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2-(Thiophen-2-yl)ethyl 4-methylbenzenesulfonate

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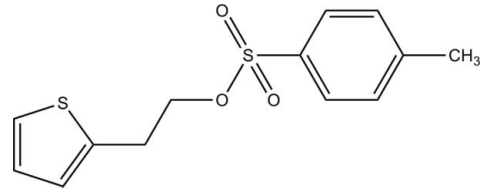
Key indicators: single-crystal X-ray study; T = 113 K; mean σ(C–C) = 0.003 Å; R factor = 0.035; wR factor = 0.088; data-to-parameter ratio = 19.3.

In the title molecule, $C_{13}H_{14}O_3S_2$, the thiophene and benzene rings form a dihedral angle of 13.86 (13)°. In the crystal, weak intermolecular C—H···O hydrogen bonds link the molecules into layers parallel to the *ab* plane.

Related literature

The title compound is an intermediate in the synthesis of the antiplatelet agent clopidogrel (systematic name (+)-(*S*)-methyl 2-(2-chlorophenyl)-2-(6,7-dihydrothieno[3,2-*c*]pyridin-5(4*H*)-yl)acetate). For background to the bioactivity and applications of clopidogrel, see: Raju *et al.* (2008). For the synthesis of the title compound, see: Sajja *et al.* (2007).



Experimental

Crystal data

$C_{13}H_{14}O_3S_2$
M_r = 282.36
Monoclinic, $P2_1$
a = 8.6130 (9) Å
b = 5.9961 (4) Å
c = 13.1284 (12) Å
β = 97.935 (19)°
V = 671.52 (10) Å^3
Z = 2
Mo $K\alpha$ radiation
μ = 0.39 mm^{-1}
T = 113 K
0.20 × 0.18 × 0.10 mm

Data collection

Rigaku Saturn CCD area-detector diffractometer
Absorption correction: multi-scan (*CrystalClear*; Rigaku/MSC, 2005)
T_{min} = 0.926, T_{max} = 0.962
6939 measured reflections
3167 independent reflections
2365 reflections with $I > 2\sigma(I)$
R_{int} = 0.048

Refinement

$R[F^2 > 2\sigma(F^2)]$ = 0.035
$wR(F^2)$ = 0.088
S = 0.83
3167 reflections
164 parameters
1 restraint
H-atom parameters constrained
$\Delta\rho_{max}$ = 0.39 e Å^{-3}
$\Delta\rho_{min}$ = −0.38 e Å^{-3}
Absolute structure: Flack (1983), 1405 Friedel pairs
Flack parameter: 0.00 (8)

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

D—H···A	D—H	H···A	D···A	D—H···A
C2—H2···O2^{i}	0.95	2.58	3.523 (3)	174
C6—H6B···O2^{ii}	0.99	2.41	3.161 (3)	132
C13—H13A···O3^{iii}	0.98	2.58	3.496 (3)	155

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

Data collection: *CrystalClear* (Rigaku/MSC, 2005); cell refinement: *CrystalClear*; data reduction: *CrystalClear*; 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: *CrystalStructure* (Rigaku/MSC, 2005).

The authors thank Mr Hai-Bin Song of Nankai University for the X-ray crystal structure determination and helpful suggestions.

Supplementary data and figures for this paper are available from the IUCr electronic archives (Reference: CV5113).

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supplementary materials

Acta Cryst. (2011). E**67**, o1787 [**doi:10.1107/S1600536811023907**]

2-(Thiophen-2-yl)ethyl 4-methylbenzenesulfonate

Y.-S. Liang, B.-N. Liu, M. Liu and D.-K. Liu

Comment

Clopidogrel, a thienopyridine class inhibitor of P2Y12 ADP platelet receptor, has been found to be particularly useful in the treatment of coronary artery disease, peripheral vascular disease and cerebrovascular disease (Raju *et al.*, 2008). Herewith we present the crystal structure of the title compound (I) used as an intermediate in the synthesis of clopidogrel (Sajja *et al.*, 2007).

In (I) (Fig. 1), the dihedral angle formed between the benzene ring plane (r.m.s. deviation 0.0029 Å) and the thiophene ring plane (r.m.s. deviation 0.0025 Å) is 13.86 (13)°. The packing of the crystal is consolidated by the weak C—H···O interactions (Table 1).

