Acta Crystallographica Section E
Structure Reports Online
ISSN 1600-5368

1-[(6-Chloro-3-pyridyl)methyl]-5-ethoxy-8-nitro-1,2,3,5,6,7-hexahydroimidazo-[1,2-*a*]pyridine

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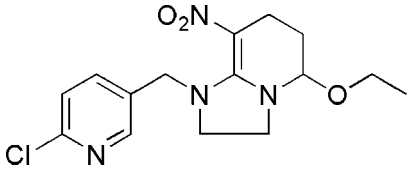
Received 26 July 2009; accepted 17 September 2009

Key indicators: single-crystal X-ray study; T = 290 K; mean σ(C–C) = 0.004 Å; R factor = 0.049; wR factor = 0.135; data-to-parameter ratio = 16.6.

In the title compound, $C_{15}H_{19}ClN_4O_3$, an active agrochemical possessing insecticidal activity, the dihedral angle between the mean planes passing through the pyridine ring and the five-membered ring is 87.3 (2)°. The fused pyridine ring adopts a twisted sofa conformation. The molecular structure features close intramolecular C—H···N and C—H···O hydrogen bonding.

Related literature

For related literature, see: Kagabu *et al.* (2002); Moriya *et al.* (1992); Tian *et al.* (2007); Tokumitsu (1990).



Experimental

Crystal data

$C_{15}H_{19}ClN_4O_3$
M_r = 338.79
Monoclinic, $P2_1/c$
a = 17.021 (3) Å
b = 5.5737 (8) Å
c = 18.334 (3) Å
β = 112.097 (3)°
V = 1611.6 (4) Å^3
Z = 4
Mo $K\alpha$ radiation
μ = 0.26 mm^{-1}
T = 290 K
0.50 × 0.24 × 0.12 mm

Data collection

Bruker SMART CCD area-detector diffractometer
Absorption correction: multi-scan (*SADABS*; Bruker, 1997)
T_{min} = 0.922, T_{max} = 0.969
8970 measured reflections
3486 independent reflections
1870 reflections with $I > 2\sigma(I)$
R_{int} = 0.082

Refinement

$R[F^2 > 2\sigma(F^2)]$ = 0.049
$wR(F^2)$ = 0.135
S = 0.82
3486 reflections
210 parameters
H-atom parameters constrained
$\Delta\rho_{max}$ = 0.32 e Å^{-3}
$\Delta\rho_{min}$ = −0.24 e Å^{-3}

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

D—H···A	D—H	H···A	D···A	D—H···A
C11—H11B···O3	0.97	2.35	2.803 (3)	108
C13—H13···N1	0.93	2.54	2.891 (3)	103

Data collection: *SMART* (Bruker, 1997); cell refinement: *SAINT* (Bruker, 1997); data reduction: *SAINT*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 2008); program(s) used to refine structure: *SHELXL97* (Sheldrick, 2008); molecular graphics: *ORTEP-3* (Farrugia, 1997); software used to prepare material for publication: *SHELXTL* (Sheldrick, 2008).

The authors thank the Opening Fund of Shanghai Key Laboratory of Chemical Biology (grant No. SKLCB-2008-08) and the Doctoral Foundation of the University of Jinan (grant No. XBS0823, B0542) for financial support.

Supplementary data and figures for this paper are available from the IUCr electronic archives (Reference: BX2230).

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supporting information

Acta Cryst. (2009). E**65**, o2517 [doi:10.1107/S1600536809037660]

1-[(6-Chloro-3-pyridyl)methyl]-5-ethoxy-8-nitro-1,2,3,5,6,7-hexahydro-imidazo[1,2-*a*]pyridine

