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5-Chloro-2-methylisothiazolin-3-one: intermolecular two-dimensional networks *via* unusual C—Cl···O=C interactions

Masaru Kato,[a] Takashi Fujihara,[b]* Daisaku Yano[c] and Akira Nagasawa[a]

[a]Department of Chemistry, Graduate School of Science and Engineering, Saitama University, Shimo-Okubo 255, Sakura-ku, Saitama City, Saitama 338-8570, Japan, [b]Molecular Analysis and Life Science Center, Saitama University, Shimo-Okubo 255, Sakura-ku, Saitama City, Saitama 338-8570, Japan, and [c]Organo Corporation, 4-1 Nishi-Onuma 4-Chome, Sagamihara City, Kanagawa 229-0012, Japan
Correspondence e-mail: fuji@chem.saitama-u.ac.jp

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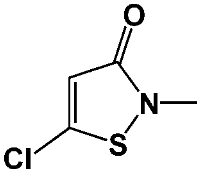
Key indicators: single-crystal X-ray study; T = 173 K; mean σ(C–C) = 0.003 Å; R factor = 0.044; wR factor = 0.098; data-to-parameter ratio = 19.9.

The title molecule, C_4H_4ClNOS, contains an essentially planar five-membered ring. The $\mathrm{C}\overset{\cdots}{-}\mathrm{C}(=\mathrm{O})$ bond is slightly longer than expected. In the crystal structure, two-dimensional networks are formed through intermolecular C—Cl···O=C interactions [Cl···O = 2.9811 (19) Å].

Related literature

Some crystal structures that contain the title molecule in cocrystals have been reported previously (Suzuki *et al.*, 1997; Sekine, Jomoto *et al.*, 2003; Sekine, Mitsumori *et al.*, 2003). For related literature, see: Frisch *et al.* (2003); Fujii *et al.* (2005); Glendening *et al.* (2001); Kato *et al.* (2007); Lewis *et al.* (1973); Wiberg (1968).



Experimental

Crystal data

C_4H_4ClNOS
M_r = 149.59
Monoclinic, $P2_1/c$
a = 8.0290 (16) Å
b = 13.978 (3) Å
c = 5.7375 (11) Å
β = 107.812 (4)°
V = 613.1 (2) Å^3
Z = 4
Mo $K\alpha$ radiation
μ = 0.86 mm^{-1}
T = 173 (2) K
0.40 × 0.09 × 0.09 mm

Data collection

Bruker SMART CCD area-detector diffractometer
Absorption correction: multi-scan (*SADABS*; Sheldrick 1996)
$T_{\min}$ = 0.726, $T_{\max}$ = 0.927
4451 measured reflections
1474 independent reflections
1157 reflections with $I > 2\sigma(I)$
$R_{\rm int}$ = 0.044

Refinement

$R[F^2 > 2\sigma(F^2)]$ = 0.044
$wR(F^2)$ = 0.098
S = 1.00
1474 reflections
74 parameters
H-atom parameters constrained
$\Delta\rho_{\max}$ = 0.33 e Å^{-3}
$\Delta\rho_{\min}$ = −0.27 e Å^{-3}

Table 1
Selected bond lengths (Å).

C1—O1	1.227 (3)	C3—Cl1	1.710 (2)
C1—N1	1.383 (3)	C3—S1	1.721 (2)
C1—C2	1.458 (3)	C4—N1	1.464 (3)
C2—C3	1.332 (3)	N1—S1	1.686 (2)

Data collection: *SMART-W2K/NT* (Bruker, 2003); cell refinement: *SAINT-W2K/NT* (Bruker, 2003); data reduction: *SAINT-W2K/NT*; program(s) used to solve structure: *SHELXTL-NT* (Bruker, 2003); program(s) used to refine structure: *SHELXTL-NT*; molecular graphics: *ORTEP-3 for Windows* (Farrugia, 1997); software used to prepare material for publication: *SHELXTL-NT*.

Supplementary data and figures for this paper are available from the IUCr electronic archives (Reference: LH2375).

