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1,5-Bis(3-thienyloxy)-3-oxapentane: a thiophene-based precursor for thiophene-based azacryptand Mannich bases

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Key indicators

Single-crystal X-ray study
T = 153 K
Mean σ(C–C) = 0.003 Å
R factor = 0.033
wR factor = 0.072
Data-to-parameter ratio = 16.3

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

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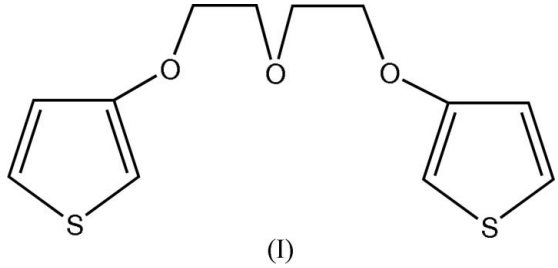
The title compound, $C_{12}H_{14}O_3S_2$, is composed of two thiophene rings bridged by an $-O(CH_2)_2O(CH_2)_2O-$ chain. The molecule is U-shaped, with the two thiophene rings inclined to one another by 83.21 (10)°. In the crystal structure, the molecules are bridged by C—H···S and C—H···O hydrogen bonds, forming a double-stranded polymer chain.

Comment

The preparation of a range of open-chain cryptand-like structures, incorporating thiophene rings, as precursors for azacryptand Mannich bases, was undertaken by Barker *et al.* (1993) and Chaffin *et al.* (2001, 2002). The title compound, (I), was synthesized by the reaction of methyl 3-hydroxythiophene-2-carboxylate with 1,5-bis(*p*-tolylsulfonyloxy)-3-oxapentane and anhydrous potassium carbonate in anhydrous *N*,*N*-dimethylformamide, followed by saponification and decarboxylation.



(I)

The molecular structure of (I) is illustrated in Fig. 1 and selected bond distances and angles are given in Table 1. The molecule is U-shaped and has pseudo-C_2 symmetry, with the central $-O(CH_2)_2O(CH_2)_2O-$ bridge having a *cis–cis* conformation. The two thiophene rings are inclined to one another by 83.21 (10)°. The thiophene bond lengths and bond angles are similar to those in an unsubstituted thiophene reported by Bonham & Momany (1963). The thienyloxy and other bond lengths and angles in (I) are in agreement with standard values (*International Tables for Crystallography*, Vol. C, 1995). In the crystal structure, symmetry-related molecules are bridged by C—H···S and C—H···O hydrogen bonds (Table 2), forming a double-stranded polymer chain (Fig. 2).

Experimental

Compound (I) was synthesized using the procedure described by Chaffin *et al.* (2001). Crystals suitable for X-ray analysis were obtained by slow evaporation of a 1:1 ethanol–dichloromethane solution.

Crystal data

$C_{12}H_{14}O_3S_2$
M_r = 270.35
Monoclinic, $P2_1/n$
a = 5.2998 (4) Å
b = 19.4005 (18) Å
c = 12.7277 (9) Å
β = 100.960 (8)°
V = 1284.78 (18) Å^3
Z = 4
D_x = 1.398 Mg m^{-3}
Mo $K\alpha$ radiation
Cell parameters from 8000 reflections
θ = 1.7–26.1°
μ = 0.41 mm^{-1}
T = 153 (2) K
Plate, colourless
0.50 × 0.25 × 0.10 mm

Data collection

Stoe IPDS diffractometer
ω scans
Absorption correction: none
10146 measured reflections
2509 independent reflections
1609 reflections with $I > 2\sigma(I)$
R_{int} = 0.066
θ_{max} = 26.0°
$h = -6 \rightarrow 6$
$k = -23 \rightarrow 23$
$l = -15 \rightarrow 15$

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)]$ = 0.033
$wR(F^2)$ = 0.072
S = 0.85
2509 reflections
154 parameters
H-atom parameters constrained
$w = 1/[\sigma^2(F_o^2) + (0.0331P)^2]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max}$ = 0.001
$\Delta\rho_{max}$ = 0.19 e Å^{-3}
$\Delta\rho_{min}$ = −0.29 e Å^{-3}

Table 1
Selected geometric parameters (Å, °).