Zhongzhen Tian, Dongmei Li and Zhong Li

S1. Comment

Since the debut of Imidacloprid in the 1990 decade (Moriya *et al.*, 1992), neonicotinoid insecticides have become rapidly an important chemical class of insecticides. Nitromethylene compounds (Kagabu *et al.*, 2002) exhibited remarkably higher biological activity but poor photostability compared with Imidacloprid. Our synthetic interest was introducing dicyclic ring into the lead structure to improve its photostability and synthesizing a series of new compounds, in which compound (I) exhibited good insecticidal activities against pea aphids and was slightly weaker than that of imidacloprid (Tian *et al.*, 2007).The dihedral angle between the mean planes passing through the pyridine ring and the five membered ring is 87.3 (2)°. The six membered N2/C3/C4/C5/C6/C7 ring adopts a twist sofa conformation. The title compound $C_{15}H_{19}ClN_4O_3$, is an active agrochemical possessing insecticidal activity. The dihedral angle between the mean planes passing through the pyridine ring and the five membered ring is 87.3 (2)°. The six membered N2/C3/C4/C5/C6/C7 ring adopts a twist sofa conformation.The molecular structure is stabilized by intramolecular C— H··· N and C— H··· O hydrogen bond, Table 1.

S2. Experimental

The synthesis of the title compoud was following the reported method by Tokumitsu, 1990. Single crystals suitable for X-ray analysis were obtained by slow evaporation of the solution of dichloromethane and petroleum ether of the title compound. m.p. 399.8–400.8 K.

S3. Refinement

H atoms were positioned geometrically and included in the refinement in the riding-model approximation, with C—H = 0.93 Å and U_{iso}(H) = 1.2 U_{eq}(C) for pyridine H atoms, C—H = 0.97 Å and U_{iso}(H) = 1.2 U_{eq}(C) for the methylene H atoms, C—H = 0.96 Å and U_{iso}(H) = 1.5 U_{eq}(C) for the methyl H atoms, C—H = 0.98 Å and U_{iso}(H) = 1.2 U_{eq}(C) for the methenyl H atoms

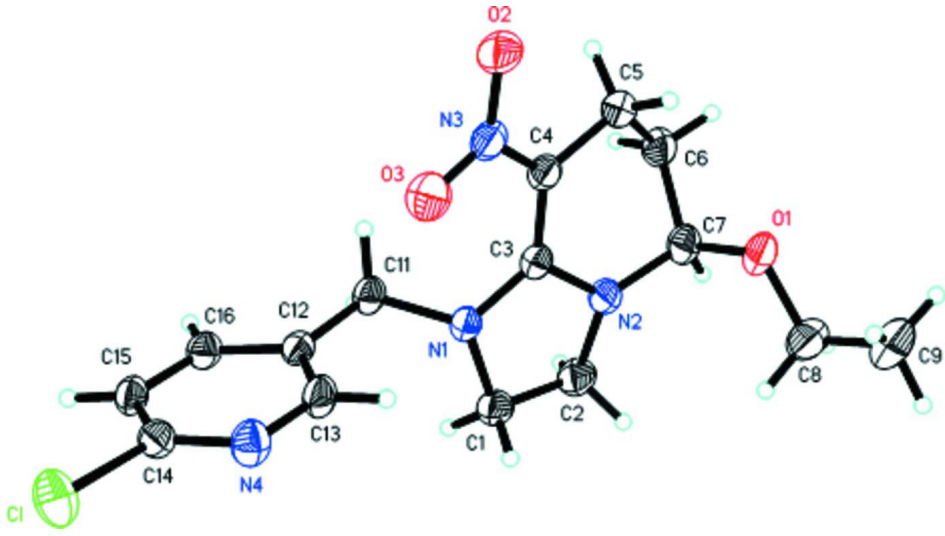

Figure 1

The molecular structure of (*a*) with atom numbering scheme. Displacement ellipsoids are drawn at the 30% probability level. The H atoms are shown as circles of arbitrary size and intramolecular hydrogen bonds are indicated by dotted lines.

