)	142
C13—H13···O1^{ii}	0.95	2.55	3.449 (2)	159
C16—H16···O1A^{iii}	0.95	2.48	3.108 (2)	124
C18—H18···O1	0.95	2.56	3.283 (2)	133

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

The H atoms of the six- and five-membered rings of carbamazepine and furfural were positioned geometrically at distances of 0.95 Å (CH) from the parent C atoms; a riding model was used during the refinement process. The U_{iso}(H) values were constrained to be 1.2 times U_{eq} of the carrier atom. The remaining H atoms were located in a difference synthesis and were refined isotropically [C—H = 0.95 (2)–1.01 (2) Å and N—H = 0.85 (3)–0.93 (2) Å].

Data collection: *APEX2* (Bruker, 2004); cell refinement: *SAINT* (Bruker, 2004); data reduction: *SAINT*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 1997); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *PLATON* (Spek, 2003); software used to prepare material for publication: *SHELXL*97.

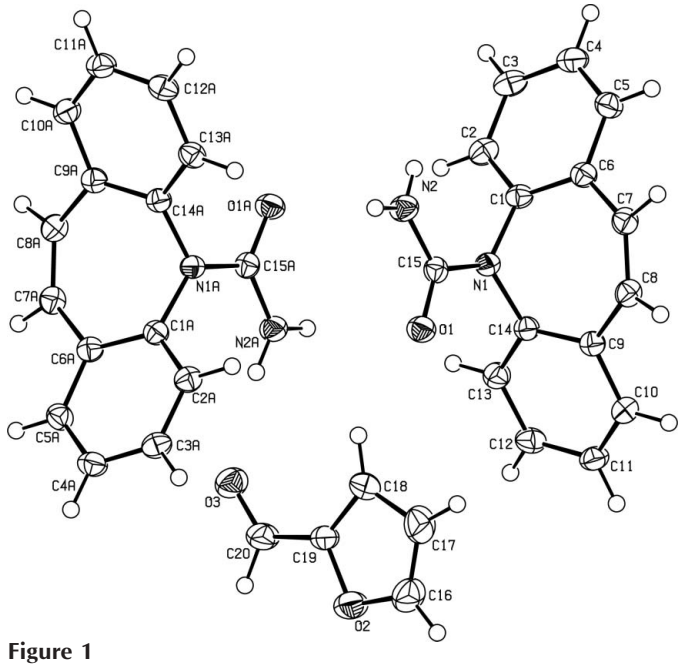


Figure 1
View of the asymmetric unit of (I), showing the atom-numbering scheme. Displacement ellipsoids are drawn at the 50% probability level.

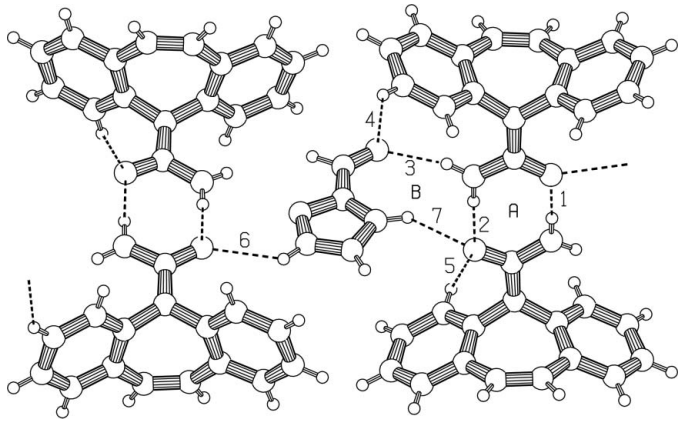


Figure 2
A packing diagram of (I). Dashed lines indicate hydrogen bonds, which produce the two ring motifs, *viz*. *A* [the $R_2^2(8)$ CBZ dimer] and *B* [an $R_3^2(9)$ motif linking one solvent molecule to the dimer].

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References

Bruker (2004). *APEX2* (Version 1.14) and *SAINT* (Version 7.06*a*). Bruker AXS Inc., Madison, Wisconsin, USA.
Cernik, R. J., Clegg, W., Catlow, C. R. A., Bushnell-Wye, G., Flaherty, J. V., Greaves, G. N., Burrows, I., Taylor, D. J., Teat, S. J. & Hamichi, M. (1997). *J. Synchrotron Rad.* **4**, 279–286.