S1—C4	1.705 (2)	O3—C8	1.428 (2)
S1—C1	1.717 (2)	C1—C2	1.356 (3)
S2—C12	1.701 (2)	C3—C4	1.353 (3)
S2—C9	1.716 (3)	C5—C6	1.503 (3)
O1—C2	1.368 (2)	C7—C8	1.490 (3)
O1—C5	1.425 (2)	C9—C10	1.362 (3)
O2—C6	1.414 (3)	C10—C11	1.414 (3)
O2—C7	1.421 (2)	C11—C12	1.346 (3)
O3—C10	1.362 (3)		
C4—S1—C1	91.89 (10)	C3—C4—S1	112.15 (16)
C12—S2—C9	91.92 (11)	O1—C5—C6	107.58 (16)
C2—O1—C5	116.42 (15)	O2—C6—C5	108.33 (17)
C6—O2—C7	111.88 (16)	O2—C7—C8	109.35 (18)
C10—O3—C8	115.46 (16)	C10—C9—S2	110.66 (17)
C2—C1—S1	110.59 (15)	C9—C10—O3	128.5 (2)
C1—C2—O1	128.80 (18)	C9—C10—C11	112.9 (2)
C1—C2—C3	113.61 (18)	O3—C10—C11	118.64 (18)
O1—C2—C3	117.59 (17)	C12—C11—C10	112.3 (2)
C4—C3—C2	111.76 (19)	C11—C12—S2	112.15 (18)

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

D—H···A	D—H	H···A	D···A	D—H···A
C9—H9A···O1^{i}	0.95	2.52	3.358 (2)	148
C12—H12A···S1^{ii}	0.95	2.86	3.787 (2)	164

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

H atoms were included in calculated positions and treated as riding atoms, with C—H = 0.95–0.99 Å and U_{iso}(H) = 1.2 or 1.5 times U_{eq}(parent atom).

Data collection: *EXPOSE* (Stoe & Cie, 2002); cell refinement: *CELL* (Stoe & Cie, 2002); data reduction: *INTEGRATE* (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*.

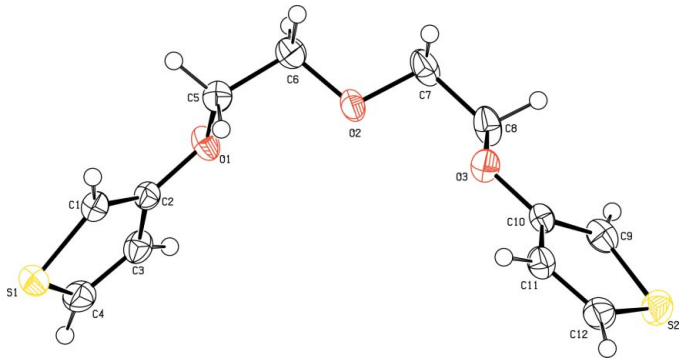


Figure 1
View of the molecular structure of compound (I), showing the atom-labelling scheme. Displacement ellipsoids are drawn at the 50% probability level.

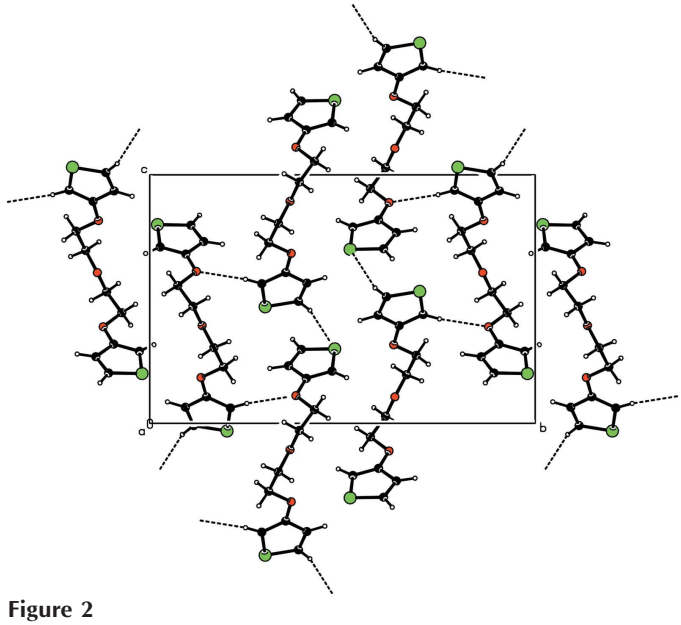


Figure 2
The crystal packing of compound (I), viewed down the *a* axis. C—H···S and C—H···O hydrogen bonds are shown as dashed lines.