1-[(6-Chloro-3-pyridyl)methyl]-5-ethoxy-8-nitro-1,2,3,5,6,7- hexahydroimidazo[1,2-*a*]pyridine

Crystal data

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$b = 5.5737\ (8)$ Å
$c = 18.334\ (3)$ Å
$\beta = 112.097\ (3)°$
$V = 1611.6\ (4)$ Å^3
$Z = 4$
$F(000) = 712$
$D_x = 1.396$ Mg m^{-3}
Mo $K\alpha$ radiation, $\lambda = 0.71073$ Å
Cell parameters from 1727 reflections
$\theta = 4.8–47.4°$
$\mu = 0.26$ mm^{-1}
$T = 290$ K
Prismatic, colourless
0.50 × 0.24 × 0.12 mm

Data collection

Bruker SMART CCD area-detector diffractometer
Radiation source: fine-focus sealed tube
Graphite monochromator
φ and ω scans
Absorption correction: multi-scan (*SADABS*; Bruker, 1997)
$T_{min} = 0.922$, $T_{max} = 0.969$
8970 measured reflections
3486 independent reflections
1870 reflections with $I > 2\sigma(I)$
$R_{int} = 0.082$
$\theta_{max} = 27.0°$, $\theta_{min} = 1.3°$
$h = -21\rightarrow21$
$k = -7\rightarrow7$
$l = -23\rightarrow13$

Refinement

Refinement on F^2
Least-squares matrix: full
$R[F^2 > 2\sigma(F^2)] = 0.049$
$wR(F^2) = 0.135$
$S = 0.82$
3486 reflections
210 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-atom parameters constrained

$w = 1/[\sigma^2(F_o^2) + (0.069P)^2]$
where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} = 0.044$
$\Delta\rho_{max} = 0.32$ e Å^{-3}
$\Delta\rho_{min} = -0.24$ e Å^{-3}
Extinction correction: *SHELXL97* (Sheldrick, 2008), $Fc^* = kFc[1+0.001xFc^2\lambda^3/\sin(2\theta)]^{-1/4}$
Extinction coefficient: 0.020 (2)

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}
Cl	1.20916 (4)	0.34129 (13)	0.43476 (5)	0.0742 (3)
O1	0.58663 (11)	0.9036 (4)	0.35790 (10)	0.0669 (5)
O2	0.69588 (12)	0.4707 (4)	0.16844 (11)	0.0739 (6)
O3	0.81680 (12)	0.5033 (3)	0.26680 (11)	0.0653 (5)
N1	0.84352 (11)	0.9213 (3)	0.35853 (10)	0.0428 (5)
N2	0.71934 (11)	1.0384 (4)	0.35902 (11)	0.0484 (5)
N3	0.74299 (13)	0.5777 (4)	0.22900 (12)	0.0517 (5)
N4	1.05820 (12)	0.4680 (4)	0.42526 (12)	0.0542 (5)
C1	0.86309 (14)	1.0659 (5)	0.43064 (14)	0.0528 (6)
H1A	0.9076	1.1814	0.4361	0.063*
H1B	0.8806	0.9645	0.4770	0.063*
C2	0.77991 (15)	1.1909 (5)	0.41832 (15)	0.0594 (7)
H2A	0.7687	1.1946	0.4664	0.071*
H2B	0.7793	1.3533	0.3991	0.071*
C3	0.75815 (13)	0.9028 (4)	0.32102 (13)	0.0406 (5)
C4	0.71043 (14)	0.7723 (4)	0.25471 (13)	0.0451 (6)
C5	0.61813 (14)	0.8220 (5)	0.21354 (14)	0.0582 (7)
H5A	0.5857	0.6921	0.2236	0.070*
H5B	0.6045	0.8293	0.1572	0.070*
C6	0.59349 (15)	1.0563 (5)	0.24097 (15)	0.0602 (7)
H6A	0.5322	1.0689	0.2210	0.072*
H6B	0.6150	1.1890	0.2197	0.072*
C7	0.62807 (15)	1.0737 (5)	0.32935 (15)	0.0552 (7)
H7	0.6161	1.2340	0.3445	0.066*
C8	0.59553 (18)	0.9382 (6)	0.43754 (16)	0.0753 (9)
H8A	0.5732	1.0941	0.4433	0.090*
H8B	0.6551	0.9334	0.4715	0.090*
C9	0.5492 (2)	0.7483 (7)	0.46073 (19)	0.1023 (12)
H9A	0.4896	0.7620	0.4299	0.123*
H9B	0.5587	0.7652	0.5155	0.123*
H9C	0.5691	0.5940	0.4519	0.123*

