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Bis(4-chloromethyl-2,5-dimethyl-3-thienyl)methane

Masataka Watanabe,[a] Asami Miura,[b] Taisuke Matsumoto,[b] Shuntaro Mataka[b] and Thies Thiemann[b]*

[a]Interdisciplinary Graduate School of Engineering, Kyushu University, 6-1 Kasuga-koh-en, Kasuga-shi, Fukuoka 816-8580, Japan, and [b]Institute of Materials Chemistry and Engineering, Kyushu University, 6-1 Kasuga-koh-en, Kasuga-shi, Fukuoka 816-8580, Japan

Correspondence e-mail:
thies@cm.kyushu-u.ac.jp

Key indicators

Single-crystal X-ray study
T = 123 K
Mean σ(C–C) = 0.003 Å
R factor = 0.030
wR factor = 0.102
Data-to-parameter ratio = 14.0

For details of how these key indicators were automatically derived from the article, see http://journals.iucr.org/e.

In the title compound, $C_{15}H_{18}Cl_2S_2$, the molecule has a crystallographic twofold axis. The dihedral angle between the symmetry-related thiophene rings is 85.54 (8)°.

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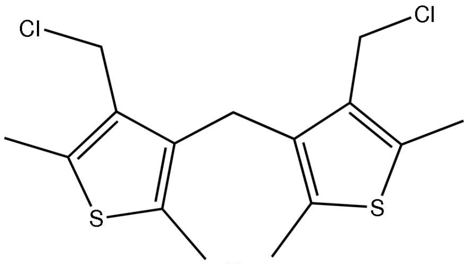
Comment

The title compound, (I), was synthesized by chloromethylation of 2,5-dimethylthiophene (Gol'dfarb & Kondakova, 1956). Compound (I) is an important starting material for bisthieno-fused ring systems (Brown & Carruthers, 1981) and has been used as a starting material for the construction of macrocyclic systems (Li *et al.*, 1994). The asymmetric unit of (I) contains one-half of the molecule (Fig. 1), with the other half generated by a crystallographic twofold axis passing through atom C6. The C3—C7 bond length is 1.491 (3) Å. While there are no comparable data available for chloromethyl-substituted thiophenes, this bond length is comparable to corresponding bonds in chloromethylarenes. The Cl1—C7 bond length in (I) is 1.828 (2) Å. In chloromethylarenes, the length of the benzylic C—Cl bond is governed by the electronic character of the arene, with a range of 1.713–1.816 Å and an average bond length of 1.793 Å [Cambridge Structural Database (CSD); Release of 2004; Allen, 2002]. In electron-rich arenes, longer C—Cl bonds are found, but these are still slightly shorter than the C7—Cl1 bond in (I).



(I)

The dihedral angle between the symmetry-related thiophene rings is 85.54 (8)°, putting the two thienyl cores virtually in an orthogonal position with respect to each other. Coplanar positioning of the rings in one molecule is impeded by the closeness of the α-substituent of one ring to either the α- or β-substituent of the second ring, while the size of the dihedral angle is governed in part by intermolecular packing. At 116.5 (2)°, the C2—C6—C2^{i} bond angle [symmetry code: (i) $1 - x, y, \frac{3}{2} - z$] is among the largest of the angles found in diarylmethanes and bis(hetero-aryl)methanes (average value 114.5°; CSD). The distance between the chloro-substituted C atoms C7 and C7^{i}, which are the reactive centers for macrocyclization reactions, is 4.766 (3) Å.

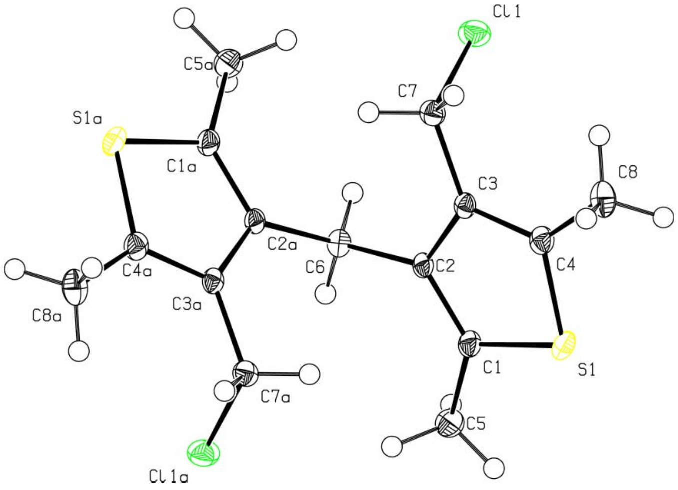


Figure 1
A view of the molecule of (I) with the atom-numbering scheme. Displacement ellipsoids are drawn at the 50% probability level. The suffix *a* corresponds to symmetry code (i) in Table 1.