Fleischman, S. G., Kuduva, S. S., McMahon, J. A., Moulton, B., Bailey Walsh, R. D., Rodríguez-Hornedo, N. & Zaworotko, M. J. (2003). *Cryst. Growth Des*. **3**, 909–919.
Florence, A. J., Baumgartner, B., Weston, C., Shankland, N., Kennedy, A. R., Shankland, K. & David, W. I. F. (2003). *J. Pharm. Sci.* **92**, 1930–1938.
Grzesiak, A. L., Lang, M., *Kim*, K. & Matzger, A. J. (2003). *J. Pharm. Sci.* **92**, 2260–2271.
Sheldrick, G. M. (1997). *SHELXS97* and *SHELXL97*. University of Göttingen, Germany.
Spek, A. L. (2003). *J. Appl. Cryst.* **36**, 7–13.

supporting information

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Carbamazepine furfural hemisolvate

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[5*H*-dibenz[b,f]azepine-5-carboxamide]2-furan carboxaldehyde hemisolvate

Crystal data

$C_{15}H_{12}N_2O{\cdot}0.5C_5H_4O_2$
$M_r = 284.31$
Monoclinic, $P2_1/n$
Hall symbol: -P 2yn
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$V = 2775.7$ (4) Å^3
$Z = 8$
$F(000) = 1192$
$D_x = 1.361$ Mg m^{-3}
Synchrotron radiation, $\lambda = 0.6902$ Å
Cell parameters from 4821 reflections
$\theta = 2.5$–29.5°
$\mu = 0.11$ mm^{-1}
$T = 120$ K
Plate, brown
0.04 × 0.04 × 0.01 mm

Data collection

Bruker SMART APEX2 CCD diffractometer
Radiation source: Daresbury SRS station 9.8
Silicon 111 monochromator
fine–slice ω scans
28844 measured reflections
8144 independent reflections
5329 reflections with $I > 2\sigma(I)$
$R_{int} = 0.053$
$\theta_{max} = 29.5°$, $\theta_{min} = 2.1°$
$h = -7\rightarrow7$
$k = -37\rightarrow35$
$l = -29\rightarrow28$

Refinement

Refinement on F^2
Least-squares matrix: full
$R[F^2 > 2\sigma(F^2)] = 0.057$
$wR(F^2) = 0.151$
$S = 1.01$
8144 reflections
424 parameters
0 restraints
Primary atom site location: structure-invariant direct methods
Secondary atom site location: difference Fourier map
Hydrogen site location: inferred from neighbouring sites
H atoms treated by a mixture of independent and constrained refinement
$w = 1/[\sigma^2(F_o^2) + (0.0702P)^2 + 0.8667P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} < 0.001$
$\Delta\rho_{max} = 0.30$ e Å^{-3}
$\Delta\rho_{min} = -0.25$ e Å^{-3}

Special details

Experimental. Collected by EPSRC service at Daresbury 9.8 (ref ssd1023) *SADABS* used to correct for beam decay.
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 $F^2 > \sigma(F^2)$ 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 (Å²)