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supplementary materials

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5-Chloro-2-methylisothiazolin-3-one: intermolecular two-dimensional networks *via* unusual C-Cl...O=C interactions

M. Kato, T. Fujihara, D. Yano and A. Nagasawa

Comment

The title compound, 5-Chloro-2-methylisothiazolin-3-one (I) is widely used as a biocide. Some molecular structures which contain (I) as co-crystals have been reported previously (Suzuki *et al.*, 1997; Sekine, Jomoto *et al.*, 2003; Sekine, Mitsumori *et al.*, 2003) but there are no reports on the crystal structure of (I) itself. We are interested in the relationship between the crystal structures of isothiazolines and their biocidal activities (Kato *et al.*, 2007) and report here the crystal structure of (I).

The molecular structure of (I), with the atom-labelling scheme, is shown in Fig. 1. Selected bond lengths and angles are shown in Table 1. The C1—C2 bond length is slightly longer than that previously reported (1.441 (3) Å, Sekine, Mitsumori *et al.*, 2003; 1.438 (4) Å, Sekine, Jomoto *et al.*, 2003; 1.437 Å, Suzuki *et al.*, 1997). The five-membered ring (S1/N1/C1—C3) is planar and the largest deviation from the plane being for atom N1 [0.0086 (12) Å]. The deviation of the C4 atom in the methyl group from the five-membered ring is 0.2214 (36) Å despite the N1 atom with sp^3-hybridization state. The planarity around the N1 atom indicates the delocalization of the lone pair of electrons on the N1 atom. An intermolecular interaction between Cl1 and O1 is observed (Fig. 2) and its distance is 2.9811 (19) Å. This distance is the same as reported previously (2.981 (2) Å, Fujii *et al.*, 2005). The Cl1 atom accepts the lone pair electrons of O1 and this intermolecular interaction stabilizes the crystal structure.

We performed the DFT calculations on (I) and 2-methylisothiazolin-3-one (II) by the B3LYP method for elucidating its electronic structure using the *Gaussian03* package program (Frisch *et al.*, 2003). The 6–31+G(d,p) basis set was used for all the elements. The optimized geometry shows a good agreement with the crystal structure. The Wiberg bond indices (Wiberg, 1968) were evaluated by natural-bond orbital (NBO) analysis (Glendening *et al.*, 2001) and these values are shown in Fig. 3. The almost Wiberg bond indices, except that of the C1—N1 bond, in (I) tend to be lower than those in (II). This may be due to the electron-withdrawing Cl on the C3 instead of H, and decreases the electron density on the five-membered ring. These results correspond to the higher activity of (I) as a biocide compared to that of (II) since the ease of cleavage of the N1—S1 bond is claimed to give rise to the biocidal activity (Lewis *et al.*, 1973).

Experimental

Single crystals of (I) suitable for X-ray diffraction were obtained as follows:

4-Chloro-2-methylisothiazolin-3-one was extracted from 'Kathon WT', which was purchased from Rohm and Hass, by 1,2-dichloroethane and was dried with anhydrous $MgSO_4$. Crude crystals were obtained by evaporation of the solvents and were recrystallized from ligroin. Elemental analysis, found: C 31.87, H 2.52, N 9.20%; calcd. for C_4H_4ClNOS: C 32.11, H 2.70, N 9.36%.

Refinement

H atoms were placed in calculated positions [C—H = 0.95 & 0.98 Å] and included in the refinement in the riding-model approximation with $U_{iso}(H) = 1.2U_{eq}(C)$ or $1.5U_{eq}(C)$ for methyl H atoms.

Figures

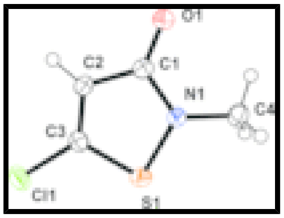


Fig. 1. The molecular structure the title compound with the atom-numbering scheme. Displacement ellipsoids are shown at the 50% probability level.

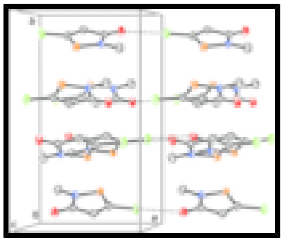


Fig. 2. Diagram showing the intermolecular C=O···Cl—C interactions (dashed line).

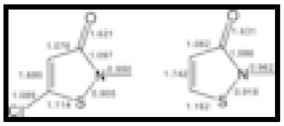


Fig. 3. Wiberg bond indecies in (I) (left) and (II) (right).