Experimental

5 g of 4-Methylbenzene-1-sulfonyl chloride and 30 ml of toluene were charged into a clean and dry reactor followed by cooling to about 5 °C. 3.4 g 2-(Thiophen-2-yl)ethanol was added at about 5 °C over about 20 minutes, followed by addition of 4.5 g of triethylamine over about 6 h. The reaction mixture temperature was raised to about 30 °C, followed by stirring for about 9 h. The reaction mass was filtered through a Nutsche filter and washed with 50 ml of toluene, and then, the reaction filtrate was transferred into another reactor followed by washing with 80 ml of water. Organic and aqueous layers were separated and the organic layer was distilled completely at about below 70 °C to afford 6.3 g of off-white solid as crude product. The solid was dissolved in methanol 30 ml at 20 °C, then colourless crystals were generated slowly.

Refinement

All H atoms were positioned geometrically (C—H 0.95 - 0.99 Å) and refined using a riding model, with U_{iso}(H) = 1.2 or 1.5U_{eq}(C).

Figures

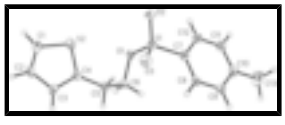

Fig. 1. The molecular structure of (I), with the atom-numbering scheme and 50% probability displacement ellipsoids.

2-(Thiophen-2-yl)ethyl 4-methylbenzenesulfonate

Crystal data

$C_{13}H_{14}O_3S_2$	$F(000) = 296$
$M_r = 282.36$	$D_x = 1.396$ Mg m^{-3}

Monoclinic, $P2_1$	Mo $K\alpha$ radiation, $\lambda = 0.71073$ Å
Hall symbol: P 2yb	Cell parameters from 2573 reflections
$a = 8.6130$ (9) Å	$\theta = 2.4$–$27.9°$
$b = 5.9961$ (4) Å	$\mu = 0.39$ mm^{-1}
$c = 13.1284$ (12) Å	$T = 113$ K
$\beta = 97.935$ (19)°	Prism, colourless
$V = 671.52$ (10) Å^3	0.20 × 0.18 × 0.10 mm
$Z = 2$	

Data collection

Rigaku Saturn CCD area-detector diffractometer	3167 independent reflections
Radiation source: rotating anode	2365 reflections with $I > 2\sigma(I)$
multilayer	$R_{int} = 0.048$
Detector resolution: 14.63 pixels mm^{-1}	$\theta_{max} = 27.9°$, $\theta_{min} = 2.4°$
ω and φ scans	$h = -11 \rightarrow 11$
Absorption correction: multi-scan (*CrystalClear*; Rigaku/MSC, 2005)	$k = -7 \rightarrow 7$
$T_{min} = 0.926$, $T_{max} = 0.962$	$l = -17 \rightarrow 13$
6939 measured reflections	

Refinement

Refinement on F^2	Secondary atom site location: difference Fourier map
Least-squares matrix: full	Hydrogen site location: inferred from neighbouring sites
$R[F^2 > 2\sigma(F^2)] = 0.035$	H-atom parameters constrained
$wR(F^2) = 0.088$	$w = 1/[\sigma^2(F_o^2) + (0.0455P)^2]$ where $P = (F_o^2 + 2F_c^2)/3$
$S = 0.83$	$(\Delta/\sigma)_{max} = 0.021$
3167 reflections	$\Delta\rho_{max} = 0.39$ e Å^{-3}
164 parameters	$\Delta\rho_{min} = -0.38$ e Å^{-3}
1 restraint	Absolute structure: Flack (1983), 1405 Friedel pairs
Primary atom site location: structure-invariant direct methods	Flack parameter: 0.00 (8)

