

1,2-Bis(3-thienyloxy)ethane: a thiophene-based precursor for thiophene-based azacryptand Mannich bases

Gaël Labat^a and Joan Halfpenny^{b*}^aInstitut de Chimie, Université de Neuchâtel, Avenue de Bellevaux 51, CH-2007 Neuchâtel, Switzerland, and ^bDepartment of Chemistry and Physics, Nottingham Trent University, Clifton Lane, Nottingham NG11 8NS, England

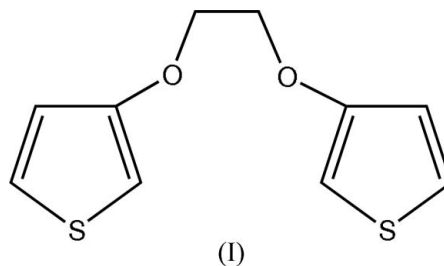
Correspondence e-mail: gael.labat@unine.ch

Key indicatorsSingle-crystal X-ray study
 $T = 153$ K
Mean $\sigma(\text{C}-\text{C}) = 0.002$ Å
 R factor = 0.031
 wR factor = 0.090
Data-to-parameter ratio = 21.8For details of how these key indicators were automatically derived from the article, see <http://journals.iucr.org/e>.

The title compound, $\text{C}_{10}\text{H}_{12}\text{O}_2\text{S}_2$, is composed of two thiophene rings bridged by an $-\text{O}(\text{CH}_2)_2\text{O}-$ chain in a *trans* arrangement. The molecule possesses C_2 symmetry with the twofold axis bisecting the central $\text{C}-\text{C}$ bond. In the crystal structure, molecules related by a centre of symmetry are bridged by $\text{C}-\text{H}\cdots\text{O}$ hydrogen bonds, forming a zigzag one-dimensional chain extending in the c -axis direction.

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The preparation of a range of open-chain cryptand-like structures, incorporating thiophene rings, as precursors for azacryptand Mannich bases, has been described by Barker *et al.* (1993) and Chaffin *et al.* (2001, 2002). The title compound, (I), was prepared by the reaction of methyl 3-hydroxythiophene-2-carboxylate with 1,2-dichloroethane and anhydrous potassium carbonate in anhydrous *N,N*-dimethylformamide, followed by saponification and decarboxylation.



The molecular structure of (I) is illustrated in Fig. 1, and selected bond distances and angles are given in Table 1. In compound (I), two thiophene rings are bridged by an $-\text{O}(\text{CH}_2)_2\text{O}-$ chain in a *trans* arrangement. A twofold axis bisects the central ethane bond [$\text{C}5-\text{C}5(1-x, y, \frac{1}{2}-z)$] and each half of the molecule is almost planar, with $\text{C}5-\text{O}1-\text{C}2-\text{C}1$ and $\text{C}5-\text{O}1-\text{C}2-\text{C}3$ torsion angles of 0.00 (18) and -178.45 (11) $^\circ$, respectively. The bond lengths and angles (Table 1) are similar to those in an unsubstituted thiophene described by Bonham & Momany (1963).

The crystal packing of compound (I) is illustrated in Fig. 2. The molecules related by centres of symmetry are linked by $\text{C}-\text{H}\cdots\text{O}$ hydrogen bonds; details are given in Table 2. It can be seen that the molecules are arranged in a such a way as to form a zigzag one-dimensional polymer extending in the crystallographic c -axis direction.

Experimental

Compound (I) was synthesized according to the procedure described by Chaffin *et al.* (2001). Suitable crystals for X-ray crystallography

analysis were obtained by slow evaporation of a 1:1 ethanol-dichloromethane solution.

Crystal data

C₁₀H₁₀O₂S₂
M_r = 226.30
 Monoclinic, *C*2/*c*
a = 22.175 (3) Å
b = 5.3918 (4) Å
c = 9.0831 (11) Å
 β = 111.362 (9)°
V = 1011.39 (19) Å³
Z = 4

D_x = 1.486 Mg m⁻³
 Mo *K*α radiation
 Cell parameters from 9090 reflections
 θ = 1.9–29.6°
 μ = 0.49 mm⁻¹
T = 153 (2) K
 Plate, colourless
 0.5 × 0.5 × 0.2 mm

Data collection

Stoe IPDS-II diffractometer
 ω scans
 Absorption correction: none
 9441 measured reflections
 1398 independent reflections
 1302 reflections with *I* > 2σ(*I*)

*R*_{int} = 0.053
 θ_{max} = 29.4°
h = -30 → 30
k = -7 → 7
l = -11 → 12

Refinement

Refinement on *F*²
R [*F*² > 2σ(*F*²)] = 0.031
wR (*F*²) = 0.090
S = 1.03
 1398 reflections
 64 parameters
 H-atom parameters constrained

w = 1/[σ²(*F_o*²) + (0.0472*P*)² + 1.0038*P*]
 where *P* = (*F_o*² + 2*F_c*²)/3
 (Δ/σ)_{max} = 0.001
 Δρ_{max} = 0.35 e Å⁻³
 Δρ_{min} = -0.35 e Å⁻³

Table 1

Selected geometric parameters (Å, °).