C11	0.89956 (13)	0.9436 (4)	0.31525 (13)	0.0455 (6)
H11A	0.9131	1.1118	0.3130	0.055*
H11B	0.8695	0.8891	0.2617	0.055*
C12	0.98050 (13)	0.8050 (4)	0.35017 (12)	0.0393 (5)
C13	0.98935 (14)	0.6091 (4)	0.39838 (13)	0.0490 (6)
H13	0.9443	0.5719	0.4134	0.059*
C14	1.12093 (14)	0.5302 (4)	0.40378 (13)	0.0454 (6)
C15	1.12235 (14)	0.7269 (4)	0.35956 (13)	0.0465 (6)
H15	1.1699	0.7651	0.3486	0.056*
C16	1.05008 (14)	0.8655 (4)	0.33212 (13)	0.0462 (6)
H16	1.0480	1.0000	0.3014	0.055*

Atomic displacement parameters (Å²)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
Cl	0.0596 (4)	0.0681 (5)	0.0967 (6)	0.0181 (3)	0.0313 (4)	0.0041 (4)
O1	0.0668 (11)	0.0879 (15)	0.0610 (12)	−0.0114 (10)	0.0413 (10)	−0.0097 (10)
O2	0.0778 (12)	0.0823 (14)	0.0702 (13)	−0.0259 (11)	0.0374 (11)	−0.0376 (11)
O3	0.0691 (12)	0.0575 (12)	0.0737 (13)	0.0125 (9)	0.0320 (10)	−0.0075 (9)
N1	0.0411 (11)	0.0494 (12)	0.0425 (11)	−0.0023 (8)	0.0210 (9)	−0.0026 (9)
N2	0.0439 (11)	0.0575 (13)	0.0477 (12)	0.0013 (9)	0.0216 (9)	−0.0130 (10)
N3	0.0583 (13)	0.0558 (13)	0.0503 (13)	−0.0090 (11)	0.0311 (11)	−0.0095 (11)
N4	0.0553 (12)	0.0513 (13)	0.0624 (14)	0.0059 (10)	0.0293 (11)	0.0106 (10)
C1	0.0529 (14)	0.0594 (16)	0.0473 (14)	−0.0102 (12)	0.0201 (12)	−0.0093 (12)
C2	0.0641 (16)	0.0623 (18)	0.0556 (16)	−0.0076 (13)	0.0269 (13)	−0.0186 (13)
C3	0.0447 (13)	0.0413 (13)	0.0407 (13)	0.0016 (10)	0.0216 (11)	0.0027 (10)
C4	0.0475 (13)	0.0493 (15)	0.0436 (14)	−0.0033 (11)	0.0231 (11)	−0.0055 (11)
C5	0.0476 (14)	0.081 (2)	0.0484 (15)	−0.0038 (13)	0.0204 (12)	−0.0060 (13)
C6	0.0466 (14)	0.082 (2)	0.0545 (16)	0.0109 (13)	0.0218 (12)	0.0084 (14)
C7	0.0500 (14)	0.0604 (17)	0.0626 (17)	0.0079 (12)	0.0297 (13)	−0.0033 (13)
C8	0.0739 (19)	0.104 (3)	0.0543 (18)	0.0098 (17)	0.0314 (15)	0.0030 (17)
C9	0.111 (3)	0.143 (3)	0.071 (2)	−0.020 (2)	0.055 (2)	0.006 (2)
C11	0.0480 (13)	0.0474 (14)	0.0479 (14)	−0.0009 (11)	0.0257 (11)	0.0059 (11)
C12	0.0426 (12)	0.0410 (13)	0.0379 (12)	−0.0033 (10)	0.0193 (10)	−0.0017 (10)
C13	0.0483 (14)	0.0533 (16)	0.0545 (15)	−0.0001 (11)	0.0299 (12)	0.0080 (12)
C14	0.0433 (13)	0.0477 (15)	0.0453 (14)	0.0016 (11)	0.0167 (11)	−0.0066 (11)
C15	0.0435 (13)	0.0538 (15)	0.0494 (14)	−0.0068 (11)	0.0257 (11)	−0.0048 (12)
C16	0.0488 (14)	0.0493 (14)	0.0451 (14)	−0.0073 (11)	0.0230 (11)	0.0045 (11)

