Acta Crystallographica Section E
Structure Reports Online
ISSN 1600-5368

2-Chloromethyl-2,3-dihydrothieno-[3,4-*b*][1,4]dioxine

Jian Xu, Hao Xu, Ji-cai Quan, Fei Sha and Cheng Yao*

College of Science, Nanjing University of Technology, Xinmofan Road No. 5, Nanjing 210009, People's Republic of China
Correspondence e-mail: yaocheng@njut.edu.cn

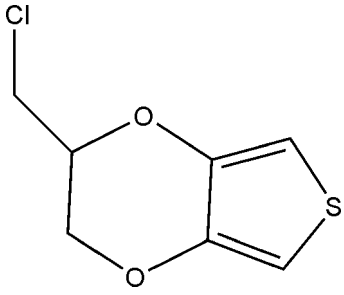
Received 24 February 2009; accepted 26 February 2009

Key indicators: single-crystal X-ray study; T = 294 K; mean σ(C–C) = 0.006 Å; R factor = 0.065; wR factor = 0.185; data-to-parameter ratio = 14.8.

In the molecule of the title compound, $C_7H_7ClO_2S$, the six-membered ring adopts a twisted conformation. In the crystal structure, weak intermolecular C—H···O hydrogen bonds link the molecules. There is also a weak C—H···π interaction.

Related literature

For a related structure, see: Jose *et al.* (2005). For bond-length data, see: Allen *et al.* (1987). For ring-puckering parameters, see: Cremer & Pople (1975).



Experimental

Crystal data

$C_7H_7ClO_2S$
M_r = 190.64
Monoclinic, $P2_1/n$
a = 10.227 (2) Å
b = 5.7500 (12) Å
c = 14.376 (3) Å
β = 105.55 (3)°
V = 814.4 (3) Å^3
Z = 4
Mo $K\alpha$ radiation
μ = 0.67 mm^{-1}
T = 294 K
0.30 × 0.20 × 0.10 mm

Data collection

Enraf–Nonius CAD-4 diffractometer
Absorption correction: ψ scan (North *et al.*, 1968)
T_{min} = 0.825, T_{max} = 0.936
1565 measured reflections
1479 independent reflections
1065 reflections with $I > 2\sigma(I)$
R_{int} = 0.067
3 standard reflections
frequency: 120 min
intensity decay: 1%

Refinement

$R[F^2 > 2\sigma(F^2)]$ = 0.065
$wR(F^2)$ = 0.185
S = 1.01
1479 reflections
100 parameters
H-atom parameters constrained
$\Delta\rho_{max}$ = 0.41 e Å^{-3}
$\Delta\rho_{min}$ = −0.29 e Å^{-3}

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

D—H···A	D—H	H···A	D···A	D—H···A
C2—H2A···O1^{i}	0.98	2.45	3.317 (5)	146
C1—H1B···$Cg1^{ii}$	0.97	2.75	3.708 (5)	168

Symmetry codes: (i) $-x-\frac{1}{2}, y-\frac{1}{2}, -z+\frac{1}{2}$; (ii) $-x+1, -y+2, -z$. $Cg1$ is the centroid of the S/C4–C7 ring.

Data collection: *CAD-4 Software* (Enraf–Nonius, 1989); cell refinement: *CAD-4 Software*; data reduction: *XCAD4* (Harms & Wocadlo, 1995); program(s) used to solve structure: *SHELXS97* (Sheldrick, 2008); program(s) used to refine structure: *SHELXL97* (Sheldrick, 2008); molecular graphics: *ORTEP-3 for Windows* (Farrugia, 1997) and *PLATON* (Spek, 2009); software used to prepare material for publication: *SHELXTL* (Sheldrick, 2008).

Supplementary data and figures for this paper are available from the IUCr electronic archives (Reference: HK2630).