	x	*y*	*z*	U_{iso}*/U_{eq}
O1	0.8341 (2)	0.29362 (5)	0.68441 (6)	0.0284 (3)
O1A	0.1984 (2)	0.20877 (5)	0.79316 (5)	0.0287 (3)
O2	0.5168 (3)	0.25216 (5)	0.43464 (6)	0.0410 (3)
O3	0.1510 (3)	0.18030 (5)	0.54430 (6)	0.0377 (3)
N1	0.5971 (3)	0.35107 (5)	0.74100 (6)	0.0224 (3)
N1A	0.4025 (3)	0.14454 (5)	0.74050 (6)	0.0222 (3)
N2	0.8039 (3)	0.28321 (6)	0.79348 (7)	0.0284 (3)
N2A	0.1982 (3)	0.21031 (6)	0.68288 (7)	0.0276 (3)
C1	0.5522 (3)	0.37620 (6)	0.80166 (7)	0.0224 (3)
C1A	0.4439 (3)	0.11601 (6)	0.68189 (7)	0.0219 (3)
C2	0.3588 (3)	0.35789 (7)	0.84140 (8)	0.0271 (3)
H2	0.2493	0.3308	0.8267	0.033*
C2A	0.6352 (3)	0.13177 (6)	0.64038 (8)	0.0253 (3)
H2A	0.7449	0.1596	0.6525	0.030*
C3	0.3258 (3)	0.37906 (7)	0.90246 (8)	0.0300 (4)
H3	0.1932	0.3667	0.9295	0.036*
C3A	0.6674 (3)	0.10730 (7)	0.58146 (8)	0.0269 (3)
H3A	0.7984	0.1182	0.5530	0.032*
C4	0.4870 (4)	0.41831 (7)	0.92385 (8)	0.0304 (4)
H4	0.4679	0.4323	0.9661	0.037*
C4A	0.5065 (3)	0.06660 (7)	0.56428 (8)	0.0283 (4)
H4A	0.5260	0.0499	0.5237	0.034*
C5	0.6762 (3)	0.43717 (7)	0.88372 (8)	0.0285 (4)
H5	0.7845	0.4643	0.8988	0.034*
C5A	0.3177 (3)	0.05037 (6)	0.60622 (8)	0.0263 (3)
H5A	0.2085	0.0226	0.5938	0.032*
C6	0.7110 (3)	0.41707 (6)	0.82125 (7)	0.0232 (3)
C6A	0.2846 (3)	0.07406 (6)	0.66663 (7)	0.0227 (3)
C7	0.9094 (3)	0.43923 (6)	0.78026 (8)	0.0256 (3)
H7	1.052 (4)	0.4576 (8)	0.8050 (9)	0.038 (5)*
C7A	0.0888 (3)	0.05455 (6)	0.71016 (8)	0.0252 (3)
H7A	−0.058 (4)	0.0351 (8)	0.6888 (9)	0.035 (5)*
C8	0.9121 (3)	0.44108 (7)	0.71528 (8)	0.0259 (3)
H8	1.051 (4)	0.4588 (8)	0.6966 (10)	0.041 (6)*
C8A	0.0889 (3)	0.05654 (6)	0.77536 (8)	0.0251 (3)
H8A	−0.053 (4)	0.0388 (7)	0.7964 (9)	0.030 (5)*
C9	0.7168 (3)	0.42180 (6)	0.66916 (7)	0.0226 (3)
C9A	0.2869 (3)	0.07840 (6)	0.81901 (7)	0.0226 (3)
C10	0.6857 (3)	0.44599 (6)	0.60853 (8)	0.0262 (3)
H10	0.7969	0.4735	0.5975	0.031*

C10A	0.3206 (3)	0.05800 (6)	0.88163 (8)	0.0263 (3)
H10A	0.2096	0.0313	0.8956	0.032*
C11	0.4949 (3)	0.43036 (7)	0.56454 (8)	0.0278 (3)
H11	0.4776	0.4468	0.5235	0.033*
C11A	0.5132 (3)	0.07599 (7)	0.92360 (8)	0.0279 (3)
H11A	0.5322	0.0618	0.9660	0.033*
C12	0.3294 (3)	0.39068 (7)	0.58046 (8)	0.0292 (4)
H12	0.1951	0.3807	0.5509	0.035*
C12A	0.6784 (3)	0.11470 (7)	0.90386 (8)	0.0276 (3)
H12A	0.8132	0.1264	0.9322	0.033*
C13	0.3597 (3)	0.36551 (7)	0.63944 (8)	0.0269 (3)
H13	0.2468	0.3382	0.6503	0.032*
C13A	0.6456 (3)	0.13617 (6)	0.84264 (8)	0.0250 (3)
H13A	0.7581	0.1627	0.8289	0.030*
C14	0.5553 (3)	0.38026 (6)	0.68259 (7)	0.0220 (3)
C14A	0.4479 (3)	0.11897 (6)	0.80119 (7)	0.0214 (3)
C15	0.7513 (3)	0.30780 (6)	0.73729 (7)	0.0223 (3)
C15A	0.2605 (3)	0.18943 (6)	0.74074 (8)	0.0230 (3)
C16	0.7073 (4)	0.28693 (8)	0.44417 (10)	0.0423 (5)
H16	0.7951	0.3041	0.4105	0.051*
C17	0.7552 (4)	0.29377 (9)	0.50783 (11)	0.0458 (5)
H17	0.8796	0.3164	0.5267	0.055*
C18	0.5852 (4)	0.26083 (7)	0.54221 (9)	0.0336 (4)
H18	0.5730	0.2570	0.5880	0.040*
C19	0.4454 (3)	0.23638 (7)	0.49529 (8)	0.0278 (3)
C20	0.2413 (4)	0.19912 (8)	0.49603 (9)	0.0371 (4)
H20	0.185 (4)	0.1879 (9)	0.4519 (11)	0.046 (6)*
H1N	0.924 (4)	0.2579 (8)	0.7947 (10)	0.040 (6)*
H2N	0.738 (5)	0.2933 (10)	0.8288 (12)	0.058 (8)*
H3N	0.088 (4)	0.2386 (9)	0.6825 (11)	0.044 (6)*
H4N	0.226 (4)	0.1963 (9)	0.6442 (11)	0.043 (6)*