Geometric parameters (Å, º)

Cl—C14	1.745 (2)	C5—H5A	0.9700
O1—C7	1.396 (3)	C5—H5B	0.9700
O1—C8	1.423 (3)	C6—C7	1.505 (4)
O2—N3	1.250 (2)	C6—H6A	0.9700
O3—N3	1.255 (2)	C6—H6B	0.9700
N1—C3	1.358 (3)	C7—H7	0.9800
N1—C11	1.458 (3)	C8—C9	1.475 (4)

N1—C1	1.475 (3)	C8—H8A	0.9700
N2—C3	1.356 (3)	C8—H8B	0.9700
N2—C7	1.453 (3)	C9—H9A	0.9600
N2—C2	1.457 (3)	C9—H9B	0.9600
N3—C4	1.379 (3)	C9—H9C	0.9600
N4—C14	1.316 (3)	C11—C12	1.497 (3)
N4—C13	1.342 (3)	C11—H11A	0.9700
C1—C2	1.517 (3)	C11—H11B	0.9700
C1—H1A	0.9700	C12—C13	1.377 (3)
C1—H1B	0.9700	C12—C16	1.386 (3)
C2—H2A	0.9700	C13—H13	0.9300
C2—H2B	0.9700	C14—C15	1.369 (3)
C3—C4	1.387 (3)	C15—C16	1.378 (3)
C4—C5	1.491 (3)	C15—H15	0.9300
C5—C6	1.514 (4)	C16—H16	0.9300

C7—O1—C8	114.8 (2)	H6A—C6—H6B	108.0
C3—N1—C11	121.70 (18)	O1—C7—N2	112.8 (2)
C3—N1—C1	109.47 (18)	O1—C7—C6	108.2 (2)
C11—N1—C1	117.89 (18)	N2—C7—C6	108.9 (2)
C3—N2—C7	122.79 (19)	O1—C7—H7	108.9
C3—N2—C2	111.33 (18)	N2—C7—H7	108.9
C7—N2—C2	123.86 (19)	C6—C7—H7	108.9
O2—N3—O3	120.5 (2)	O1—C8—C9	109.7 (3)
O2—N3—C4	118.2 (2)	O1—C8—H8A	109.7
O3—N3—C4	121.2 (2)	C9—C8—H8A	109.7
C14—N4—C13	115.5 (2)	O1—C8—H8B	109.7
N1—C1—C2	103.53 (17)	C9—C8—H8B	109.7
N1—C1—H1A	111.1	H8A—C8—H8B	108.2
C2—C1—H1A	111.1	C8—C9—H9A	109.5
N1—C1—H1B	111.1	C8—C9—H9B	109.5
C2—C1—H1B	111.1	H9A—C9—H9B	109.5
H1A—C1—H1B	109.0	C8—C9—H9C	109.5
N2—C2—C1	101.66 (19)	H9A—C9—H9C	109.5
N2—C2—H2A	111.4	H9B—C9—H9C	109.5
C1—C2—H2A	111.4	N1—C11—C12	114.11 (18)
N2—C2—H2B	111.4	N1—C11—H11A	108.7
C1—C2—H2B	111.4	C12—C11—H11A	108.7
H2A—C2—H2B	109.3	N1—C11—H11B	108.7
N2—C3—N1	109.43 (19)	C12—C11—H11B	108.7
N2—C3—C4	120.32 (19)	H11A—C11—H11B	107.6
N1—C3—C4	130.3 (2)	C13—C12—C16	116.7 (2)
N3—C4—C3	122.3 (2)	C13—C12—C11	123.00 (19)
N3—C4—C5	117.1 (2)	C16—C12—C11	120.3 (2)
C3—C4—C5	120.3 (2)	N4—C13—C12	124.8 (2)
C4—C5—C6	111.3 (2)	N4—C13—H13	117.6
C4—C5—H5A	109.4	C12—C13—H13	117.6
C6—C5—H5A	109.4	N4—C14—C15	125.8 (2)