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supporting information

Acta Cryst. (2009). E**65**, o668 [doi:10.1107/S1600536809007156]

2-Chloromethyl-2,3-dihydrothieno[3,4-*b*][1,4]dioxine

Jian Xu, Hao Xu, Ji-cai Quan, Fei Sha and Cheng Yao

S1. Comment

A great deal of interest has been devoted in recent years to the synthesis and investigation of functionalized 3,4-ethylenedioxythiophene (EDOT) systems because of their potential as active materials in applications such as light-emitting diodes (OLEDs), plastic lasers, field-effect transistors and photovoltaic devices (Jose *et al.*, 2005). The title compound is an important intermediate in the synthesis of functionalized 3,4-ethylenedioxy- thiophene (EDOT) systems, and we report herein its crystal structure.

In the molecule of the title compound (Fig. 1), the bond lengths (Allen *et al.*, 1987) and angles are within normal ranges. Ring B (S/C4-C7) is, of course, planar. Ring A (O1/O2/C2-C5) is not planar, having total puckering amplitude, Q_T, of 0.659 (3) Å and twisted conformation [φ = -149.80 (3)° and θ = 154.28 (3)°] (Cremer & Pople, 1975).

In the crystal structure, intermolecular C-H···O hydrogen bonds (Table 1) link the molecules (Fig. 2), in which they may be effective in the stabilization of the structure. There is also a weak C—H···π interaction (Table 1).

S2. Experimental

For the preparation of the title compound, 3,4-dimethoxythiophene (1.14 g, 7.9 mmol), 3-chloro-1,2-propanediol (2.45 g, 22.2 mmol), *p*-toluene- sulfonic acid monohydrate (0.151 g, 0.81 mmol) and dry toluene (27 ml) were added into a three necked flask equipped with an argon purge. The mixture was refluxed for 12 h. Then, diol (2.45 g, 22.2 mmol) was added and refluxed for 3 h. It was allowed to cool to room temperature. After removal of the solvent, the remaining crude product was isolated by flash chromatography [silica gel, hexane/dichloromethane (8:2)] to isolate the title compound, as a colorless solid (yield; 58%) (Jose *et al.*, 2005). Crystals suitable for X-ray analysis were obtained by dissolving the title compound (0.1 g) in hexane (25 ml) and evaporating the solvent slowly at room temperature for about 3 d.

S3. Refinement

H atoms were positioned geometrically, with C-H = 0.93, 0.98 and 0.97 Å for aromatic, methine and methylene H, respectively, and constrained to ride on their parent atoms, with $U_{iso}(H) = 1.2U_{eq}(C)$.