Atomic displacement parameters (Å²)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
O1	0.0326 (6)	0.0281 (6)	0.0245 (6)	0.0052 (5)	0.0000 (5)	−0.0007 (5)
O1A	0.0343 (7)	0.0291 (6)	0.0227 (6)	0.0073 (5)	0.0001 (5)	−0.0017 (5)
O2	0.0488 (8)	0.0477 (8)	0.0267 (7)	−0.0142 (7)	0.0030 (6)	0.0017 (6)
O3	0.0380 (7)	0.0422 (8)	0.0328 (7)	−0.0091 (6)	0.0011 (5)	0.0041 (6)
N1	0.0256 (7)	0.0222 (7)	0.0193 (6)	0.0012 (5)	−0.0006 (5)	0.0010 (5)
N1A	0.0259 (7)	0.0219 (7)	0.0187 (6)	0.0012 (5)	0.0010 (5)	0.0000 (5)
N2	0.0315 (8)	0.0286 (8)	0.0250 (8)	0.0061 (6)	0.0002 (6)	0.0027 (6)
N2A	0.0337 (8)	0.0258 (7)	0.0231 (7)	0.0053 (6)	0.0007 (6)	0.0011 (5)
C1	0.0213 (7)	0.0259 (8)	0.0202 (7)	0.0036 (6)	−0.0010 (6)	0.0016 (6)
C1A	0.0223 (7)	0.0220 (7)	0.0214 (7)	0.0027 (6)	−0.0018 (6)	0.0001 (6)
C2	0.0227 (8)	0.0321 (9)	0.0266 (8)	−0.0005 (6)	−0.0017 (6)	0.0047 (6)
C2A	0.0234 (8)	0.0283 (8)	0.0240 (8)	−0.0007 (6)	0.0001 (6)	0.0015 (6)
C3	0.0256 (8)	0.0401 (10)	0.0245 (8)	0.0046 (7)	0.0033 (6)	0.0056 (7)