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}
S1	0.19325 (6)	0.31172 (10)	0.75706 (4)	0.02115 (14)
S2	0.22445 (7)	0.29779 (13)	0.39671 (4)	0.03087 (17)
O1	0.15911 (18)	0.3941 (3)	0.64203 (11)	0.0213 (4)
O2	0.1803 (2)	0.0753 (3)	0.75046 (13)	0.0330 (5)
O3	0.33583 (19)	0.4105 (3)	0.80406 (12)	0.0278 (4)
C1	0.3827 (2)	0.3018 (6)	0.33242 (16)	0.0278 (5)
H1	0.4116	0.1822	0.2915	0.033*
C2	0.4623 (3)	0.4953 (5)	0.34661 (18)	0.0275 (6)
H2	0.5542	0.5244	0.3163	0.033*
C3	0.3976 (2)	0.6547 (4)	0.41104 (16)	0.0193 (5)
H3	0.4385	0.7991	0.4282	0.023*
C4	0.2621 (3)	0.5599 (4)	0.44481 (16)	0.0201 (5)
C5	0.1556 (3)	0.6739 (4)	0.51055 (16)	0.0263 (6)
H5A	0.1611	0.8368	0.4993	0.032*
H5B	0.0465	0.6263	0.4870	0.032*
C6	0.1919 (3)	0.6291 (4)	0.62353 (17)	0.0221 (5)
H6A	0.3035	0.6624	0.6477	0.027*
H6B	0.1265	0.7255	0.6617	0.027*
C7	0.0366 (3)	0.4163 (4)	0.81555 (16)	0.0202 (5)
C8	0.0527 (3)	0.6179 (4)	0.86654 (16)	0.0207 (5)
H8	0.1479	0.6996	0.8707	0.025*
C9	−0.0732 (3)	0.7003 (4)	0.91203 (16)	0.0232 (5)
H9	−0.0638	0.8400	0.9465	0.028*
C10	−0.2126 (3)	0.5795 (5)	0.90745 (16)	0.0269 (6)
C11	−0.2247 (3)	0.3748 (4)	0.85539 (17)	0.0261 (6)
H11	−0.3190	0.2912	0.8518	0.031*
C12	−0.1017 (2)	0.2926 (5)	0.80928 (15)	0.0233 (5)
H12	−0.1110	0.1540	0.7739	0.028*
C13	−0.3486 (3)	0.6686 (5)	0.9550 (2)	0.0415 (8)
H13A	−0.4457	0.6455	0.9078	0.062*
H13B	−0.3336	0.8284	0.9687	0.062*
H13C	−0.3554	0.5901	1.0197	0.062*

Atomic displacement parameters (Å^2)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
S1	0.0254 (3)	0.0184 (3)	0.0206 (3)	0.0022 (3)	0.0066 (2)	0.0007 (3)
S2	0.0249 (3)	0.0325 (4)	0.0362 (3)	−0.0035 (4)	0.0080 (2)	−0.0007 (4)
O1	0.0264 (9)	0.0206 (9)	0.0176 (8)	−0.0047 (7)	0.0059 (7)	−0.0013 (6)
O2	0.0464 (11)	0.0142 (11)	0.0429 (12)	0.0044 (8)	0.0224 (9)	0.0026 (8)
O3	0.0240 (9)	0.0355 (11)	0.0228 (9)	0.0015 (8)	−0.0004 (7)	0.0032 (8)
C1	0.0266 (12)	0.0343 (14)	0.0230 (11)	0.0024 (15)	0.0053 (9)	−0.0027 (15)
C2	0.0210 (13)	0.0330 (16)	0.0301 (13)	0.0011 (11)	0.0097 (10)	0.0086 (12)
C3	0.0179 (11)	0.0230 (15)	0.0163 (11)	0.0085 (10)	0.0000 (8)	0.0010 (10)

C4	0.0235 (12)	0.0206 (14)	0.0160 (11)	0.0033 (10)	0.0018 (9)	0.0051 (10)
C5	0.0282 (13)	0.0274 (16)	0.0245 (12)	0.0073 (11)	0.0080 (10)	0.0070 (11)
C6	0.0246 (12)	0.0189 (14)	0.0236 (12)	−0.0014 (10)	0.0056 (9)	−0.0005 (10)
C7	0.0245 (13)	0.0214 (14)	0.0149 (11)	0.0018 (10)	0.0032 (9)	0.0009 (10)
C8	0.0277 (13)	0.0196 (14)	0.0149 (11)	−0.0032 (10)	0.0041 (9)	0.0017 (9)
C9	0.0317 (13)	0.0192 (13)	0.0185 (11)	0.0031 (11)	0.0026 (9)	−0.0029 (11)
C10	0.0283 (14)	0.0343 (17)	0.0182 (12)	0.0025 (12)	0.0036 (10)	−0.0009 (11)
C11	0.0251 (13)	0.0309 (17)	0.0225 (12)	−0.0049 (10)	0.0039 (10)	−0.0049 (10)
C12	0.0300 (12)	0.0200 (13)	0.0196 (10)	−0.0027 (13)	0.0023 (8)	−0.0010 (12)
C13	0.0290 (14)	0.059 (2)	0.0373 (15)	0.0042 (15)	0.0080 (11)	−0.0180 (16)

Geometric parameters (Å, °)

