organic compounds

2-(2-Chloropyrimidin-4-yl)-3,5,6,7,8,9-hexahydro-2*H*-1,2,4-triazolo[4,3-*a*]-azepin-3-one

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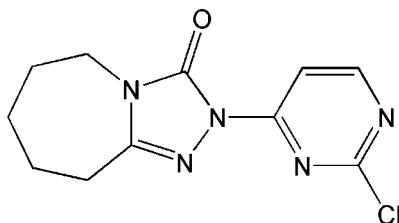Correspondence e-mail: yfling2000cn@yahoo.com.cn

In the title compound, $C_{11}H_{12}ClN_5O$, the triazolone and pyrimidine rings are almost coplanar [dihedral angle = 2.98 (14)°]. The total puckering amplitude Q_T of the seven-membered lactam ring is 0.706 (3) Å.

Related literature

For the applications of pyrimidine derivatives as pesticides and pharmaceutical agents, see: Condon *et al.* (1993); as agrochemicals, see: Maeno *et al.* (1990); as antiviral agents, see: Gilchrist (1997); as herbicides, see: Selby *et al.* (2002). For puckering paramteres, see: Cremer & Pople (1975).

Experimental

Crystal data

$C_{11}H_{12}ClN_5O$	$V = 1203.2$ (4) Å^3
$M_r = 265.71$	$Z = 4$
Monoclinic, $P2_1/n$	Mo $K\alpha$ radiation
$a = 8.6810$ (16) Å	$\mu = 0.31$ mm^{-1}
$b = 14.718$ (3) Å	$T = 294$ (2) K
$c = 9.4251$ (17) Å	$0.24 \times 0.16 \times 0.10$ mm
$\beta = 92.359$ (3)°	

Data collection

Bruker SMART CCD area-detector diffractometer	6734 measured reflections
Absorption correction: multi-scan (*SADABS*; Sheldrick, 1996)	2461 independent reflections
$T_{min} = 0.926$, $T_{max} = 0.969$	1291 reflections with $I > 2\sigma(I)$
	$R_{int} = 0.047$

Refinement

$R[F^2 > 2\sigma(F^2)] = 0.045$	163 parameters
$wR(F^2) = 0.130$	H-atom parameters constrained
$S = 1.01$	$\Delta\rho_{max} = 0.21$ e Å^{-3}
2461 reflections	$\Delta\rho_{min} = -0.23$ e Å^{-3}

Data collection: *SMART* (Bruker, 1999); cell refinement: *SAINT* (Bruker, 1999); data reduction: *SAINT*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 2008); program(s) used to refine structure: *SHELXL97* (Sheldrick, 2008); molecular graphics: *SHELXTL* (Sheldrick, 2008); software used to prepare material for publication: *SHELXTL*.

References

Bruker (1999). *SMART* and *SAINT*. Bruker AXS Inc., Madison, Wisconsin, USA.

Condon, M. E., Brady, T. E., Feist, D., Malefyt, T., Marc, P., Quakenbush, L. S., Rodaway, S. J., Shaner, D. L. & Tecle, B. (1993). *Brighton Crop Protection Conference on Weeds*, pp. 41–46. Alton, Hampshire, England: BCPC Publications.

Cremer, D. & Pople, J. A. (1975). *J. Am. Chem. Soc.* **97**, 1354–1358.

Gilchrist, T. L. (1997). *Heterocyclic Chemistry*, 3rd ed., pp. 261–276. Singapore: Addison Wesley Longman.

Maeno, S., Miura, I., Masuda, K. & Nagata, T. (1990). *Brighton Crop Protection Conference on Pests and Diseases*, pp. 415–422. Alton, Hampshire, England: BCPC Publications.

Selby, T. P., Drumm, J. E., Coats, R. A., Coppo, F. T., Gee, S. K., Hay, J. V., Pasteris, R. J. & Stevenson, T. M. (2002). *ACS Symposium Series*, Vol. 800, *Synthesis and Chemistry of Agrochemicals VI*, pp. 74–84. Washington DC: American Chemical Society.

Sheldrick, G. M. (1996). *SADABS*. University of Göttingen, Germany.

Sheldrick, G. M. (2008). *Acta Cryst.* A**64**, 112–122.

supplementary materials

2-(2-Chloropyrimidin-4-yl)-3,5,6,7,8,9-hexahydro-2*H*-1,2,4-triazolo[4,3-*a*]azepin-3-one

G.-C. Li, L.-Y. Wang, Z.-Y. Li and F.-L. Yang

Comment

Pyrimidine derivatives are very important molecules in biology and have many application in the areas of pesticide and pharmaceutical agents (Condon *et al.*, 1993). For example, imazosulfuron, ethirmol and mepanipyrim have been commercialized as agrochemicals (Maeno *et al.*, 1990). Pyrimidine derivatives have also been developed as antiviral agents, such as azidothymidine (AZT), which is the most widely used anti-AIDS drug (Gilchrist, 1997). Recently, a new series of highly active herbicides of substituted azolylpyrimidines were reported (Selby *et al.*, 2002). In order to discover further biologically active pyrimidine compounds, the title compound, (I), was synthesized and its crystal structure determined (Fig. 1).