C3A	0.0245 (8)	0.0322 (9)	0.0243 (8)	0.0014 (6)	0.0038 (6)	0.0025 (6)
C4	0.0368 (10)	0.0332 (9)	0.0214 (8)	0.0100 (7)	0.0024 (6)	0.0015 (6)
C4A	0.0324 (9)	0.0312 (9)	0.0213 (8)	0.0037 (7)	0.0016 (6)	−0.0028 (6)
C5	0.0350 (9)	0.0266 (8)	0.0238 (8)	0.0038 (7)	−0.0037 (6)	−0.0022 (6)
C5A	0.0272 (8)	0.0261 (8)	0.0254 (8)	−0.0014 (6)	−0.0026 (6)	−0.0024 (6)
C6	0.0235 (8)	0.0239 (8)	0.0222 (7)	0.0036 (6)	−0.0023 (6)	0.0005 (6)
C6A	0.0212 (8)	0.0246 (8)	0.0223 (7)	0.0023 (6)	−0.0007 (6)	0.0011 (6)
C7	0.0244 (8)	0.0254 (8)	0.0269 (8)	−0.0016 (6)	−0.0022 (6)	0.0008 (6)
C7A	0.0219 (8)	0.0255 (8)	0.0280 (8)	−0.0013 (6)	−0.0011 (6)	0.0006 (6)
C8	0.0229 (8)	0.0271 (8)	0.0275 (8)	−0.0030 (6)	−0.0008 (6)	0.0022 (6)
C8A	0.0217 (8)	0.0268 (8)	0.0270 (8)	−0.0006 (6)	0.0021 (6)	0.0016 (6)
C9	0.0223 (8)	0.0233 (8)	0.0221 (7)	0.0012 (6)	0.0007 (6)	0.0000 (6)
C9A	0.0212 (8)	0.0242 (8)	0.0226 (7)	0.0022 (6)	0.0019 (6)	−0.0007 (6)
C10	0.0276 (8)	0.0262 (8)	0.0249 (8)	−0.0007 (6)	0.0016 (6)	0.0031 (6)
C10A	0.0293 (9)	0.0265 (8)	0.0233 (8)	0.0014 (6)	0.0027 (6)	0.0025 (6)
C11	0.0330 (9)	0.0302 (9)	0.0202 (8)	0.0021 (7)	−0.0004 (6)	0.0038 (6)
C11A	0.0321 (9)	0.0304 (9)	0.0212 (8)	0.0053 (7)	−0.0012 (6)	0.0011 (6)
C12	0.0289 (9)	0.0352 (9)	0.0233 (8)	−0.0009 (7)	−0.0052 (6)	−0.0010 (7)
C12A	0.0257 (8)	0.0329 (9)	0.0239 (8)	0.0016 (7)	−0.0038 (6)	−0.0033 (7)
C13	0.0274 (8)	0.0281 (8)	0.0250 (8)	−0.0026 (6)	−0.0010 (6)	0.0007 (6)
C13A	0.0233 (8)	0.0271 (8)	0.0246 (8)	−0.0007 (6)	0.0017 (6)	−0.0031 (6)
C14	0.0232 (8)	0.0224 (7)	0.0204 (7)	0.0018 (6)	0.0004 (6)	0.0001 (6)
C14A	0.0219 (7)	0.0220 (7)	0.0204 (7)	0.0031 (6)	0.0012 (5)	0.0000 (6)
C15	0.0203 (7)	0.0218 (7)	0.0246 (8)	−0.0022 (6)	−0.0014 (6)	−0.0002 (6)
C15A	0.0225 (8)	0.0222 (8)	0.0242 (8)	−0.0008 (6)	0.0003 (6)	0.0008 (6)
C16	0.0411 (11)	0.0443 (12)	0.0415 (11)	−0.0113 (9)	0.0027 (9)	0.0062 (9)
C17	0.0447 (12)	0.0409 (12)	0.0514 (13)	−0.0177 (9)	−0.0092 (9)	0.0000 (9)
C18	0.0391 (10)	0.0353 (10)	0.0262 (9)	−0.0026 (8)	−0.0054 (7)	−0.0027 (7)
C19	0.0316 (9)	0.0313 (9)	0.0205 (8)	−0.0038 (7)	0.0009 (6)	0.0002 (6)
C20	0.0417 (11)	0.0441 (11)	0.0253 (9)	−0.0127 (9)	−0.0039 (7)	−0.0011 (8)

Geometric parameters (Å, º)

O1—C15	1.2351 (19)	C6A—C7A	1.459 (2)
O1A—C15A	1.2395 (19)	C7—C8	1.338 (2)
O2—C16	1.351 (2)	C7—H7	1.01 (2)
O2—C19	1.372 (2)	C7A—C8A	1.342 (2)
O3—C20	1.211 (2)	C7A—H7A	1.01 (2)
N1—C15	1.385 (2)	C8—C9	1.460 (2)
N1—C1	1.433 (2)	C8—H8	0.95 (2)
N1—C14	1.4342 (19)	C8A—C9A	1.463 (2)
N1A—C15A	1.382 (2)	C8A—H8A	0.977 (19)
N1A—C14A	1.4298 (19)	C9—C14	1.399 (2)
N1A—C1A	1.4366 (19)	C9—C10	1.404 (2)
N2—C15	1.344 (2)	C9A—C14A	1.400 (2)
N2—H1N	0.91 (2)	C9A—C10A	1.401 (2)
N2—H2N	0.85 (3)	C10—C11	1.386 (2)
N2A—C15A	1.342 (2)	C10—H10	0.9500