S1—O2	1.4236 (19)	C6—H6A	0.9900
S1—O3	1.4250 (17)	C6—H6B	0.9900
S1—O1	1.5776 (15)	C7—C8	1.379 (3)
S1—C7	1.758 (2)	C7—C12	1.396 (3)
S2—C1	1.700 (2)	C8—C9	1.399 (3)
S2—C4	1.708 (3)	C8—H8	0.9500
O1—C6	1.464 (3)	C9—C10	1.396 (3)
C1—C2	1.347 (4)	C9—H9	0.9500
C1—H1	0.9500	C10—C11	1.402 (4)
C2—C3	1.438 (3)	C10—C13	1.500 (3)
C2—H2	0.9500	C11—C12	1.382 (3)
C3—C4	1.423 (3)	C11—H11	0.9500
C3—H3	0.9500	C12—H12	0.9500
C4—C5	1.507 (3)	C13—H13A	0.9800
C5—C6	1.497 (3)	C13—H13B	0.9800
C5—H5A	0.9900	C13—H13C	0.9800
C5—H5B	0.9900		
O2—S1—O3	119.74 (12)	C5—C6—H6A	110.0
O2—S1—O1	104.53 (10)	O1—C6—H6B	110.0
O3—S1—O1	108.65 (9)	C5—C6—H6B	110.0
O2—S1—C7	108.87 (12)	H6A—C6—H6B	108.4
O3—S1—C7	109.28 (11)	C8—C7—C12	121.5 (2)
O1—S1—C7	104.69 (10)	C8—C7—S1	119.52 (18)
C1—S2—C4	92.64 (13)	C12—C7—S1	119.0 (2)
C6—O1—S1	116.46 (14)	C7—C8—C9	119.0 (2)
C2—C1—S2	111.8 (2)	C7—C8—H8	120.5
C2—C1—H1	124.1	C9—C8—H8	120.5
S2—C1—H1	124.1	C10—C9—C8	120.8 (2)
C1—C2—C3	115.0 (2)	C10—C9—H9	119.6
C1—C2—H2	122.5	C8—C9—H9	119.6
C3—C2—H2	122.5	C9—C10—C11	118.7 (2)
C4—C3—C2	108.6 (2)	C9—C10—C13	120.9 (3)
C4—C3—H3	125.7	C11—C10—C13	120.3 (2)
C2—C3—H3	125.7	C12—C11—C10	121.1 (2)
C3—C4—C5	126.0 (2)	C12—C11—H11	119.5
C3—C4—S2	111.98 (17)	C10—C11—H11	119.5

C5—C4—S2	121.96 (18)	C11—C12—C7	118.9 (3)
C6—C5—C4	115.19 (19)	C11—C12—H12	120.5
C6—C5—H5A	108.5	C7—C12—H12	120.5
C4—C5—H5A	108.5	C10—C13—H13A	109.5
C6—C5—H5B	108.5	C10—C13—H13B	109.5
C4—C5—H5B	108.5	H13A—C13—H13B	109.5
H5A—C5—H5B	107.5	C10—C13—H13C	109.5
O1—C6—C5	108.57 (19)	H13A—C13—H13C	109.5
O1—C6—H6A	110.0	H13B—C13—H13C	109.5
O2—S1—O1—C6	−169.41 (15)	O3—S1—C7—C8	22.3 (2)
O3—S1—O1—C6	−40.48 (18)	O1—S1—C7—C8	−93.96 (19)
C7—S1—O1—C6	76.18 (17)	O2—S1—C7—C12	−25.2 (2)
C4—S2—C1—C2	0.0 (2)	O3—S1—C7—C12	−157.67 (17)
S2—C1—C2—C3	−0.4 (3)	O1—S1—C7—C12	86.1 (2)
C1—C2—C3—C4	0.7 (3)	C12—C7—C8—C9	−0.6 (3)
C2—C3—C4—C5	−177.6 (2)	S1—C7—C8—C9	179.48 (17)
C2—C3—C4—S2	−0.6 (2)	C7—C8—C9—C10	0.9 (3)
C1—S2—C4—C3	0.37 (17)	C8—C9—C10—C11	−0.6 (3)
C1—S2—C4—C5	177.50 (18)	C8—C9—C10—C13	−179.2 (2)
C3—C4—C5—C6	−94.9 (3)	C9—C10—C11—C12	0.0 (3)
S2—C4—C5—C6	88.4 (2)	C13—C10—C11—C12	178.6 (2)
S1—O1—C6—C5	178.83 (14)	C10—C11—C12—C7	0.3 (3)
C4—C5—C6—O1	−67.3 (3)	C8—C7—C12—C11	0.0 (3)
O2—S1—C7—C8	154.71 (18)	S1—C7—C12—C11	179.91 (17)

Hydrogen-bond geometry (Å, °)

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
C2—H2···O2^{i}	0.95	2.58	3.523 (3)	174
C6—H6B···O2^{ii}	0.99	2.41	3.161 (3)	132
C13—H13A···O3^{iii}	0.98	2.58	3.496 (3)	155

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

Fig. 1