Acta Cryst E STRUCTURE REPORTS

OPEN ACCESS

ISSN 1600-5368

Crystal structure of 2-[(dichloromethane)sulfonyl]pyridine

Zhiqiu Chen, Hembat Bolat, Xing Wan and Ya Li*

College of Chemistry and Chemical Engineering, Shanghai University of Engineering Science, 333 Longteng Road, Shanghai, People's Republic of China. *Correspondence e-mail: ya.li@sues.edu.cn

Received 13 November 2014; accepted 17 November 2014

Edited by W. T. A. Harrison, University of Aberdeen, Scotland

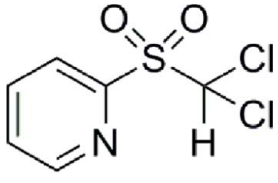
The asymmetric unit of the title compound, $C_6H_5Cl_2NO_2S$, contains two molecules with similar conformations (r.m.s. overlay fit for the non-H atoms = 0.067 Å). Atoms attached to the pendent Csp^3—S bond are arranged in a staggered conformation with one of the Cl atoms *anti* to the C atom in the aromatic ring [C—S—C—Cl torsion angles = 178.41 (11) and −176.70 (13)°]. In the crystal, molecules are linked by C—H···N and C—H···O hydrogen bonds, generating a three-dimensional network, and weak aromatic π–π stacking is also observed [centroid–centroid separation = 3.8902 (17) Å].

Keywords: crystal structure; sulfone; pyridine derivative; hydrogen bonding; π–π stacking.

CCDC reference: 1034519

1. Related literature

For the biological activity of sulfone derivatives, see: Chen *et al.* (2012); Drews (2000); Raja *et al.* (2009). For the uses of halomethyl sulfone derivatives in organic synthesis, see: Li & Hu (2005); Prakash *et al.* (2013); Zhao *et al.* (2010). For the synthesis of the starting material, see: Kamiyama *et al.* (1988).



2. Experimental

2.1. Crystal data

$C_6H_5Cl_2NO_2S$
M_r = 226.07
Monoclinic, $P2_1/n$
a = 9.9647 (10) Å
b = 12.2131 (11) Å
c = 15.7158 (15) Å
β = 108.483 (1)°
V = 1814.0 (3) Å^3
Z = 8
Mo $K\alpha$ radiation
μ = 0.90 mm^{-1}
T = 293 K
0.21 × 0.16 × 0.12 mm

2.2. Data collection

Bruker SMART CCD diffractometer
Absorption correction: multi-scan (*SADABS*; Bruker, 2007)
T_{min} = 0.615, T_{max} = 0.746
10817 measured reflections
3570 independent reflections
2907 reflections with $I > 2\sigma(I)$
R_{int} = 0.034

2.3. Refinement

$R[F^2 > 2\sigma(F^2)]$ = 0.037
$wR(F^2)$ = 0.102
S = 1.03
3570 reflections
218 parameters
H-atom parameters constrained
$\Delta\rho_{max}$ = 0.37 e Å^{-3}
$\Delta\rho_{min}$ = −0.37 e Å^{-3}

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

D—H···A	D—H	H···A	D···A	D—H···A
C1—H1···N2^{i}	0.98	2.37	3.321 (3)	163
C5—H5···O3^{ii}	0.93	2.64	3.220 (3)	121
C6—H6···O3^{ii}	0.93	2.54	3.177 (3)	126
C7—H7···N1^{i}	0.98	2.36	3.303 (3)	162
C11—H11···O1^{iii}	0.93	2.64	3.292 (3)	128

Symmetry codes: (i) $-x+1, -y+1, -z+1$; (ii) $x+\frac{1}{2}, -y+\frac{3}{2}, z-\frac{1}{2}$; (iii) $x+\frac{1}{2}, -y+\frac{1}{2}, z+\frac{1}{2}$.