N2A—H4N	0.89 (2)	C10A—C11A	1.386 (2)
N2A—H3N	0.93 (2)	C10A—H10A	0.9500
C1—C2	1.392 (2)	C11—C12	1.387 (2)
C1—C6	1.399 (2)	C11—H11	0.9500
C1A—C2A	1.385 (2)	C11A—C12A	1.389 (2)
C1A—C6A	1.401 (2)	C11A—H11A	0.9500
C2—C3	1.386 (2)	C12—C13	1.385 (2)
C2—H2	0.9500	C12—H12	0.9500
C2A—C3A	1.383 (2)	C12A—C13A	1.385 (2)
C2A—H2A	0.9500	C12A—H12A	0.9500
C3—C4	1.386 (3)	C13—C14	1.386 (2)
C3—H3	0.9500	C13—H13	0.9500
C3A—C4A	1.389 (2)	C13A—C14A	1.392 (2)
C3A—H3A	0.9500	C13A—H13A	0.9500
C4—C5	1.386 (2)	C16—C17	1.339 (3)
C4—H4	0.9500	C16—H16	0.9500
C4A—C5A	1.385 (2)	C17—C18	1.428 (3)
C4A—H4A	0.9500	C17—H17	0.9500
C5—C6	1.403 (2)	C18—C19	1.353 (2)
C5—H5	0.9500	C18—H18	0.9500
C5A—C6A	1.402 (2)	C19—C20	1.436 (2)
C5A—H5A	0.9500	C20—H20	0.99 (2)
C6—C7	1.463 (2)		

C16—O2—C19	106.27 (14)	C7A—C8A—H8A	116.2 (11)
C15—N1—C1	121.68 (13)	C9A—C8A—H8A	115.9 (11)
C15—N1—C14	117.50 (13)	C14—C9—C10	117.74 (14)
C1—N1—C14	117.59 (13)	C14—C9—C8	123.11 (14)
C15A—N1A—C14A	117.90 (13)	C10—C9—C8	119.15 (15)
C15A—N1A—C1A	122.05 (13)	C14A—C9A—C10A	117.68 (14)
C14A—N1A—C1A	117.86 (12)	C14A—C9A—C8A	123.12 (14)
C15—N2—H1N	119.7 (13)	C10A—C9A—C8A	119.20 (15)
C15—N2—H2N	120.6 (17)	C11—C10—C9	120.96 (15)
H1N—N2—H2N	119 (2)	C11—C10—H10	119.5
C15A—N2A—H4N	125.9 (14)	C9—C10—H10	119.5
C15A—N2A—H3N	117.6 (14)	C11A—C10A—C9A	121.17 (16)
H4N—N2A—H3N	115.4 (19)	C11A—C10A—H10A	119.4
C2—C1—C6	121.19 (15)	C9A—C10A—H10A	119.4
C2—C1—N1	119.25 (14)	C10—C11—C12	120.01 (15)
C6—C1—N1	119.49 (14)	C10—C11—H11	120.0
C2A—C1A—C6A	121.29 (14)	C12—C11—H11	120.0
C2A—C1A—N1A	119.14 (14)	C10A—C11A—C12A	120.18 (15)
C6A—C1A—N1A	119.53 (14)	C10A—C11A—H11A	119.9
C3—C2—C1	120.11 (16)	C12A—C11A—H11A	119.9
C3—C2—H2	119.9	C13—C12—C11	120.09 (15)
C1—C2—H2	119.9	C13—C12—H12	120.0
C3A—C2A—C1A	120.42 (15)	C11—C12—H12	120.0
C3A—C2A—H2A	119.8	C13A—C12A—C11A	119.69 (15)