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supporting information

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Crystal data

$C_{12}H_{14}O_3S_2$
$M_r = 270.35$
Monoclinic, $P2_1/n$
Hall symbol: -P 2yn
$a = 5.2998$ (4) Å
$b = 19.4005$ (18) Å
$c = 12.7277$ (9) Å
$\beta = 100.960$ (8)°
$V = 1284.78$ (18) Å^3
$Z = 4$
$F(000) = 568$
$D_x = 1.398$ Mg m^{-3}
Mo $K\alpha$ radiation, $\lambda = 0.71073$ Å
Cell parameters from 8000 reflections
$\theta = 1.7$–$26.1°$
$\mu = 0.41$ mm^{-1}
$T = 153$ K
Plate, colourless
0.50 × 0.25 × 0.10 mm

Data collection

Stoe IPDS diffractometer
Radiation source: fine-focus sealed tube
Graphite monochromator
Detector resolution: 0.81Å pixels mm^{-1}
ω scans
10146 measured reflections
2509 independent reflections
1609 reflections with $I > 2\sigma(I)$
$R_{int} = 0.066$
$\theta_{max} = 26.0°$, $\theta_{min} = 1.9°$
$h = -6 \rightarrow 6$
$k = -23 \rightarrow 23$
$l = -15 \rightarrow 15$

Refinement

Refinement on F^2
Least-squares matrix: full
$R[F^2 > 2\sigma(F^2)] = 0.033$
$wR(F^2) = 0.072$
$S = 0.85$
2509 reflections
154 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
$w = 1/[\sigma^2(F_o^2) + (0.0331P)^2]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} = 0.001$
$\Delta\rho_{max} = 0.19$ 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}
S1	0.16435 (11)	0.52004 (3)	0.70026 (4)	0.03420 (16)
S2	0.63304 (12)	0.70048 (3)	1.53098 (5)	0.03781 (17)
O1	−0.2011 (3)	0.62079 (7)	0.88858 (11)	0.0283 (3)
O2	−0.2260 (3)	0.63598 (7)	1.10645 (10)	0.0294 (4)
O3	0.0678 (3)	0.63305 (7)	1.31584 (11)	0.0278 (3)
C1	−0.0383 (4)	0.52702 (11)	0.79012 (15)	0.0257 (5)
H1A	−0.1231	0.4894	0.8162	0.031*
C2	−0.0605 (4)	0.59373 (10)	0.81876 (15)	0.0240 (4)
C3	0.0848 (4)	0.63996 (11)	0.76818 (16)	0.0298 (5)
H3A	0.0888	0.6884	0.7790	0.036*
C4	0.2175 (4)	0.60675 (12)	0.70255 (17)	0.0353 (6)
H4A	0.3274	0.6291	0.6624	0.042*
C5	−0.3283 (4)	0.57264 (10)	0.94515 (16)	0.0267 (5)
H5B	−0.2057	0.5371	0.9793	0.032*
H5A	−0.4691	0.5495	0.8954	0.032*
C6	−0.4344 (4)	0.61194 (11)	1.02881 (16)	0.0303 (5)
H6A	−0.5387	0.6513	0.9955	0.036*
H6B	−0.5459	0.5816	1.0628	0.036*
C7	−0.3098 (5)	0.66629 (12)	1.19548 (16)	0.0370 (6)
H7A	−0.4051	0.6318	1.2301	0.044*
H7B	−0.4268	0.7053	1.1711	0.044*
C8	−0.0825 (5)	0.69130 (11)	1.27361 (16)	0.0335 (5)
H8A	0.0214	0.7227	1.2377	0.040*
H8B	−0.1395	0.7169	1.3322	0.040*
C9	0.3544 (4)	0.70933 (11)	1.43801 (16)	0.0309 (5)
H9A	0.2668	0.7517	1.4202	0.037*
C10	0.2762 (4)	0.64727 (10)	1.39336 (15)	0.0242 (5)
C11	0.4412 (4)	0.59251 (11)	1.43531 (16)	0.0295 (5)
H11A	0.4134	0.5458	1.4138	0.035*
C12	0.6421 (5)	0.61409 (12)	1.50917 (17)	0.0351 (5)
H12A	0.7737	0.5845	1.5450	0.042*