Data collection: *SMART* (Bruker, 2007); cell refinement: *SAINT* (Bruker, 2007); data reduction: *SAINT*; program(s) used to solve structure: *SHELXTL* (Sheldrick, 2008); program(s) used to refine structure: *SHELXL2013* (Sheldrick, 2008); molecular graphics: *SHELXTL*; software used to prepare material for publication: *SHELXTL*.

Acknowledgements

Financial support from the Innovation Program of the Shanghai University Students (cs1304009) is gratefully acknowledged.

Supporting information for this paper is available from the IUCr electronic archives (Reference: HB7316).

References

Bruker (2007). *SMART*, *SAINT* and *SADABS*. Bruker AXS Inc., Madison, Wisconsin, USA.
Chen, X., Hussain, S., Parveen, S., Zhang, S., Yang, Y. & Zhu, C. (2012). *CMC*, **19**, 3578–3604.
Drews, J. (2000). *Science*, **287**, 1960–1964.
Kamiyama, T., Enomoto, S. & Inoue, M. (1988). *Chem. Pharm. Bull.* **36**, 2652–2653.
Li, Y. & Hu, J. (2005). *Angew. Chem. Int. Ed.* **44**, 5882–5886.
Prakash, G. K. S., Ni, C., Wang, F., Zhang, Z., Haiges, R. & Olah, G. A. (2013). *Angew. Chem. Int. Ed.* **52**, 10835–10839.
Raja, S. N., Surber, B. W., Du, J. & Cross, J. L. (2009). *J. Label Compd Radiopharm.*, **52**, 98–102.
Sheldrick, G. M. (2008). *Acta Cryst.* A**64**, 112–122.
Zhao, Y., Huang, W., Zhu, L. & Hu, J. (2010). *Org. Lett.* **12**, 1444–1447.

supporting information

Acta Cryst. (2014). E**70**, o1272 [doi:10.1107/S1600536814025148]

Crystal structure of 2-[(dichloromethane)sulfonyl]pyridine

Zhiqiu Chen, Hembat Bolat, Xing Wan and Ya Li

S1. Comment

Sulfonyl groups are well-known for imparting biological activities to a lot of natural and unnatural molecules (Chen, *et al.*, 2012; Drews, 2000; Raja, *et al.*, 2009). Besides, halomethyl sulfones have been widely used in the preparation of a wide variety of halogenated compounds (Li & Hu, 2005; Prakash, *et al.*, 2013; Zhao, *et al.*, 2010). Here, we report the crystal structure of 2-(dichloromethylsulfonyl)pyridine, the title compound, which may find potential use in the synthesis of interesting chlorinated compounds.

S2. Experimental

A mixture of sodium pyridine-2-sulfinate (660 mg, 4.0 mmol), chloroform (10.0 ml) and 1N KOH (5.0 ml) was refluxed over 5h. Then the orgainc layer was separated and dried over anhydrous $MgSO_4$. Evaporation of the solvent under vacuum, followed by flash chromatography, gave the title compound (white solid, 560 mg, 62 %). The obtained powder was recrystalized from ethyl acetate/hexane(1:10) solution to give colourless prisms.

S2.1. Refinement

The H atoms of the pyridine group were placed at calculated positions and treated as riding on the parent atoms, with Uiso(H) = 1.2Ueq(C). The dichloromethyl H atom was placed at calculated position with Uiso(H) = 1.2Ueq(C).