5-Chloro-2-methylisothiazolin-3-one

Crystal data

C_4H_4ClNOS

$M_r = 149.59$

Monoclinic, $P2_1/c$

Hall symbol: -P 2ybc

$a = 8.0290$ (16) Å

$b = 13.978$ (3) Å

$c = 5.7375$ (11) Å

$\beta = 107.812$ (4)°

$V = 613.1$ (2) Å^3

$Z = 4$

$F_{000} = 304$

$D_x = 1.621$ Mg m^{-3}

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

Cell parameters from 824 reflections

$\theta = 2.7$–24.8°

$\mu = 0.86$ mm^{-1}

$T = 173$ (2) K

Needle, colorless

0.40 × 0.09 × 0.09 mm

Data collection

Bruker SMART CCD area-detector diffractometer

Radiation source: fine-focus sealed tube

1474 independent reflections

1157 reflections with $I > 2\sigma(I)$

Monochromator: graphite

Detector resolution: 8.366 pixels mm^{-1}

T = 173(2) K

φ and ω scans

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

$T_{\min}$ = 0.726, $T_{\max}$ = 0.927

4451 measured reflections

R_{int} = 0.044

$\theta_{\max}$ = 28.0°

$\theta_{\min}$ = 2.7°

$h = -10 \rightarrow 10$

$k = -14 \rightarrow 18$

$l = -7 \rightarrow 7$

Refinement

Refinement on F^2

Least-squares matrix: full

$R[F^2 > 2\sigma(F^2)]$ = 0.044

$wR(F^2)$ = 0.098

S = 1.00

1474 reflections

74 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

$w = 1/[\sigma^2(F_o^2) + (0.0484P)^2]$
where $P = (F_o^2 + 2F_c^2)/3$

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

$\Delta\rho_{\max}$ = 0.33 e Å^{-3}

$\Delta\rho_{\min}$ = −0.27 e Å^{-3}

Extinction correction: none

Special details

Geometry. Distance SDEV

2.9811 (0.0019) O1 - Cl1_$1

Least-squares planes (x,y,z in crystal coordinates) and deviations from them (* indicates atom used to define plane)

$- 0.2147 (0.0078)\, x + 12.2058 (0.0061)\, y - 2.6112 (0.0038)\, z = 5.0659 (0.0082)$

* −0.0061 (0.0013) C1 * −0.0006 (0.0014) C2 * 0.0052 (0.0013) C3 * 0.0086 (0.0012) N1 * −0.0071 (0.0010) S1 − 0.0161 (0.0029) O1 − 0.2214 (0.0036) C4 0.0272 (0.0032) Cl1

Rms deviation of fitted atoms = 0.0061

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}
C1	0.5852 (3)	0.59959 (15)	0.8169 (4)	0.0214 (5)
C2	0.4002 (3)	0.57570 (16)	0.7183 (4)	0.0222 (5)

H1	0.3505	0.5427	0.5683	0.027*
C3	0.3088 (3)	0.60554 (16)	0.8631 (4)	0.0229 (5)
C4	0.7856 (3)	0.66864 (17)	1.2057 (4)	0.0287 (6)
H2A	0.8755	0.6419	1.1412	0.043*
H2B	0.7960	0.6397	1.3651	0.043*
H2C	0.8014	0.7380	1.2246	0.043*
Cl1	0.08933 (8)	0.59406 (5)	0.81908 (12)	0.0338 (2)
N1	0.6122 (2)	0.64805 (13)	1.0356 (4)	0.0229 (4)
O1	0.7041 (2)	0.58234 (11)	0.7303 (3)	0.0289 (4)
S1	0.43218 (8)	0.66265 (4)	1.12464 (11)	0.02660 (19)

Atomic displacement parameters (Å^2)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
C1	0.0250 (12)	0.0201 (11)	0.0199 (12)	−0.0007 (9)	0.0080 (10)	0.0019 (9)
C2	0.0236 (12)	0.0230 (12)	0.0192 (12)	−0.0016 (9)	0.0051 (10)	−0.0019 (9)
C3	0.0206 (12)	0.0241 (12)	0.0239 (12)	−0.0002 (9)	0.0067 (10)	0.0021 (9)
C4	0.0272 (14)	0.0339 (14)	0.0231 (13)	−0.0033 (11)	0.0049 (11)	−0.0032 (10)
Cl1	0.0209 (3)	0.0439 (4)	0.0370 (4)	0.0012 (3)	0.0094 (3)	0.0014 (3)
N1	0.0209 (10)	0.0271 (11)	0.0210 (10)	−0.0021 (8)	0.0069 (8)	−0.0039 (8)
O1	0.0247 (9)	0.0386 (10)	0.0253 (10)	−0.0027 (7)	0.0103 (7)	−0.0061 (7)
S1	0.0271 (3)	0.0308 (4)	0.0248 (3)	−0.0009 (3)	0.0123 (3)	−0.0056 (2)