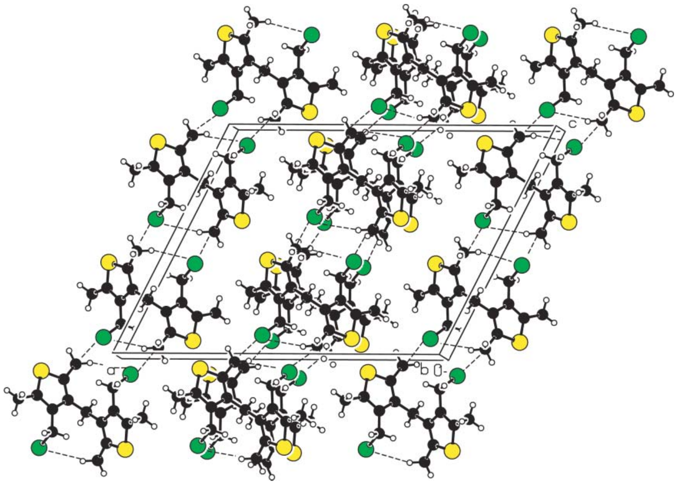


Figure 2
A view, down the *b* axis, of the unit cell contents of (I). Inter- and intramolecular contacts are shown as dashed lines.

In the crystal structure, molecules form chains in a stepwise fashion parallel to the *c* axis (Fig. 2). The governing factor in the chain is the intermolecular carbon–halogen interaction between atoms Cl1 and C5^{iv} [symmetry code: (iv) $x, -y, \frac{1}{2} + z$] [3.324 (2) Å, the sum of the van der Waals radii of C and Cl being 3.45 Å (Bondi, 1964)]. The intramolecular distance between atoms Cl1 and C5^{i} is longer, at 3.826 (2) Å, and does not qualify as a close contact [a Cl···C close contact is taken as equal to or smaller than 3.45 Å (Desiraju & Parthasarathy, 1989)]. However, the distance to the corresponding H atom is within the range of a close contact [Cl1···H5*B*^{i} = 2.92 Å; a Cl···H close contact is taken as equal to or shorter than 2.96 Å (Desiraju & Parthasarathy, 1989)]. Furthermore, there are two weak C—H···π interactions (Table 2) involving both methyl groups of both thienyl units [for C—H···π interactions, the H···π distance is proposed as equal to or shorter than 3.1 Å (Nishio & Hirota, 1989)].

Experimental

Compound (I) was prepared by the reaction of 2,5-dimethylthiophene (20.0 g, 0.18 mol) and chloromethyl methyl ether (50.0 g, 0.62 mol) in acetic acid (100 ml) (Gol'dfarb & Kondakova, 1956; Li *et al.*, 1994) and crystallized from benzene by slow evaporation (yield 13%).

Crystal data

$C_{15}H_{18}Cl_2S_2$
$M_r = 333.33$
Monoclinic, $C2/c$
$a = 20.797$ (4) Å
$b = 5.068$ (1) Å
$c = 16.253$ (3) Å
$\beta = 116.42$ (1)°
$V = 1534.1$ (5) Å^3
$Z = 4$

$D_x = 1.443$ Mg m^{-3}
Cu $K\alpha$ radiation
Cell parameters from 8753 reflections
$\theta = 3.0$–68.2°
$\mu = 6.20$ mm^{-1}
$T = 123.1$ K
Prism, colorless
0.30 × 0.30 × 0.12 mm

Data collection

Rigaku R-AXIS RAPID diffractometer
ω scans
Absorption correction: numerical (*ABSCOR*; Higashi, 1999)
$T_{\min} = 0.431$, $T_{\max} = 0.475$
9291 measured reflections

1382 independent reflections
1278 reflections with $F^2 > 2\sigma(F^2)$
$R_{\rm int} = 0.048$
$\theta_{\max} = 68.2°$
$h = -24 \rightarrow 24$
$k = -5 \rightarrow 5$
$l = -19 \rightarrow 18$

Refinement

Refinement on F^2
$R(F) = 0.030$
$wR(F^2) = 0.102$
$S = 1.00$
1382 reflections
99 parameters
H-atom parameters constrained

$w = 1/[0.001F_o^2 + \sigma(F_o^2)]/(4F_o^2)$
$(\Delta/\sigma)_{\max} < 0.001$
$\Delta\rho_{\max} = 0.36$ e Å^{-3}
$\Delta\rho_{\min} = -0.43$ e Å^{-3}
Extinction correction: Larson (1970)
Extinction coefficient: 44 (4)

Table 1
Selected geometric parameters (Å, °).

Cl1—C7	1.828 (2)	C3—C7	1.491 (3)
C2—C6	1.517 (2)		
C2—C6—C2^{i}	116.5 (2)		

Symmetry code: (i) $1 - x, y, \frac{3}{2} - z$.

Table 2
Hydrogen-bond geometry (Å, °).

D—H···*A*	*D*—H	H···*A*	*D*···A	*D*—H··· *A*
C5—H5A···Cg1^{ii}	0.95	2.84	3.767 (2)	166
C8—H8B···Cg1^{iii}	0.95	3.16	4.060 (2)	158

Symmetry codes: (ii) $x, 1 + y, z$; (iii) $x, y - 1, z$.

All H atoms were placed in calculated positions and refined as riding on their parent atoms, with $U_{\rm iso}$(H) = $1.2U_{\rm eq}$(C) and with C—H = 0.95 Å. The methyl groups were not allowed to rotate. *Cg*1 is the centroid of the thiophene ring.

Data collection and cell refinement: *CrystalClear* (Rigaku, 1999); data reduction: *CrystalStructure* (Rigaku/MSC, 2004); structure solution: *SIR97* (Altomare *et al.*, 1999); structure refinement: *SHELXL97* (Sheldrick, 1997); molecular graphics: *PLATON* (Spek, 2003); publication material: *CrystalStructure*.

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