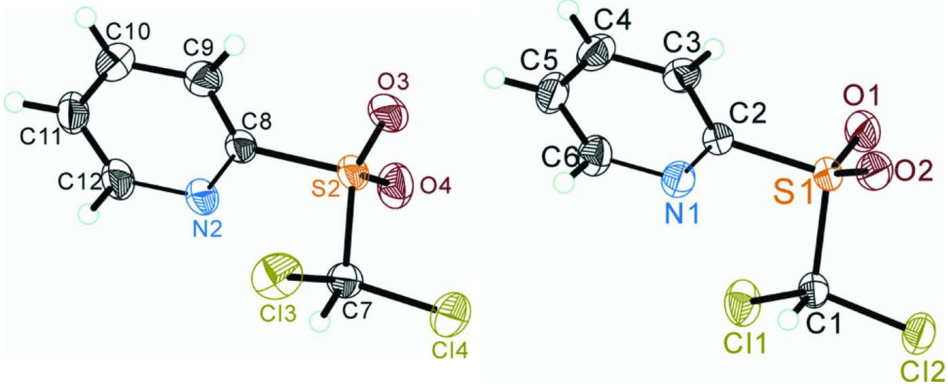


Figure 1

Molecular structure of the title compound. The displacement ellipsoids are drawn at the 50% probability level.

2-[(Dichloromethane)sulfonyl]pyridine

Crystal data

$C_6H_5Cl_2NO_2S$
M_r = 226.07
Monoclinic, $P2_1/n$

a = 9.9647 (10) Å
b = 12.2131 (11) Å
c = 15.7158 (15) Å

β = 108.483 (1)°
V = 1814.0 (3) Å^3
Z = 8
F(000) = 912
D_x = 1.656 Mg m^{-3}
Mo $K\alpha$ radiation, λ = 0.71073 Å

Cell parameters from 4116 reflections
θ = 4.3–54.4°
μ = 0.90 mm^{-1}
T = 293 K
Prism, colorless
0.21 × 0.16 × 0.12 mm

Data collection

Bruker SMART CCD diffractometer
phi and ω scans
Absorption correction: multi-scan (*SADABS*; Bruker, 2007)
T_{min} = 0.615, T_{max} = 0.746
10817 measured reflections

3570 independent reflections
2907 reflections with $I > 2\sigma(I)$
R_{int} = 0.034
θ_{max} = 26.0°, θ_{min} = 2.2°
h = −12→12
k = −15→13
l = −19→14

Refinement

Refinement on F^2
Least-squares matrix: full
$R[F^2 > 2\sigma(F^2)]$ = 0.037
$wR(F^2)$ = 0.102
S = 1.03
3570 reflections
218 parameters
0 restraints
Hydrogen site location: inferred from neighbouring sites

H-atom parameters constrained
$w = 1/[\sigma^2(F_o^2) + (0.048P)^2 + 0.7592P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max}$ = 0.001
$\Delta\rho_{max}$ = 0.37 e Å^{-3}
$\Delta\rho_{min}$ = −0.37 e Å^{-3}
Extinction correction: *SHELXL2013* (Sheldrick, 2013), $Fc^*=kFc[1+0.001xFc^2\lambda^3/\sin(2\theta)]^{-1/4}$
Extinction coefficient: 0.0286 (15)

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.

Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (Å^2)

	x	y	z	U_{iso}*/U_{eq}
S1	0.22031 (6)	0.33604 (5)	0.12351 (4)	0.04809 (18)
S2	0.34445 (7)	0.72345 (5)	0.63426 (4)	0.05073 (19)
Cl1	0.13628 (8)	0.50108 (5)	0.23115 (5)	0.0676 (2)
Cl2	0.16196 (8)	0.27131 (5)	0.28379 (5)	0.0647 (2)
Cl3	0.19229 (9)	0.60561 (8)	0.73732 (6)	0.0850 (3)
Cl4	0.32582 (10)	0.81316 (7)	0.79958 (5)	0.0874 (3)
N1	0.4188 (2)	0.47686 (16)	0.13024 (13)	0.0499 (5)
N2	0.4604 (2)	0.53408 (16)	0.62759 (13)	0.0517 (5)
O1	0.0757 (2)	0.32158 (16)	0.07175 (13)	0.0733 (6)
O2	0.3169 (2)	0.24747 (14)	0.13497 (12)	0.0672 (5)
O3	0.2167 (2)	0.77708 (15)	0.58491 (13)	0.0734 (6)
O4	0.4775 (2)	0.77492 (15)	0.64783 (14)	0.0699 (5)
C1	0.2303 (2)	0.37906 (17)	0.23599 (15)	0.0447 (5)
H1	0.3296	0.3910	0.2713	0.054*
C2	0.2870 (2)	0.45238 (18)	0.08275 (14)	0.0429 (5)