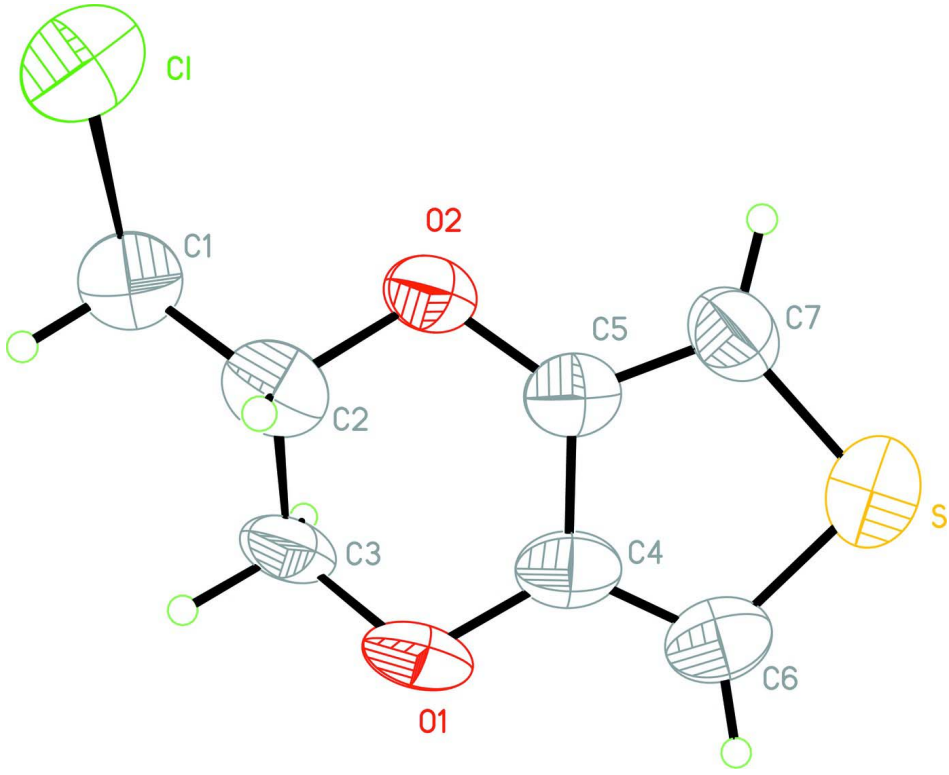

Figure 1

The molecular structure of the title molecule, with the atom-numbering scheme. Displacement ellipsoids are drawn at the 50% probability level.

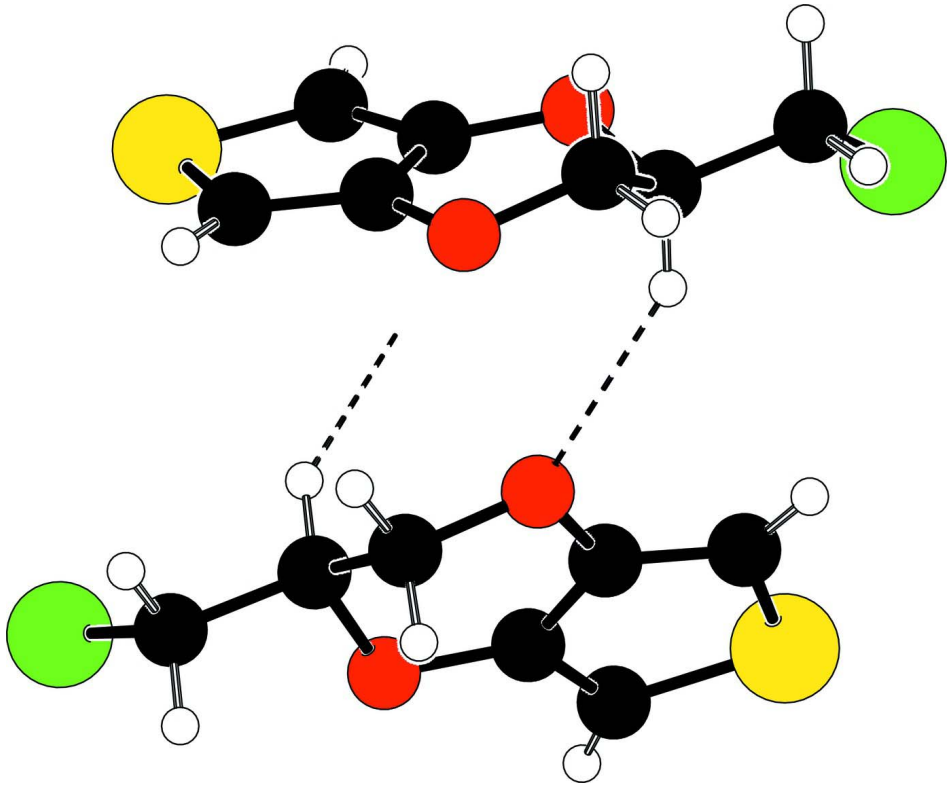

Figure 2

A partial packing diagram of the title compound. Hydrogen bonds are shown as dashed lines.