C4—C5—H5B	109.4	N4—C14—Cl	116.08 (18)
C6—C5—H5B	109.4	C15—C14—Cl	118.11 (18)
H5A—C5—H5B	108.0	C14—C15—C16	117.0 (2)
C5—C6—C7	111.6 (2)	C14—C15—H15	121.5
C5—C6—H6A	109.3	C16—C15—H15	121.5
C7—C6—H6A	109.3	C15—C16—C12	120.1 (2)
C5—C6—H6B	109.3	C15—C16—H16	119.9
C7—C6—H6B	109.3	C12—C16—H16	119.9
C3—N1—C1—C2	−16.3 (3)	C8—O1—C7—N2	75.1 (3)
C11—N1—C1—C2	128.5 (2)	C8—O1—C7—C6	−164.3 (2)
C3—N2—C2—C1	−19.3 (3)	C3—N2—C7—O1	91.2 (3)
C7—N2—C2—C1	176.5 (2)	C2—N2—C7—O1	−106.4 (3)
N1—C1—C2—N2	20.5 (2)	C3—N2—C7—C6	−28.9 (3)
C7—N2—C3—N1	174.3 (2)	C2—N2—C7—C6	133.5 (2)
C2—N2—C3—N1	9.9 (3)	C5—C6—C7—O1	−67.8 (3)
C7—N2—C3—C4	−6.0 (3)	C5—C6—C7—N2	55.2 (3)
C2—N2—C3—C4	−170.4 (2)	C7—O1—C8—C9	180.0 (2)
C11—N1—C3—N2	−138.6 (2)	C3—N1—C11—C12	−140.6 (2)
C1—N1—C3—N2	4.7 (3)	C1—N1—C11—C12	79.0 (2)
C11—N1—C3—C4	41.7 (4)	N1—C11—C12—C13	23.2 (3)
C1—N1—C3—C4	−175.0 (2)	N1—C11—C12—C16	−159.4 (2)
O2—N3—C4—C3	−179.6 (2)	C14—N4—C13—C12	1.3 (3)
O3—N3—C4—C3	3.1 (3)	C16—C12—C13—N4	−3.6 (3)
O2—N3—C4—C5	7.1 (3)	C11—C12—C13—N4	173.9 (2)
O3—N3—C4—C5	−170.2 (2)	C13—N4—C14—C15	2.3 (3)
N2—C3—C4—N3	−158.8 (2)	C13—N4—C14—Cl	−177.37 (17)
N1—C3—C4—N3	20.8 (4)	N4—C14—C15—C16	−3.2 (3)
N2—C3—C4—C5	14.3 (3)	Cl—C14—C15—C16	176.44 (17)
N1—C3—C4—C5	−166.1 (2)	C14—C15—C16—C12	0.6 (3)
N3—C4—C5—C6	−173.1 (2)	C13—C12—C16—C15	2.4 (3)
C3—C4—C5—C6	13.5 (3)	C11—C12—C16—C15	−175.1 (2)
C4—C5—C6—C7	−48.2 (3)		

Hydrogen-bond geometry (Å, º)

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
C11—H11*B*···O3	0.97	2.35	2.803 (3)	108
C13—H13···N1	0.93	2.54	2.891 (3)	103