C3	0.2047 (3)	0.5082 (2)	0.00872 (16)	0.0529 (6)
H3	0.1126	0.4864	−0.0220	0.064*
C4	0.2646 (3)	0.5977 (2)	−0.01787 (17)	0.0592 (6)
H4	0.2135	0.6385	−0.0675	0.071*
C5	0.4002 (3)	0.6258 (2)	0.02950 (19)	0.0607 (7)
H5	0.4425	0.6861	0.0123	0.073*
C6	0.4741 (3)	0.5646 (2)	0.10274 (18)	0.0578 (6)
H6	0.5663	0.5851	0.1345	0.069*
C7	0.3368 (3)	0.6905 (2)	0.74546 (16)	0.0523 (6)
H7	0.4239	0.6524	0.7792	0.063*
C8	0.3445 (2)	0.59091 (18)	0.58779 (15)	0.0454 (5)
C9	0.2333 (3)	0.5566 (2)	0.51689 (17)	0.0596 (6)
H9	0.1550	0.6010	0.4916	0.072*
C10	0.2428 (3)	0.4520 (2)	0.48428 (19)	0.0691 (8)
H10	0.1695	0.4238	0.4367	0.083*
C11	0.3620 (3)	0.3912 (2)	0.52340 (19)	0.0648 (7)
H11	0.3718	0.3217	0.5019	0.078*
C12	0.4667 (3)	0.4344 (2)	0.59470 (19)	0.0612 (7)
H12	0.5463	0.3918	0.6215	0.073*

Atomic displacement parameters (Å²)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
S1	0.0590 (4)	0.0370 (3)	0.0447 (3)	−0.0097 (2)	0.0115 (3)	−0.0018 (2)
S2	0.0659 (4)	0.0382 (3)	0.0499 (3)	0.0138 (3)	0.0209 (3)	0.0044 (2)
Cl1	0.0791 (5)	0.0434 (3)	0.0909 (5)	0.0082 (3)	0.0420 (4)	0.0000 (3)
Cl2	0.0849 (5)	0.0483 (4)	0.0719 (4)	−0.0087 (3)	0.0407 (4)	0.0051 (3)
Cl3	0.0800 (5)	0.1064 (7)	0.0806 (5)	−0.0173 (5)	0.0426 (4)	−0.0035 (5)
Cl4	0.1221 (7)	0.0714 (5)	0.0727 (5)	0.0256 (5)	0.0367 (5)	−0.0173 (4)
N1	0.0482 (11)	0.0488 (11)	0.0503 (11)	−0.0034 (9)	0.0123 (9)	0.0050 (9)
N2	0.0576 (12)	0.0422 (10)	0.0543 (11)	0.0135 (9)	0.0164 (9)	0.0040 (9)
O1	0.0736 (13)	0.0696 (12)	0.0613 (11)	−0.0329 (10)	−0.0005 (10)	0.0030 (9)
O2	0.1029 (15)	0.0415 (9)	0.0640 (11)	0.0094 (9)	0.0362 (11)	0.0002 (8)
O3	0.0935 (14)	0.0607 (11)	0.0617 (11)	0.0395 (10)	0.0183 (10)	0.0112 (9)
O4	0.0863 (14)	0.0513 (10)	0.0810 (13)	−0.0130 (9)	0.0390 (11)	−0.0032 (9)
C1	0.0474 (12)	0.0372 (11)	0.0512 (13)	−0.0037 (9)	0.0182 (10)	−0.0011 (9)
C2	0.0505 (13)	0.0383 (11)	0.0400 (11)	−0.0032 (9)	0.0145 (10)	−0.0009 (9)
C3	0.0541 (14)	0.0567 (14)	0.0444 (12)	0.0023 (11)	0.0104 (11)	0.0039 (11)
C4	0.0749 (18)	0.0531 (14)	0.0522 (14)	0.0128 (13)	0.0240 (13)	0.0148 (11)
C5	0.0749 (18)	0.0466 (13)	0.0696 (17)	−0.0037 (12)	0.0357 (15)	0.0081 (12)
C6	0.0539 (14)	0.0545 (14)	0.0655 (16)	−0.0086 (12)	0.0198 (12)	0.0043 (12)
C7	0.0574 (14)	0.0522 (13)	0.0493 (13)	0.0141 (11)	0.0195 (11)	0.0013 (11)
C8	0.0556 (13)	0.0390 (11)	0.0437 (12)	0.0071 (10)	0.0187 (10)	0.0023 (9)
C9	0.0640 (16)	0.0594 (15)	0.0512 (14)	0.0108 (12)	0.0124 (12)	0.0016 (12)
C10	0.083 (2)	0.0644 (17)	0.0554 (15)	−0.0077 (15)	0.0154 (14)	−0.0098 (13)
C11	0.093 (2)	0.0406 (13)	0.0681 (17)	0.0037 (13)	0.0359 (16)	−0.0039 (12)
C12	0.0751 (18)	0.0419 (13)	0.0687 (17)	0.0158 (12)	0.0259 (14)	0.0032 (12)