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Crystal data

$C_7H_7ClO_2S$
$M_r = 190.64$
Monoclinic, $P2_1/n$
Hall symbol: -P 2yn
$a = 10.227\ (2)$ Å
$b = 5.7500\ (12)$ Å
$c = 14.376\ (3)$ Å
$\beta = 105.55\ (3)°$
$V = 814.4\ (3)$ Å^3
$Z = 4$
$F(000) = 392$
$D_x = 1.555$ Mg m^{-3}
Mo $K\alpha$ radiation, $\lambda = 0.71073$ Å
Cell parameters from 25 reflections
$\theta = 10–13°$
$\mu = 0.67$ mm^{-1}
$T = 294$ K
Block, colorless
0.30 × 0.20 × 0.10 mm

Data collection

Enraf–Nonius CAD-4 diffractometer
Radiation source: fine-focus sealed tube
Graphite monochromator
$\omega/2\theta$ scans
Absorption correction: ψ scan (North *et al.*, 1968)
$T_{min} = 0.825$, $T_{max} = 0.936$
1565 measured reflections
1479 independent reflections
1065 reflections with $I > 2\sigma(I)$
$R_{int} = 0.067$
$\theta_{max} = 25.4°$, $\theta_{min} = 2.2°$
$h = 0\rightarrow12$
$k = 0\rightarrow6$
$l = -17\rightarrow16$
3 standard reflections every 120 min
intensity decay: 1%

Refinement

Refinement on F^2
Least-squares matrix: full
$R[F^2 > 2\sigma(F^2)] = 0.065$
$wR(F^2) = 0.185$
$S = 1.01$
1479 reflections
100 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
$w = 1/[\sigma^2(F_o^2) + (0.1P)^2 + 0.92P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} < 0.001$
$\Delta\rho_{max} = 0.41$ e Å^{-3}
$\Delta\rho_{min} = -0.29$ e Å^{-3}

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 (Å²)

	x	*y*	*z*	U_{iso}*/U_{eq}
Cl	−0.37084 (12)	0.1937 (2)	0.51615 (9)	0.0759 (5)
S	0.12047 (12)	0.1840 (2)	0.27636 (9)	0.0740 (5)
O1	−0.1425 (3)	0.6480 (5)	0.29741 (19)	0.0619 (8)
O2	−0.1277 (2)	0.2762 (4)	0.43358 (19)	0.0505 (7)
C1	−0.2959 (4)	0.4560 (8)	0.4923 (3)	0.0569 (10)
H1A	−0.3636	0.5786	0.4805	0.068*
H1B	−0.2238	0.4991	0.5486	0.068*
C2	−0.2397 (4)	0.4363 (7)	0.4079 (3)	0.0524 (9)
H2A	−0.3096	0.3729	0.3531	0.063*
C3	−0.1903 (4)	0.6650 (6)	0.3787 (3)	0.0539 (10)
H3A	−0.2641	0.7765	0.3663	0.065*
H3B	−0.1181	0.7236	0.4320	0.065*
C4	−0.0539 (4)	0.4634 (7)	0.3034 (3)	0.0515 (9)
C5	−0.0507 (4)	0.2828 (6)	0.3683 (3)	0.0477 (9)
C6	0.0309 (4)	0.4363 (8)	0.2481 (3)	0.0632 (11)
H6A	0.0400	0.5405	0.2008	0.076*
C7	0.0424 (4)	0.1179 (7)	0.3626 (3)	0.0591 (10)
H7A	0.0605	−0.0143	0.4012	0.071*

Atomic displacement parameters (Å²)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
Cl	0.0794 (8)	0.0787 (9)	0.0741 (8)	−0.0128 (6)	0.0285 (6)	−0.0007 (6)
S	0.0758 (8)	0.0812 (9)	0.0696 (8)	0.0012 (6)	0.0275 (6)	−0.0095 (6)
O1	0.0693 (18)	0.0601 (18)	0.0461 (16)	0.0112 (14)	−0.0024 (13)	0.0218 (13)