C1A—C2A—H2A	119.8	C13A—C12A—H12A	120.2
C4—C3—C2	119.69 (16)	C11A—C12A—H12A	120.2
C4—C3—H3	120.2	C12—C13—C14	119.77 (16)
C2—C3—H3	120.2	C12—C13—H13	120.1
C2A—C3A—C4A	119.39 (15)	C14—C13—H13	120.1
C2A—C3A—H3A	120.3	C12A—C13A—C14A	120.03 (15)
C4A—C3A—H3A	120.3	C12A—C13A—H13A	120.0
C3—C4—C5	120.11 (16)	C14A—C13A—H13A	120.0
C3—C4—H4	119.9	C13—C14—C9	121.31 (14)
C5—C4—H4	119.9	C13—C14—N1	118.95 (14)
C5A—C4A—C3A	120.17 (15)	C9—C14—N1	119.71 (14)
C5A—C4A—H4A	119.9	C13A—C14A—C9A	121.13 (14)
C3A—C4A—H4A	119.9	C13A—C14A—N1A	119.29 (14)
C4—C5—C6	121.40 (16)	C9A—C14A—N1A	119.53 (14)
C4—C5—H5	119.3	O1—C15—N2	123.20 (15)
C6—C5—H5	119.3	O1—C15—N1	120.29 (14)
C4A—C5A—C6A	121.38 (15)	N2—C15—N1	116.51 (14)
C4A—C5A—H5A	119.3	O1A—C15A—N2A	123.05 (15)
C6A—C5A—H5A	119.3	O1A—C15A—N1A	119.74 (14)
C1—C6—C5	117.42 (15)	N2A—C15A—N1A	117.20 (14)
C1—C6—C7	123.40 (14)	C17—C16—O2	110.46 (18)
C5—C6—C7	119.18 (15)	C17—C16—H16	124.8
C1A—C6A—C5A	117.28 (15)	O2—C16—H16	124.8
C1A—C6A—C7A	123.25 (14)	C16—C17—C18	107.56 (17)
C5A—C6A—C7A	119.47 (15)	C16—C17—H17	126.2
C8—C7—C6	127.84 (15)	C18—C17—H17	126.2
C8—C7—H7	117.6 (11)	C19—C18—C17	104.81 (16)
C6—C7—H7	114.4 (11)	C19—C18—H18	127.6
C8A—C7A—C6A	127.99 (15)	C17—C18—H18	127.6
C8A—C7A—H7A	116.0 (11)	C18—C19—O2	110.89 (15)
C6A—C7A—H7A	115.9 (11)	C18—C19—C20	133.89 (17)
C7—C8—C9	127.88 (16)	O2—C19—C20	115.21 (15)
C7—C8—H8	116.7 (13)	O3—C20—C19	125.49 (17)
C9—C8—H8	115.3 (12)	O3—C20—H20	121.4 (13)
C7A—C8A—C9A	127.76 (15)	C19—C20—H20	113.0 (13)

C15—N1—C1—C2	−83.90 (19)	C9—C10—C11—C12	0.8 (3)
C14—N1—C1—C2	116.94 (16)	C9A—C10A—C11A—C12A	−0.4 (3)
C15—N1—C1—C6	93.10 (18)	C10—C11—C12—C13	−2.1 (3)
C14—N1—C1—C6	−66.05 (19)	C10A—C11A—C12A—C13A	1.7 (3)
C15A—N1A—C1A—C2A	80.79 (19)	C11—C12—C13—C14	0.3 (3)
C14A—N1A—C1A—C2A	−116.38 (16)	C11A—C12A—C13A—C14A	0.0 (2)
C15A—N1A—C1A—C6A	−96.86 (18)	C12—C13—C14—C9	2.9 (3)
C14A—N1A—C1A—C6A	65.96 (19)	C12—C13—C14—N1	−174.91 (15)
C6—C1—C2—C3	−2.0 (2)	C10—C9—C14—C13	−4.2 (2)
N1—C1—C2—C3	174.91 (15)	C8—C9—C14—C13	175.20 (16)
C6A—C1A—C2A—C3A	2.2 (2)	C10—C9—C14—N1	173.66 (14)
N1A—C1A—C2A—C3A	−175.40 (15)	C8—C9—C14—N1	−7.0 (2)