Geometric parameters (Å, º)

S1—O2	1.4212 (19)	C2—C3	1.373 (3)
S1—O1	1.4235 (19)	C3—C4	1.372 (4)
S1—C2	1.772 (2)	C3—H3	0.9300
S1—C1	1.816 (2)	C4—C5	1.364 (4)
S2—O4	1.421 (2)	C4—H4	0.9300
S2—O3	1.4231 (19)	C5—C6	1.374 (4)
S2—C8	1.776 (2)	C5—H5	0.9300
S2—C7	1.818 (2)	C6—H6	0.9300
Cl1—C1	1.749 (2)	C7—H7	0.9800
Cl2—C1	1.756 (2)	C8—C9	1.364 (3)
Cl3—C7	1.746 (3)	C9—C10	1.390 (4)
Cl4—C7	1.743 (2)	C9—H9	0.9300
N1—C2	1.323 (3)	C10—C11	1.370 (4)
N1—C6	1.338 (3)	C10—H10	0.9300
N2—C8	1.323 (3)	C11—C12	1.371 (4)
N2—C12	1.332 (3)	C11—H11	0.9300
C1—H1	0.9800	C12—H12	0.9300
O2—S1—O1	120.03 (13)	C3—C4—H4	120.5
O2—S1—C2	109.84 (11)	C4—C5—C6	119.7 (2)
O1—S1—C2	108.69 (11)	C4—C5—H5	120.2
O2—S1—C1	105.72 (10)	C6—C5—H5	120.2
O1—S1—C1	108.98 (12)	N1—C6—C5	122.7 (2)
C2—S1—C1	102.05 (10)	N1—C6—H6	118.6
O4—S2—O3	120.59 (13)	C5—C6—H6	118.6
O4—S2—C8	110.07 (11)	Cl4—C7—Cl3	111.61 (13)
O3—S2—C8	108.19 (12)	Cl4—C7—S2	107.87 (13)
O4—S2—C7	105.97 (12)	Cl3—C7—S2	110.24 (13)
O3—S2—C7	108.84 (12)	Cl4—C7—H7	109.0
C8—S2—C7	101.49 (11)	Cl3—C7—H7	109.0
C2—N1—C6	115.8 (2)	S2—C7—H7	109.0
C8—N2—C12	116.0 (2)	N2—C8—C9	125.9 (2)
Cl1—C1—Cl2	112.46 (13)	N2—C8—S2	113.44 (17)
Cl1—C1—S1	109.92 (12)	C9—C8—S2	120.67 (18)
Cl2—C1—S1	106.89 (11)	C8—C9—C10	116.8 (2)
Cl1—C1—H1	109.2	C8—C9—H9	121.6
Cl2—C1—H1	109.2	C10—C9—H9	121.6
S1—C1—H1	109.2	C11—C10—C9	118.9 (3)
N1—C2—C3	125.8 (2)	C11—C10—H10	120.6
N1—C2—S1	113.34 (16)	C9—C10—H10	120.6
C3—C2—S1	120.84 (18)	C10—C11—C12	119.0 (2)
C4—C3—C2	116.9 (2)	C10—C11—H11	120.5
C4—C3—H3	121.5	C12—C11—H11	120.5
C2—C3—H3	121.5	N2—C12—C11	123.4 (2)
C5—C4—C3	119.1 (2)	N2—C12—H12	118.3
C5—C4—H4	120.5	C11—C12—H12	118.3

