

Acta Crystallographica Section E

## Structure Reports

Online

ISSN 1600-5368

4,5-Dichloro-2*H*-1,3-oxazine-2,6(3*H*)-dione

Damon Parrish, Brian Glass, Gretchen M. Rehberg and Margaret E. Kastner\*

Department of Chemistry, Bucknell University, Lewisburg, PA 17837, USA  
Correspondence e-mail: kastner@bucknell.edu

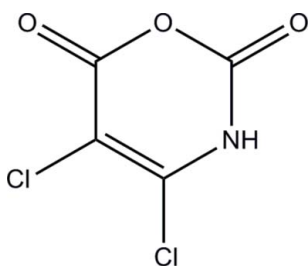
Received 13 August 2009; accepted 28 August 2009

Key indicators: single-crystal X-ray study;  $T = 293$  K; mean  $\sigma(\text{C}-\text{C}) = 0.003$  Å;  $R$  factor = 0.034;  $wR$  factor = 0.100; data-to-parameter ratio = 15.3.

In the title compound,  $\text{C}_4\text{HCl}_2\text{NO}_3$ , the essentially planar (maximum deviation = 0.023 Å for the ring O atom) molecules form  $\text{N}-\text{H}\cdots\text{O}$  hydrogen bonds between molecules lying about inversion centers, forming eight-membered rings with an  $R_2^2(8)$  motif in graph-set notation.

## Related literature

For synthetic background, see: Warren *et al.* (1975); Rehberg & Glass (1995). For related structures, see: Copley *et al.* (2005); Parrish, Leuschner *et al.* (2009); Parrish, Tivitmahaisoon *et al.* (2009). For graph-set notation in hydrogen bonding, see: Bernstein *et al.* (1994).



## Experimental

## Crystal data

 $\text{C}_4\text{HCl}_2\text{NO}_3$   
 $M_r = 181.96$ Monoclinic,  $P2_1/c$   
 $a = 10.2290$  (16) Å $b = 5.2549$  (8) Å  
 $c = 12.2766$  (16) Å  
 $\beta = 112.359$  (11)°  
 $V = 610.28$  (16) Å<sup>3</sup>  
 $Z = 4$ Mo  $K\alpha$  radiation  
 $\mu = 1.00$  mm<sup>-1</sup>  
 $T = 293$  K  
 $0.38 \times 0.33 \times 0.15$  mm

## Data collection

Siemens R3m/V diffractometer  
Absorption correction: none  
1566 measured reflections  
1405 independent reflections  
1235 reflections with  $I > 2\sigma(I)$  $R_{\text{int}} = 0.053$   
3 standard reflections  
every 97 reflections  
intensity decay: none

## Refinement

 $R[F^2 > 2\sigma(F^2)] = 0.034$   
 $wR(F^2) = 0.100$   
 $S = 0.95$   
1405 reflections92 parameters  
H-atom parameters constrained  
 $\Delta\rho_{\text{max}} = 0.41$  e Å<sup>-3</sup>  
 $\Delta\rho_{\text{min}} = -0.38$  e Å<sup>-3</sup>

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

$D-H\cdots A$	$D-H$	$H\cdots A$	$D\cdots A$	$D-H\cdots A$
$\text{N3}-\text{H3}\cdots\text{O2}^i$	0.86	1.99	2.845 (2)	174

Symmetry code: (i)  $-x + 2, -y + 1, -z$ .

Data collection: *XSCANS* (Bruker, 1996); cell refinement: *XSCANS*; data reduction: *XSCANS*; 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*.

The authors thank the National Science Foundation for grant No. ILI8951058.

Supplementary data and figures for this paper are available from the IUCr electronic archives (Reference: PV2198).

## References

- Bernstein, J., Etter, M. C. & Leiserowitz, L. (1994). *Structure Correlation*, edited by H.-B. Bürgi & J. D. Dunitz, Vol. 2, p. 431–507. New York: VCH.
- Bruker (1996). *XSCANS*. Bruker AXS Inc., Madison, Wisconsin, USA.
- Copley, R. C. B., Deprez, L. S., Lewis, T. C. & Price, S. L. (2005). *CrystEngComm*, **7**, 421–428.
- Parrish, D., Leuschner, F., Rehberg, G. M. & Kastner, M. E. (2009). *Acta Cryst.* **E65**, o2354.
- Parrish, D., Tivitmahaisoon, P., Rehberg, G. M. & Kastner, M. E. (2009). *Acta Cryst.* **E65**, o2355.
- Rehberg, G. M. & Glass, B. M. (1995). *Org. Prep. Proced. Int.* **27**, 651–652.
- Sheldrick, G. M. (2008). *Acta Cryst.* **A64**, 112–122.
- Warren, J. D., MacMillan, J. H. & Washburne, S. S. (1975). *J. Org. Chem.* **40**, 743–746.