O2	0.0571 (15)	0.0440 (14)	0.0484 (15)	0.0044 (12)	0.0110 (12)	0.0090 (12)
C1	0.061 (2)	0.066 (3)	0.0370 (19)	−0.005 (2)	0.0014 (17)	−0.0062 (18)
C2	0.051 (2)	0.053 (2)	0.042 (2)	−0.0049 (17)	−0.0081 (16)	−0.0067 (17)
C3	0.068 (2)	0.047 (2)	0.040 (2)	0.0146 (18)	0.0034 (17)	0.0132 (17)
C4	0.055 (2)	0.057 (2)	0.0329 (18)	−0.0073 (18)	−0.0059 (16)	0.0042 (17)
C5	0.059 (2)	0.044 (2)	0.0355 (18)	−0.0114 (17)	0.0042 (15)	−0.0069 (16)
C6	0.069 (3)	0.073 (3)	0.044 (2)	−0.004 (2)	0.0078 (19)	0.006 (2)
C7	0.064 (2)	0.051 (2)	0.059 (2)	0.0111 (19)	0.012 (2)	0.001 (2)

Geometric parameters (Å, º)

Cl—C1	1.766 (4)	C2—C3	1.508 (5)
S—C7	1.688 (4)	C2—H2A	0.9800
S—C6	1.706 (5)	C3—H3A	0.9700
O1—C4	1.384 (5)	C3—H3B	0.9700
O1—C3	1.386 (5)	C4—C6	1.333 (5)
O2—C5	1.377 (5)	C4—C5	1.391 (5)
O2—C2	1.439 (5)	C5—C7	1.362 (5)
C1—C2	1.480 (5)	C6—H6A	0.9300
C1—H1A	0.9700	C7—H7A	0.9300
C1—H1B	0.9700		
C7—S—C6	92.1 (2)	C2—C3—H3A	108.9
C4—O1—C3	112.0 (3)	O1—C3—H3B	108.9
C5—O2—C2	111.6 (3)	C2—C3—H3B	108.9
C2—C1—Cl	112.2 (3)	H3A—C3—H3B	107.8
C2—C1—H1A	109.2	C6—C4—O1	124.9 (4)
Cl—C1—H1A	109.2	C6—C4—C5	114.3 (4)
C2—C1—H1B	109.2	O1—C4—C5	120.8 (3)
Cl—C1—H1B	109.2	C7—C5—O2	124.0 (3)
H1A—C1—H1B	107.9	C7—C5—C4	111.7 (4)
O2—C2—C1	107.2 (3)	O2—C5—C4	124.3 (3)
O2—C2—C3	109.0 (3)	C4—C6—S	110.5 (3)
C1—C2—C3	113.2 (3)	C4—C6—H6A	124.7
O2—C2—H2A	109.1	S—C6—H6A	124.7
C1—C2—H2A	109.1	C5—C7—S	111.3 (3)
C3—C2—H2A	109.1	C5—C7—H7A	124.3
O1—C3—C2	113.2 (3)	S—C7—H7A	124.3
O1—C3—H3A	108.9		
C5—O2—C2—C1	−167.2 (3)	C6—C4—C5—C7	1.5 (5)
C5—O2—C2—C3	−44.3 (4)	O1—C4—C5—C7	179.5 (3)
Cl—C1—C2—O2	−66.6 (3)	C6—C4—C5—O2	178.7 (3)
Cl—C1—C2—C3	173.1 (3)	O1—C4—C5—O2	−3.2 (5)
C4—O1—C3—C2	−48.0 (4)	O1—C4—C6—S	−178.8 (3)
O2—C2—C3—O1	63.1 (4)	C5—C4—C6—S	−0.8 (5)
C1—C2—C3—O1	−177.6 (3)	C7—S—C6—C4	0.0 (3)
C3—O1—C4—C6	−163.6 (4)	O2—C5—C7—S	−178.7 (3)

C3—O1—C4—C5	18.6 (5)	C4—C5—C7—S	−1.4 (4)
C2—O2—C5—C7	−165.2 (4)	C6—S—C7—C5	0.8 (3)
C2—O2—C5—C4	17.9 (5)		

Hydrogen-bond geometry (Å, º)

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
C2—H2*A*···O1^{i}	0.98	2.45	3.317 (5)	146
C1—H1*B*···*Cg*1^{ii}	0.97	2.75	3.708 (5)	169

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