Geometric parameters (Å, °)

C1—O1	1.227 (3)	C3—S1	1.721 (2)
C1—N1	1.383 (3)	C4—N1	1.464 (3)
C1—C2	1.458 (3)	C4—H2A	0.9800
C2—C3	1.332 (3)	C4—H2B	0.9800
C2—H1	0.9500	C4—H2C	0.9800
C3—Cl1	1.710 (2)	N1—S1	1.686 (2)
O1—C1—N1	122.5 (2)	N1—C4—H2B	109.5
O1—C1—C2	128.7 (2)	H2A—C4—H2B	109.5
N1—C1—C2	108.8 (2)	N1—C4—H2C	109.5
C3—C2—C1	112.1 (2)	H2A—C4—H2C	109.5
C3—C2—H1	123.9	H2B—C4—H2C	109.5
C1—C2—H1	123.9	C1—N1—C4	123.7 (2)
C2—C3—Cl1	128.16 (19)	C1—N1—S1	115.04 (16)
C2—C3—S1	114.15 (18)	C4—N1—S1	120.17 (16)
Cl1—C3—S1	117.69 (14)	N1—S1—C3	89.86 (10)
N1—C4—H2A	109.5		
O1—C1—C2—C3	179.8 (2)	O1—C1—N1—S1	−178.96 (17)
N1—C1—C2—C3	−0.5 (3)	C2—C1—N1—S1	1.3 (2)
C1—C2—C3—Cl1	179.39 (17)	C1—N1—S1—C3	−1.33 (17)
C1—C2—C3—S1	−0.4 (3)	C4—N1—S1—C3	−169.62 (18)
O1—C1—N1—C4	−11.1 (3)	C2—C3—S1—N1	0.99 (19)
C2—C1—N1—C4	169.1 (2)	Cl1—C3—S1—N1	−178.85 (14)