C1—C2—C3—C4	−0.4 (2)	C15—N1—C14—C13	84.83 (18)
C1A—C2A—C3A—C4A	−0.2 (2)	C1—N1—C14—C13	−115.13 (17)
C2—C3—C4—C5	1.6 (3)	C15—N1—C14—C9	−93.05 (18)
C2A—C3A—C4A—C5A	−0.8 (3)	C1—N1—C14—C9	66.99 (19)
C3—C4—C5—C6	−0.5 (3)	C12A—C13A—C14A—C9A	−3.0 (2)
C3A—C4A—C5A—C6A	−0.3 (3)	C12A—C13A—C14A—N1A	174.56 (14)
C2—C1—C6—C5	3.1 (2)	C10A—C9A—C14A—C13A	4.1 (2)
N1—C1—C6—C5	−173.89 (14)	C8A—C9A—C14A—C13A	−175.45 (15)
C2—C1—C6—C7	−177.24 (15)	C10A—C9A—C14A—N1A	−173.41 (14)
N1—C1—C6—C7	5.8 (2)	C8A—C9A—C14A—N1A	7.0 (2)
C4—C5—C6—C1	−1.8 (2)	C15A—N1A—C14A—C13A	−81.11 (19)
C4—C5—C6—C7	178.51 (15)	C1A—N1A—C14A—C13A	115.34 (16)
C2A—C1A—C6A—C5A	−3.2 (2)	C15A—N1A—C14A—C9A	96.46 (17)
N1A—C1A—C6A—C5A	174.42 (14)	C1A—N1A—C14A—C9A	−67.08 (19)
C2A—C1A—C6A—C7A	177.01 (15)	C1—N1—C15—O1	−163.76 (14)
N1A—C1A—C6A—C7A	−5.4 (2)	C14—N1—C15—O1	−4.6 (2)
C4A—C5A—C6A—C1A	2.2 (2)	C1—N1—C15—N2	16.0 (2)
C4A—C5A—C6A—C7A	−177.95 (15)	C14—N1—C15—N2	175.16 (14)
C1—C6—C7—C8	28.6 (3)	C14A—N1A—C15A—O1A	6.8 (2)
C5—C6—C7—C8	−151.69 (18)	C1A—N1A—C15A—O1A	169.65 (14)
C1A—C6A—C7A—C8A	−28.7 (3)	C14A—N1A—C15A—N2A	−173.72 (14)
C5A—C6A—C7A—C8A	151.50 (17)	C1A—N1A—C15A—N2A	−10.9 (2)
C6—C7—C8—C9	0.5 (3)	C19—O2—C16—C17	−0.6 (2)
C6A—C7A—C8A—C9A	−0.6 (3)	O2—C16—C17—C18	0.5 (3)
C7—C8—C9—C14	−28.6 (3)	C16—C17—C18—C19	−0.1 (2)
C7—C8—C9—C10	150.75 (18)	C17—C18—C19—O2	−0.3 (2)
C7A—C8A—C9A—C14A	28.7 (3)	C17—C18—C19—C20	−179.1 (2)
C7A—C8A—C9A—C10A	−150.86 (17)	C16—O2—C19—C18	0.6 (2)
C14—C9—C10—C11	2.3 (2)	C16—O2—C19—C20	179.61 (17)
C8—C9—C10—C11	−177.09 (16)	C18—C19—C20—O3	−1.4 (4)
C14A—C9A—C10A—C11A	−2.4 (2)	O2—C19—C20—O3	179.8 (2)
C8A—C9A—C10A—C11A	177.16 (15)		

Hydrogen-bond geometry (Å, º)

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
N2—H1*N*···O1*A*^{i}	0.91 (2)	1.91 (2)	2.817 (2)	175 (2)
N2*A*—H3*N*···O1^{ii}	0.93 (2)	1.95 (2)	2.876 (2)	175 (2)
N2*A*—H4*N*···O3	0.89 (2)	2.13 (2)	2.961 (2)	156 (2)
C3*A*—H3*A*···O3^{i}	0.95	2.45	3.250 (2)	142
C13—H13···O1^{ii}	0.95	2.55	3.449 (2)	159
C16—H16···O1*A*^{iii}	0.95	2.48	3.108 (2)	124
C18—H18···O1	0.95	2.56	3.283 (2)	133

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