O2—S1—C1—Cl1	170.96 (12)	O4—S2—C7—Cl4	68.31 (15)
O1—S1—C1—Cl1	−58.75 (15)	O3—S2—C7—Cl4	−62.76 (16)
C2—S1—C1—Cl1	56.09 (14)	C8—S2—C7—Cl4	−176.70 (13)
O2—S1—C1—Cl2	−66.71 (14)	O4—S2—C7—Cl3	−169.59 (13)
O1—S1—C1—Cl2	63.58 (14)	O3—S2—C7—Cl3	59.34 (16)
C2—S1—C1—Cl2	178.41 (11)	C8—S2—C7—Cl3	−54.61 (15)
C6—N1—C2—C3	0.5 (4)	C12—N2—C8—C9	−0.3 (4)
C6—N1—C2—S1	−179.51 (18)	C12—N2—C8—S2	−179.28 (19)
O2—S1—C2—N1	−50.8 (2)	O4—S2—C8—N2	45.1 (2)
O1—S1—C2—N1	176.04 (17)	O3—S2—C8—N2	178.72 (18)
C1—S1—C2—N1	61.00 (19)	C7—S2—C8—N2	−66.86 (19)
O2—S1—C2—C3	129.1 (2)	O4—S2—C8—C9	−134.0 (2)
O1—S1—C2—C3	−4.0 (2)	O3—S2—C8—C9	−0.3 (2)
C1—S1—C2—C3	−119.0 (2)	C7—S2—C8—C9	114.1 (2)
N1—C2—C3—C4	−0.4 (4)	N2—C8—C9—C10	0.6 (4)
S1—C2—C3—C4	179.66 (18)	S2—C8—C9—C10	179.4 (2)
C2—C3—C4—C5	0.2 (4)	C8—C9—C10—C11	−1.1 (4)
C3—C4—C5—C6	−0.1 (4)	C9—C10—C11—C12	1.5 (4)
C2—N1—C6—C5	−0.5 (4)	C8—N2—C12—C11	0.7 (4)
C4—C5—C6—N1	0.3 (4)	C10—C11—C12—N2	−1.3 (4)

Hydrogen-bond geometry (Å, º)

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
C1—H1···N2^{i}	0.98	2.37	3.321 (3)	163
C5—H5···O3^{ii}	0.93	2.64	3.220 (3)	121
C6—H6···O3^{ii}	0.93	2.54	3.177 (3)	126
C7—H7···N1^{i}	0.98	2.36	3.303 (3)	162
C11—H11···O1^{iii}	0.93	2.64	3.292 (3)	128

Symmetry codes: (i) −*x*+1, −*y*+1, −*z*+1; (ii) *x*+1/2, −*y*+3/2, *z*−1/2; (iii) *x*+1/2, −*y*+1/2, *z*+1/2.