**supplementary materials**

*Acta Cryst.* (2009). E65, o2356 [ doi:10.1107/S1600536809034606 ]

## 4,5-Dichloro-2*H*-1,3-oxazine-2,6(3*H*)-dione

D. Parrish, B. Glass, G. M. Rehberg and M. E. Kastner

### Comment

The synthesis of derivatives of 3-oxauracil has previously been reported (Warren *et al.*, 1975) and an improved synthesis of the unsubstituted 3-oxauracil was reported by Rehberg & Glass (1995). The structure of the unsubstituted 3-oxauracil and its monohydrate have been reported (Copley *et al.*, 2005). Three derivatives of 3-oxauracil (4-methyl, 4-bromo, and 4,5-dichloro) have been prepared in our laboratory in route to the synthesis of 1-aza-1,3-butadienes. In this paper, we report the crystal structure of the title compound, (I).

Unlike the hydrogen bonding observed in 4-methyl derivative (Parrish, Leuschner *et al.*, 2009) resulting in staggered chains of molecules, in the crystal structure of of the title compound (Fig. 1), the molecules of (I) are held together by classical intermolecular hydrogen bonds of the type N—H···O resulting in dimeric units about inversion centers, forming eight membered ring systems which may be described in terms of graph set notation (Bernstein *et al.* 1994) as  $R_2^2(8)$  ring motif (details have been given in Table 1 and Figure 2). The molecular dimensions in (I) agree well with the corresponding bond distances and angles reported for the above mentioned structures and 4-bromo derivative of 3-oxauracil (Parrish, Tivitmahaisoon *et al.*, 2009).

### Experimental

Dichloromaleic anhydride (3,4-dichlorofuran-2,5-dione) and trimethylsilyl azide were treated analogously to the syntheses reported for the 4-methyl (Parrish, Leuschner *et al.*, 2009) and 4-bromo derivatives. Crystals of the title compound were grown from a solution of acetone at room temperature by slow evaporation.

### Refinement

Hydrogen atom bonded to N3 was calculated and refined using a riding model using the N—H distance 0.88 Å with  $U_{iso}(H) = 1.2U_{eq}(N)$ .

### Figures

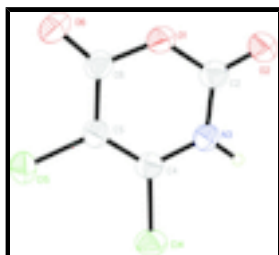


Fig. 1. The molecular structure of the title compound, with atom labels and 50% probability displacement ellipsoids for non-H atoms.

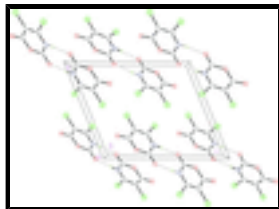


Fig. 2. The packing of the title compound viewed along the *b* axis and showing the H-bonded dimer formed by inversion related molecules.