S1–C4	1.7129 (14)	C3–C4	1.3674 (19)
S1–C1	1.7178 (13)	C3–C2	1.4227 (17)
O1–C2	1.3597 (15)	C2–C1	1.3672 (17)
O1–C5	1.4288 (15)	C5–C5 ⁱ	1.500 (2)
C4–S1–C1	92.55 (6)	O1–C2–C3	118.83 (11)
C2–O1–C5	115.12 (10)	C3–C4–S1	111.56 (10)
C4–C3–C2	111.88 (11)	O1–C5–C5 ⁱ	108.13 (9)
C1–C2–O1	127.57 (12)	C2–C1–S1	110.43 (10)
C1–C2–C3	113.59 (12)		

Symmetry code: (i) -x + 1, y, -z + ½.

Table 2

Hydrogen-bond geometry (Å, °).

<i>D</i> –H... <i>A</i>	<i>D</i> –H	H... <i>A</i>	<i>D</i> ... <i>A</i>	<i>D</i> –H... <i>A</i>
C3–H3...O1 ⁱⁱ	1.00	2.41	3.3940 (16)	170

Symmetry code: (ii) -x + 1, -y, -z.

H atoms were located in difference Fourier maps and held fixed with *U*_{iso}(H) = 0.05 Å² and C–H = 0.94–1.05 Å.

Data collection: *X*-AREA (Stoe & Cie, 2002); cell refinement: *X*-AREA; data reduction: *X*-RED32 (Stoe & Cie, 2002); program(s) used to solve structure: *SHELXS97* (Sheldrick, 1997); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *PLATON* (Spek, 2003); software used to prepare material for publication: *SHELXL97*.

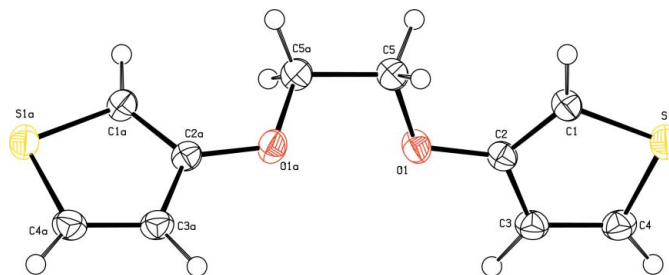


Figure 1

View of compound (I), showing the atom-labelling scheme. Displacement ellipsoids are drawn at the 50% probability level. [Symmetry code: (a) 1 - x, y, ½ - z.]

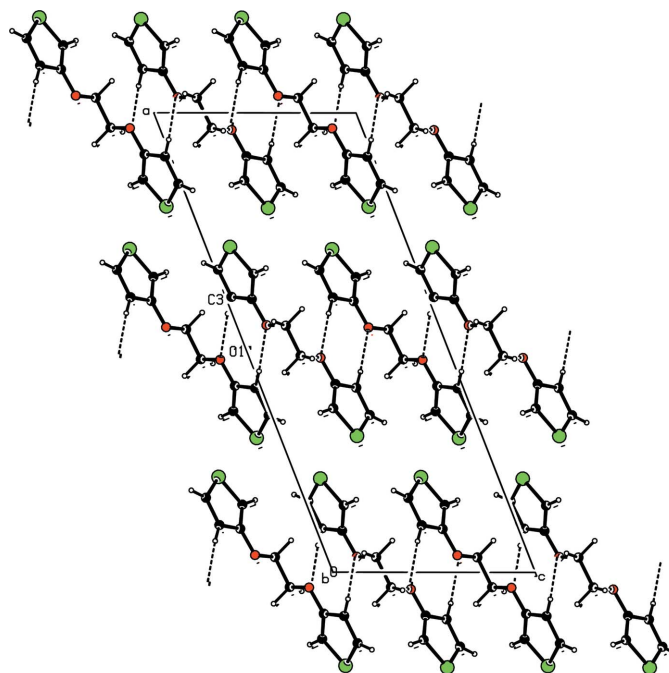


Figure 2

The crystal packing of compound (I), viewed down the *b* axis. C–H...O hydrogen bonds are shown as dashed lines (details are given in Table 2).

The authors thank Professor Helen Stoeckli-Evans (Université de Neuchâtel) for making available the Stoe *IPDS* diffractometer for data collection.