In the crystal structure of (I), the triazolone and pyrimidine rings are almost coplanar. The dihedral angle between them is 2.99 (18)°. The total puckering amplitude Q_T (Cremer & Pople, 1975) of the seven-membered lactam ring gives a quantitative evaluation of puckering being 0.706 (3) Å.

Experimental

The reaction of 6,7,8,9-tetrahydro-2*H*-[1,2,4]triazolo[4,3-*a*]azepin-3(5*H*)-one (0.184 g, 1.2 mmol) with 4-(3-chlorophenoxy)-2-chloropyrimidine (0.241 g, 1 mmol) in the precence of potassium carbonate (0.207 g, 1.5 mmol) was carried out in N,*N*-dimethylformamide (20 ml) at 343 K overnight. The reaction was cooled and partitioned between 20 ml dichloromethane and 20 ml water. The aqueous layer was extracted with dichloromethane. After removal of the solvent, colourless crystals were obtained by recrystallization from ethyl acetate solution by slow evaporation (yield 30%).

Refinement

All H atoms were placed in calculated positions, with C—H = 0.93 or 0.97 Å, and refined using a riding model, with $U_{iso}(H)$ = $1.2U_{eq}(C)$.
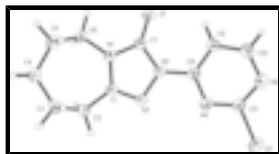
Figures

Fig. 1. The asymmetric unit of (I), with displacement ellipsoids drawn at the 30% probability level.

2-(2-Chloropyrimidin-4-yl)-3,5,6,7,8,9-hexahydro-2*H*-1,2,4- triazolo[4,3-*a*]azepin-3-one

Crystal data

$C_{11}H_{12}ClN_5O$ $F_{000} = 552$

$M_r = 265.71$

Monoclinic, $P2_1/n$

Hall symbol: -P 2yn

$a = 8.6810$ (16) Å

$b = 14.718$ (3) Å

$c = 9.4251$ (17) Å

$\beta = 92.359$ (3)°

$V = 1203.2$ (4) Å^3

$Z = 4$

$D_x = 1.467$ Mg m^{-3}

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

Cell parameters from 1409 reflections

$\theta = 2.6–21.9$°

$\mu = 0.31$ mm^{-1}

$T = 294$ (2) K

Prism, colourless

$0.24 \times 0.16 \times 0.10$ mm

Data collection

Bruker SMART CCD area-detector diffractometer

Radiation source: fine-focus sealed tube

Monochromator: graphite

$T = 294(2)$ K

φ and oω scans

Absorption correction: multi-scan (SADABS; Sheldrick, 1996)