Fig. 1

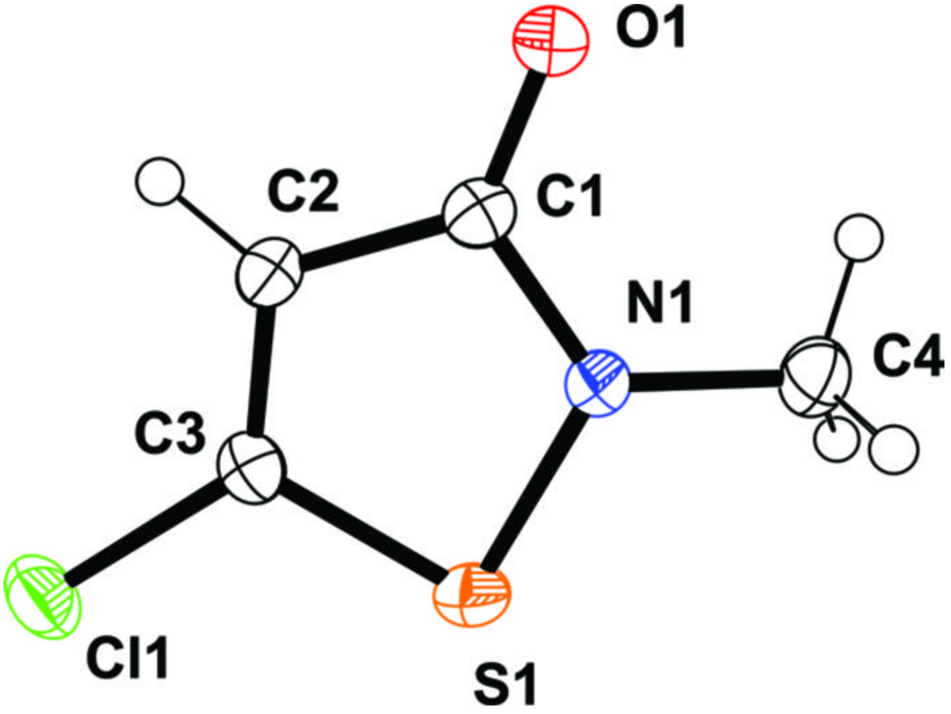


Fig. 2

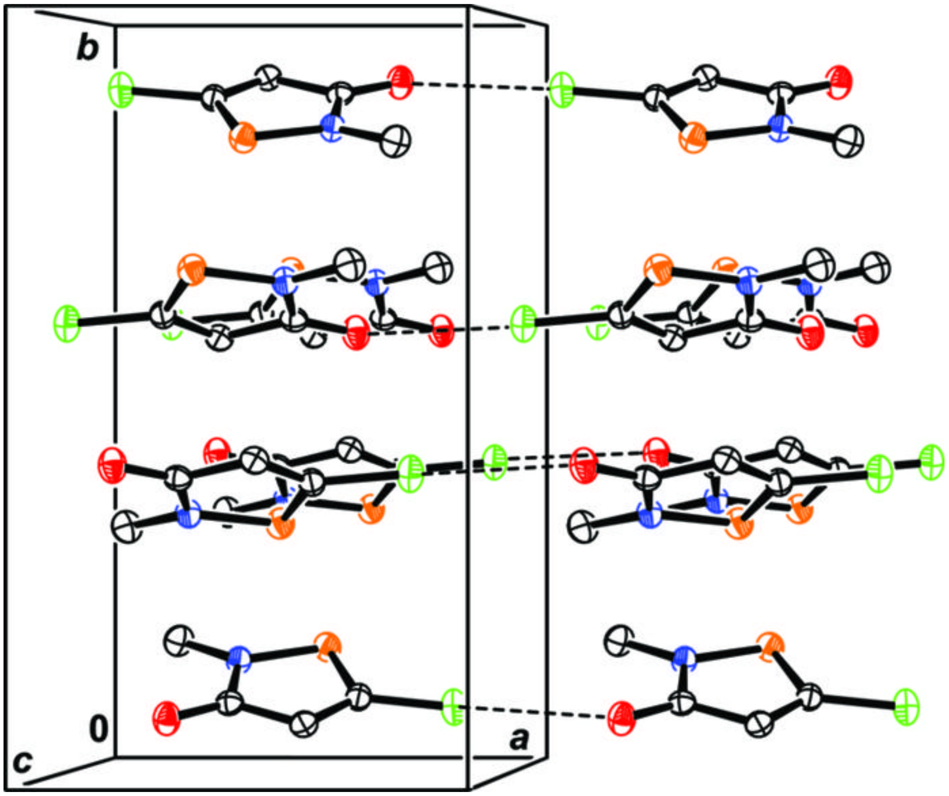
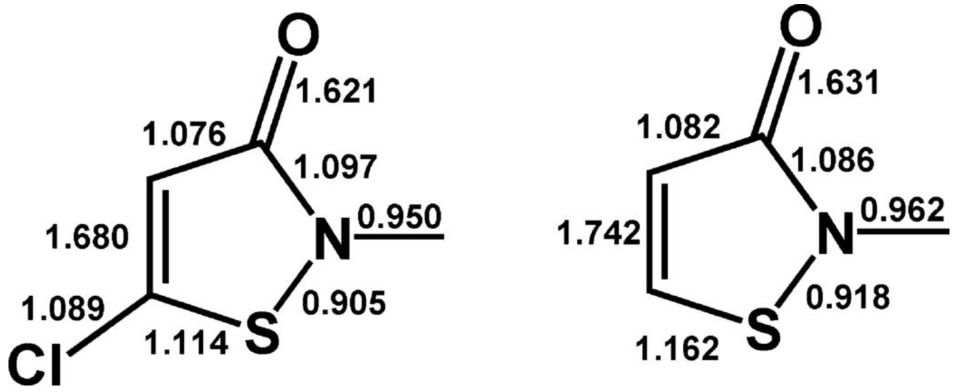


Fig. 3


O
1.621
1.076
1.097
N
0.950
1.680
1.089
0.905
Cl
1.114
S
O
1.631
1.082
1.086
N
0.962
1.742
0.918
1.162
S