## 4,5-Dichloro-2*H*-1,3-oxazine-2,6(3*H*)-dione

### Crystal data

$C_4HCl_2NO_3$

$M_r = 181.96$

Monoclinic,  $P2_1/c$

Hall symbol: -P 2ybc

$a = 10.2290$  (16) Å

$b = 5.2549$  (8) Å

$c = 12.2766$  (16) Å

$\beta = 112.359$  (11)°

$V = 610.28$  (16) Å<sup>3</sup>

$Z = 4$

$F_{000} = 360$

$D_x = 1.980$  Mg m<sup>-3</sup>

$D_m = 1.92$  Mg m<sup>-3</sup>

$D_m$  measured by floatation

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

Cell parameters from 20 reflections

$\theta = 10\text{--}12.5^\circ$

$\mu = 1.00$  mm<sup>-1</sup>

$T = 293$  K

Plates, colorless

$0.38 \times 0.33 \times 0.15$  mm

### Data collection

Siemens R3m/V  
diffractometer

Radiation source: fine-focus sealed tube

Monochromator: graphite

$T = 293$  K

$\theta$ - $2\theta$  scans

Absorption correction: none

1566 measured reflections

1405 independent reflections

1235 reflections with  $I > 2\sigma(I)$

$R_{int} = 0.053$

$\theta_{max} = 27.6^\circ$

$\theta_{min} = 2.2^\circ$

$h = 0 \rightarrow 13$

$k = 0 \rightarrow 6$

$l = -15 \rightarrow 14$

3 standard reflections

every 97 reflections

intensity decay: none

### Refinement

Refinement on  $F^2$

Least-squares matrix: full

$R[F^2 > 2\sigma(F^2)] = 0.034$

$wR(F^2) = 0.100$

$S = 0.95$

1405 reflections

Hydrogen site location: inferred from neighbouring sites

H-atom parameters constrained

$$w = 1/[\sigma^2(F_o^2) + (0.0666P)^2 + 0.3617P]$$

where  $P = (F_o^2 + 2F_c^2)/3$

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

$\Delta\rho_{max} = 0.41$  e Å<sup>-3</sup>

$\Delta\rho_{min} = -0.38$  e Å<sup>-3</sup>

92 parameters

Extinction correction: SHELXL97 (Sheldrick, 2008),

$$F_c^* = kF_c [1 + 0.001 \times F_c^2 \lambda^3 / \sin(2\theta)]^{-1/4}$$

Primary atom site location: structure-invariant direct methods

Extinction coefficient: 0.042 (5)

Secondary atom site location: difference Fourier map

### 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 ( $\text{\AA}^2$ )

	$x$	$y$	$z$	$U_{\text{iso}}^*/U_{\text{eq}}$
O1	0.89484 (14)	0.7547 (3)	0.20549 (12)	0.0405 (4)
C2	0.9358 (2)	0.6588 (4)	0.12050 (17)	0.0362 (4)
O2	1.03514 (16)	0.7544 (3)	0.10600 (14)	0.0474 (4)
N3	0.86084 (17)	0.4586 (3)	0.05845 (14)	0.0363 (4)
H3	0.8864	0.3892	0.0062	0.044*
C4	0.74604 (19)	0.3625 (3)	0.07572 (15)	0.0325 (4)
Cl4	0.66660 (6)	0.11274 (10)	-0.01234 (4)	0.0453 (2)
C5	0.7009 (2)	0.4611 (4)	0.15609 (16)	0.0347 (4)
Cl5	0.55557 (6)	0.35198 (11)	0.17764 (5)	0.0491 (2)
C6	0.7780 (2)	0.6694 (4)	0.22914 (17)	0.0366 (4)
O6	0.75456 (18)	0.7746 (3)	0.30575 (15)	0.0533 (4)

### Atomic displacement parameters ( $\text{\AA}^2$ )

	$U^{11}$	$U^{22}$	$U^{33}$	$U^{12}$	$U^{13}$	$U^{23}$
O1	0.0479 (8)	0.0401 (8)	0.0369 (7)	-0.0084 (6)	0.0199 (6)	-0.0094 (6)
C2	0.0401 (10)	0.0363 (9)	0.0321 (9)	-0.0007 (8)	0.0138 (8)	0.0003 (7)
O2	0.0479 (8)	0.0484 (9)	0.0515 (9)	-0.0126 (7)	0.0251 (7)	-0.0079 (7)
N3	0.0405 (8)	0.0411 (9)	0.0317 (8)	-0.0050 (7)	0.0188 (6)	-0.0060 (7)
C4	0.0366 (9)	0.0333 (9)	0.0256 (8)	-0.0020 (7)	0.0097 (7)	0.0002 (7)
Cl4	0.0530 (3)	0.0453 (3)	0.0375 (3)	-0.0132 (2)	0.0172 (2)	-0.0125 (2)
C5	0.0387 (9)	0.0387 (10)	0.0286 (8)	-0.0019 (8)	0.0148 (7)	0.0005 (7)
Cl5	0.0526 (3)	0.0587 (4)	0.0464 (3)	-0.0136 (2)	0.0303 (3)	-0.0082 (2)
C6	0.0442 (10)	0.0362 (9)	0.0317 (9)	-0.0008 (8)	0.0171 (8)	-0.0007 (7)
O6	0.0691 (10)	0.0521 (9)	0.0484 (9)	-0.0073 (8)	0.0334 (8)	-0.0166 (7)