$T_{min} = 0.926$, $T_{max} = 0.969$

6734 measured reflections

2461 independent reflections

1291 reflections with $I > 2\sigma(I)$

$R_{int} = 0.047$

$\theta_{max} = 26.4$°

$\theta_{min} = 2.6$°

$h = -10 \rightarrow 8$

$k = -18 \rightarrow 17$

$l = -11 \rightarrow 11$

Refinement

Refinement on F^2

Least-squares matrix: full

$R[F^2 > 2\sigma(F^2)] = 0.045$

$wR(F^2) = 0.130$

$S = 1.01$

2461 reflections

163 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

$w = 1/[\sigma^2(F_o^2) + (0.0559P)^2 + 0.1252P]$
where $P = (F_o^2 + 2F_c^2)/3$

$(\Delta/\sigma)_{max} = 0.002$

$\Delta\rho_{max} = 0.21$ e Å^{-3}

$\Delta\rho_{min} = -0.23$ 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 $F^2 > \sigma(F^2)$ 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}
Cl1	1.10477 (10)	0.59079 (6)	0.12418 (10)	0.0753 (3)
O1	0.6140 (2)	0.37929 (13)	0.5659 (2)	0.0643 (6)
N1	0.7797 (2)	0.25640 (15)	0.5395 (2)	0.0446 (6)
N2	0.8353 (3)	0.38014 (15)	0.4293 (2)	0.0462 (6)
N3	0.9482 (3)	0.31650 (15)	0.3968 (2)	0.0505 (6)
N4	0.9548 (3)	0.48516 (15)	0.2886 (2)	0.0488 (6)
N5	0.8656 (3)	0.63806 (16)	0.2619 (3)	0.0603 (7)
C1	0.9097 (3)	0.24464 (18)	0.4640 (3)	0.0463 (7)
C2	0.9975 (4)	0.1581 (2)	0.4627 (3)	0.0600 (9)
H2A	1.0848	0.1655	0.4028	0.072*
H2B	0.9318	0.1111	0.4206	0.072*
C3	1.0563 (3)	0.1263 (2)	0.6091 (3)	0.0580 (8)
H3A	1.1356	0.0808	0.5974	0.070*
H3B	1.1035	0.1775	0.6591	0.070*
C4	0.9327 (4)	0.0867 (2)	0.6996 (3)	0.0596 (8)
H4A	0.9824	0.0608	0.7844	0.072*
H4B	0.8829	0.0373	0.6472	0.072*
C5	0.8092 (4)	0.1522 (2)	0.7447 (3)	0.0582 (8)
H5A	0.7464	0.1216	0.8127	0.070*
H5B	0.8593	0.2029	0.7933	0.070*
C6	0.7045 (3)	0.18922 (19)	0.6280 (3)	0.0517 (8)
H6A	0.6676	0.1394	0.5684	0.062*
H6B	0.6157	0.2171	0.6696	0.062*
C7	0.7269 (3)	0.34300 (19)	0.5188 (3)	0.0456 (7)
C8	0.8418 (3)	0.46838 (18)	0.3766 (3)	0.0431 (7)
C9	0.7356 (3)	0.53480 (18)	0.4117 (3)	0.0492 (7)
H9	0.6562	0.5230	0.4723	0.059*
C10	0.7550 (4)	0.6178 (2)	0.3520 (3)	0.0601 (9)
H10	0.6869	0.6637	0.3752	0.072*
C11	0.9571 (3)	0.5687 (2)	0.2385 (3)	0.0502 (7)

Atomic displacement parameters ($Å^2$)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
Cl1	0.0592 (6)	0.0746 (6)	0.0940 (7)	−0.0024 (5)	0.0242 (5)	0.0263 (5)
O1	0.0519 (13)	0.0689 (14)	0.0746 (14)	0.0205 (11)	0.0324 (11)	0.0145 (11)
N1	0.0400 (14)	0.0512 (14)	0.0438 (13)	0.0063 (11)	0.0147 (11)	0.0071 (11)
N2	0.0433 (14)	0.0459 (14)	0.0508 (14)	0.0082 (11)	0.0167 (11)	0.0065 (11)
N3	0.0451 (15)	0.0494 (14)	0.0587 (15)	0.0120 (12)	0.0224 (12)	0.0085 (12)
N4	0.0409 (14)	0.0527 (15)	0.0535 (15)	0.0011 (11)	0.0097 (12)	0.0097 (12)
N5	0.0670 (19)	0.0487 (15)	0.0658 (17)	0.0016 (13)	0.0091 (14)	0.0049 (13)
C1	0.0444 (17)	0.0501 (17)	0.0456 (16)	0.0077 (14)	0.0171 (13)	0.0042 (14)

C2	0.062 (2)	0.0566 (18)	0.064 (2)	0.0175 (16)	0.0283 (16)	0.0089 (16)
C3	0.0465 (19)	0.0531 (18)	0.075 (2)	0.0107 (15)	0.0113 (16)	0.0119 (16)
C4	0.058 (2)	0.0604 (19)	0.0612 (19)	0.0065 (16)	0.0093 (16)	0.0161 (16)
C5	0.060 (2)	0.067 (2)	0.0485 (17)	0.0048 (16)	0.0130 (15)	0.0141 (16)
C6	0.0426 (17)	0.0586 (18)	0.0551 (18)	−0.0039 (15)	0.0166 (14)	0.0098 (15)
C7	0.0424 (17)	0.0532 (17)	0.0418 (16)	0.0049 (14)	0.0102 (13)	0.0054 (14)
C8	0.0407 (16)	0.0493 (17)	0.0393 (16)	−0.0002 (13)	0.0015 (13)	0.0012 (13)
C9	0.0495 (18)	0.0514 (18)	0.0472 (17)	0.0023 (15)	0.0100 (14)	−0.0039 (14)
C10	0.070 (2)	0.0496 (18)	0.061 (2)	0.0104 (17)	0.0104 (18)	−0.0016 (16)
C11	0.0445 (18)	0.0543 (19)	0.0520 (18)	−0.0051 (15)	0.0045 (14)	0.0060 (15)

Geometric parameters (Å, °)