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supporting information

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D_x = 1.486 Mg m⁻³
 Mo *K*α radiation, λ = 0.71073 Å
 Cell parameters from 9090 reflections
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 Plate, colourless
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 Graphite monochromator
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 ω scans
 9441 measured reflections

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 1302 reflections with $I > 2\sigma(I)$
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 θ_{max} = 29.4°, θ_{min} = 2.0°
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 k = -7→7
 l = -11→12

Refinement

Refinement on *F*²
 Least-squares matrix: full
 $R[F^2 > 2\sigma(F^2)]$ = 0.031
 $wR(F^2)$ = 0.090
 S = 1.03
 1398 reflections
 64 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
 $w = 1/[\sigma^2(F_o^2) + (0.0472P)^2 + 1.0038P]$
 where $P = (F_o^2 + 2F_c^2)/3$
 $(\Delta/\sigma)_{\text{max}}$ = 0.001
 $\Delta\rho_{\text{max}}$ = 0.35 e Å⁻³
 $\Delta\rho_{\text{min}}$ = -0.35 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 (\AA^2)

	x	y	z	$U_{\text{iso}}^*/U_{\text{eq}}$
S1	0.705495 (15)	0.30108 (6)	0.11836 (4)	0.02820 (13)
O1	0.53539 (5)	0.28858 (18)	0.14777 (11)	0.0259 (2)
C3	0.59883 (6)	0.0614 (2)	0.02934 (16)	0.0261 (3)
H3	0.5630	-0.0585	-0.0223	0.050*
C2	0.59236 (6)	0.2606 (2)	0.12527 (14)	0.0216 (2)
C4	0.65818 (7)	0.0611 (2)	0.01542 (16)	0.0282 (3)
H4	0.6733	-0.0522	-0.0426	0.050*
C5	0.53252 (6)	0.4969 (2)	0.24223 (15)	0.0247 (3)
H5A	0.5691	0.4837	0.3545	0.050*
H5B	0.5403	0.6558	0.1910	0.050*
C1	0.64618 (6)	0.4075 (2)	0.18219 (14)	0.0236 (2)
H1	0.6573	0.5546	0.2544	0.050*

Atomic displacement parameters (\AA^2)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
S1	0.02423 (18)	0.0307 (2)	0.0318 (2)	-0.00172 (11)	0.01271 (14)	-0.00265 (12)
O1	0.0246 (4)	0.0290 (5)	0.0272 (5)	-0.0060 (3)	0.0133 (4)	-0.0087 (3)
C3	0.0301 (6)	0.0217 (5)	0.0275 (6)	-0.0026 (5)	0.0119 (5)	-0.0034 (5)
C2	0.0240 (5)	0.0222 (5)	0.0194 (5)	-0.0016 (4)	0.0091 (4)	0.0006 (4)
C4	0.0323 (6)	0.0231 (6)	0.0306 (6)	0.0008 (5)	0.0132 (5)	-0.0032 (5)
C5	0.0280 (6)	0.0258 (6)	0.0224 (5)	-0.0027 (5)	0.0118 (5)	-0.0040 (4)
C1	0.0245 (5)	0.0252 (6)	0.0222 (5)	-0.0031 (4)	0.0098 (4)	-0.0023 (4)

Geometric parameters (\AA , $^\circ$)

S1—C4	1.7129 (14)	C2—C1	1.3672 (17)
S1—C1	1.7178 (13)	C4—H4	0.9445
O1—C2	1.3597 (15)	C5—C5 ⁱ	1.500 (2)
O1—C5	1.4288 (15)	C5—H5A	1.0489
C3—C4	1.3674 (19)	C5—H5B	1.0193
C3—C2	1.4227 (17)	C1—H1	1.0012
C3—H3	0.9989		
C4—S1—C1	92.55 (6)	S1—C4—H4	121.5
C2—O1—C5	115.12 (10)	O1—C5—C5 ⁱ	108.13 (9)
C4—C3—C2	111.88 (11)	O1—C5—H5A	110.0
C4—C3—H3	125.7	C5 ⁱ —C5—H5A	109.8
C2—C3—H3	122.4	O1—C5—H5B	109.6
C1—C2—O1	127.57 (12)	C5 ⁱ —C5—H5B	111.8

C1—C2—C3	113.59 (12)	H5A—C5—H5B	107.5
O1—C2—C3	118.83 (11)	C2—C1—S1	110.43 (10)
C3—C4—S1	111.56 (10)	C2—C1—H1	132.8
C3—C4—H4	127.0	S1—C1—H1	116.7
C5—O1—C2—C1	0.00 (18)	C1—S1—C4—C3	-0.11 (11)
C5—O1—C2—C3	-178.45 (11)	C2—O1—C5—C5 ⁱ	-178.84 (11)
C4—C3—C2—C1	0.06 (17)	O1—C2—C1—S1	-178.66 (10)
C4—C3—C2—O1	178.73 (12)	C3—C2—C1—S1	-0.14 (14)
C2—C3—C4—S1	0.05 (15)	C4—S1—C1—C2	0.14 (10)

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

Hydrogen-bond geometry (\AA , $^\circ$)

$D-H\cdots A$	$D-H$	$H\cdots A$	$D\cdots A$	$D-H\cdots A$
C3—H3 \cdots O1 ⁱⁱ	1.00	2.41	3.3940 (16)	170

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