## supplementary materials

---

### Geometric parameters ( $\text{\AA}$ , $^\circ$ )

O1—C2	1.360 (2)	C4—C5	1.342 (3)
O1—C6	1.406 (2)	C4—C14	1.698 (2)
C2—O2	1.206 (2)	C5—C6	1.444 (3)
C2—N3	1.353 (3)	C5—C15	1.706 (2)
N3—C4	1.367 (2)	C6—O6	1.192 (2)
N3—H3	0.8600		
C2—O1—C6	125.02 (15)	C5—C4—C14	123.46 (15)
O2—C2—N3	124.69 (18)	N3—C4—C14	114.72 (14)
O2—C2—O1	118.79 (18)	C4—C5—C6	119.33 (17)
N3—C2—O1	116.51 (16)	C4—C5—C15	123.23 (15)
C2—N3—C4	122.41 (16)	C6—C5—C15	117.44 (14)
C2—N3—H3	118.8	O6—C6—O1	117.20 (18)
C4—N3—H3	118.8	O6—C6—C5	127.99 (19)
C5—C4—N3	121.82 (17)	O1—C6—C5	114.81 (16)
C6—O1—C2—O2	177.41 (18)	N3—C4—C5—C15	178.26 (14)
C6—O1—C2—N3	-3.1 (3)	C14—C4—C5—C15	-1.5 (3)
O2—C2—N3—C4	-177.81 (19)	C2—O1—C6—O6	-179.15 (19)
O1—C2—N3—C4	2.7 (3)	C2—O1—C6—C5	1.0 (3)
C2—N3—C4—C5	-0.3 (3)	C4—C5—C6—O6	-178.2 (2)
C2—N3—C4—C14	179.47 (15)	C15—C5—C6—O6	1.5 (3)
N3—C4—C5—C6	-2.0 (3)	C4—C5—C6—O1	1.6 (3)
C14—C4—C5—C6	178.29 (14)	C15—C5—C6—O1	-178.62 (13)

### Hydrogen-bond geometry ( $\text{\AA}$ , $^\circ$ )

$D-H\cdots A$	$D-H$	$H\cdots A$	$D\cdots A$	$D-H\cdots A$
N3—H3 $\cdots$ O2 <sup>i</sup>	0.86	1.99	2.845 (2)	174

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

Fig. 1

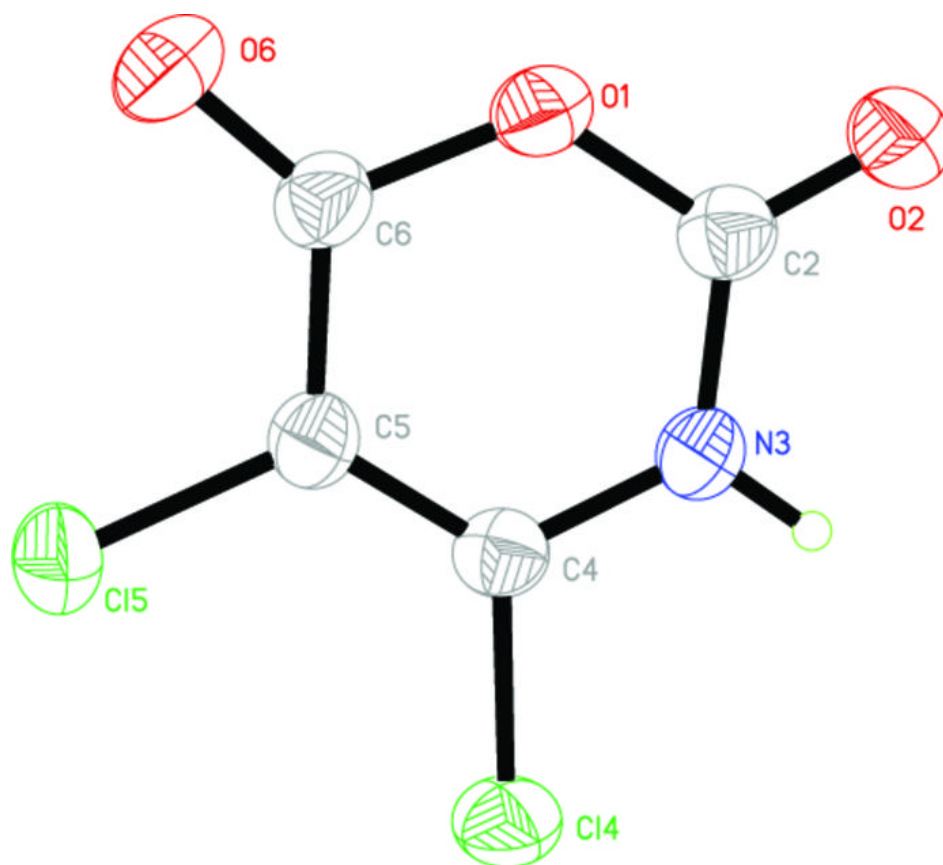


Fig. 2