Cl1—C11	1.739 (3)	C2—H2B	0.9700
O1—C7	1.216 (3)	C3—C4	1.514 (4)
N1—C7	1.366 (3)	C3—H3A	0.9700
N1—C1	1.370 (3)	C3—H3B	0.9700
N1—C6	1.465 (3)	C4—C5	1.516 (4)
N2—C8	1.392 (3)	C4—H4A	0.9700
N2—N3	1.399 (3)	C4—H4B	0.9700
N2—C7	1.400 (3)	C5—C6	1.500 (4)
N3—C1	1.284 (3)	C5—H5A	0.9700
N4—C11	1.318 (3)	C5—H5B	0.9700
N4—C8	1.333 (3)	C6—H6A	0.9700
N5—C11	1.317 (4)	C6—H6B	0.9700
N5—C10	1.341 (4)	C8—C9	1.393 (4)
C1—C2	1.485 (4)	C9—C10	1.358 (4)
C2—C3	1.525 (4)	C9—H9	0.9300
C2—H2A	0.9700	C10—H10	0.9300
C7—N1—C1	108.8 (2)	H4A—C4—H4B	107.4
C7—N1—C6	123.8 (2)	C6—C5—C4	116.1 (2)
C1—N1—C6	127.4 (2)	C6—C5—H5A	108.3
C8—N2—N3	120.5 (2)	C4—C5—H5A	108.3
C8—N2—C7	128.1 (2)	C6—C5—H5B	108.3
N3—N2—C7	111.4 (2)	C4—C5—H5B	108.3
C1—N3—N2	104.1 (2)	H5A—C5—H5B	107.4
C11—N4—C8	114.7 (2)	N1—C6—C5	113.1 (2)
C11—N5—C10	112.7 (2)	N1—C6—H6A	109.0
N3—C1—N1	112.9 (2)	C5—C6—H6A	109.0
N3—C1—C2	124.0 (2)	N1—C6—H6B	109.0
N1—C1—C2	123.2 (2)	C5—C6—H6B	109.0
C1—C2—C3	114.1 (2)	H6A—C6—H6B	107.8
C1—C2—H2A	108.7	O1—C7—N1	128.9 (2)
C3—C2—H2A	108.7	O1—C7—N2	128.3 (3)
C1—C2—H2B	108.7	N1—C7—N2	102.8 (2)
C3—C2—H2B	108.7	N4—C8—N2	115.9 (2)
H2A—C2—H2B	107.6	N4—C8—C9	121.9 (3)
C4—C3—C2	114.1 (3)	N2—C8—C9	122.2 (2)
C4—C3—H3A	108.7	C10—C9—C8	116.0 (3)

C2—C3—H3A	108.7	C10—C9—H9	122.0
C4—C3—H3B	108.7	C8—C9—H9	122.0
C2—C3—H3B	108.7	N5—C10—C9	124.5 (3)
H3A—C3—H3B	107.6	N5—C10—H10	117.8
C3—C4—C5	116.0 (3)	C9—C10—H10	117.8
C3—C4—H4A	108.3	N5—C11—N4	130.2 (3)
C5—C4—H4A	108.3	N5—C11—Cl1	115.1 (2)
C3—C4—H4B	108.3	N4—C11—Cl1	114.7 (2)
C5—C4—H4B	108.3		
C8—N2—N3—C1	178.5 (2)	C6—N1—C7—N2	179.7 (2)
C7—N2—N3—C1	−0.2 (3)	C8—N2—C7—O1	2.1 (5)
N2—N3—C1—N1	−0.3 (3)	N3—N2—C7—O1	−179.3 (3)
N2—N3—C1—C2	−179.5 (3)	C8—N2—C7—N1	−177.9 (3)
C7—N1—C1—N3	0.8 (3)	N3—N2—C7—N1	0.7 (3)
C6—N1—C1—N3	−179.7 (3)	C11—N4—C8—N2	179.0 (2)
C7—N1—C1—C2	179.9 (3)	C11—N4—C8—C9	0.0 (4)
C6—N1—C1—C2	−0.6 (4)	N3—N2—C8—N4	3.9 (4)
N3—C1—C2—C3	120.7 (3)	C7—N2—C8—N4	−177.6 (2)
N1—C1—C2—C3	−58.3 (4)	N3—N2—C8—C9	−177.1 (2)
C1—C2—C3—C4	75.0 (4)	C7—N2—C8—C9	1.4 (4)
C2—C3—C4—C5	−65.9 (4)	N4—C8—C9—C10	−0.6 (4)
C3—C4—C5—C6	66.4 (4)	N2—C8—C9—C10	−179.6 (3)
C7—N1—C6—C5	−122.9 (3)	C11—N5—C10—C9	−1.2 (5)
C1—N1—C6—C5	57.7 (4)	C8—C9—C10—N5	1.3 (5)
C4—C5—C6—N1	−73.1 (4)	C10—N5—C11—N4	0.4 (5)
C1—N1—C7—O1	179.1 (3)	C10—N5—C11—Cl1	−179.2 (2)
C6—N1—C7—O1	−0.4 (5)	C8—N4—C11—N5	0.1 (5)
C1—N1—C7—N2	−0.8 (3)	C8—N4—C11—Cl1	179.8 (2)

Fig. 1