Atomic displacement parameters (Å²)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
S1	0.0308 (3)	0.0404 (3)	0.0319 (3)	0.0047 (3)	0.0074 (3)	−0.0062 (2)
S2	0.0401 (4)	0.0398 (3)	0.0344 (3)	−0.0119 (3)	0.0093 (3)	−0.0054 (3)
O1	0.0409 (9)	0.0179 (7)	0.0296 (8)	−0.0022 (6)	0.0157 (7)	−0.0021 (6)
O2	0.0338 (9)	0.0334 (8)	0.0222 (7)	0.0027 (7)	0.0084 (7)	−0.0061 (6)
O3	0.0325 (9)	0.0216 (7)	0.0272 (7)	0.0070 (6)	0.0004 (7)	0.0002 (6)

C1	0.0273 (12)	0.0237 (11)	0.0247 (10)	0.0001 (9)	0.0014 (9)	−0.0004 (8)
C2	0.0242 (11)	0.0259 (11)	0.0212 (9)	0.0000 (9)	0.0022 (9)	−0.0004 (9)
C3	0.0340 (13)	0.0265 (12)	0.0282 (11)	−0.0085 (10)	0.0038 (10)	−0.0010 (9)
C4	0.0312 (14)	0.0454 (14)	0.0299 (11)	−0.0095 (11)	0.0072 (11)	0.0023 (10)
C5	0.0320 (13)	0.0221 (11)	0.0265 (11)	−0.0052 (9)	0.0070 (10)	0.0016 (9)
C6	0.0326 (13)	0.0317 (12)	0.0276 (11)	0.0002 (10)	0.0084 (11)	0.0014 (9)
C7	0.0430 (15)	0.0444 (14)	0.0236 (11)	0.0221 (12)	0.0066 (11)	−0.0005 (10)
C8	0.0488 (16)	0.0271 (12)	0.0237 (10)	0.0174 (11)	0.0042 (11)	0.0006 (9)
C9	0.0392 (13)	0.0251 (11)	0.0317 (11)	0.0009 (10)	0.0150 (11)	0.0027 (9)
C10	0.0287 (12)	0.0249 (11)	0.0205 (10)	0.0002 (9)	0.0087 (10)	−0.0005 (8)
C11	0.0341 (14)	0.0276 (11)	0.0271 (10)	0.0033 (10)	0.0062 (10)	−0.0028 (9)
C12	0.0321 (13)	0.0413 (13)	0.0313 (12)	0.0063 (11)	0.0047 (11)	0.0001 (10)

Geometric parameters (Å, º)

S1—C4	1.705 (2)	C5—C6	1.503 (3)
S1—C1	1.717 (2)	C5—H5B	0.9900
S2—C12	1.701 (2)	C5—H5A	0.9900
S2—C9	1.716 (3)	C6—H6A	0.9900
O1—C2	1.368 (2)	C6—H6B	0.9900
O1—C5	1.425 (2)	C7—C8	1.490 (3)
O2—C6	1.414 (3)	C7—H7A	0.9900
O2—C7	1.421 (2)	C7—H7B	0.9900
O3—C10	1.362 (3)	C8—H8A	0.9900
O3—C8	1.428 (2)	C8—H8B	0.9900
C1—C2	1.356 (3)	C9—C10	1.362 (3)
C1—H1A	0.9500	C9—H9A	0.9500
C2—C3	1.414 (3)	C10—C11	1.414 (3)
C3—C4	1.353 (3)	C11—C12	1.346 (3)
C3—H3A	0.9500	C11—H11A	0.9500
C4—H4A	0.9500	C12—H12A	0.9500
C4—S1—C1	91.89 (10)	C5—C6—H6B	110.0
C12—S2—C9	91.92 (11)	H6A—C6—H6B	108.4
C2—O1—C5	116.42 (15)	O2—C7—C8	109.35 (18)
C6—O2—C7	111.88 (16)	O2—C7—H7A	109.8
C10—O3—C8	115.46 (16)	C8—C7—H7A	109.8
C2—C1—S1	110.59 (15)	O2—C7—H7B	109.8
C2—C1—H1A	124.7	C8—C7—H7B	109.8
S1—C1—H1A	124.7	H7A—C7—H7B	108.3
C1—C2—O1	128.80 (18)	O3—C8—C7	108.41 (18)
C1—C2—C3	113.61 (18)	O3—C8—H8A	110.0
O1—C2—C3	117.59 (17)	C7—C8—H8A	110.0
C4—C3—C2	111.76 (19)	O3—C8—H8B	110.0
C4—C3—H3A	124.1	C7—C8—H8B	110.0
C2—C3—H3A	124.1	H8A—C8—H8B	108.4
C3—C4—S1	112.15 (16)	C10—C9—S2	110.66 (17)
C3—C4—H4A	123.9	C10—C9—H9A	124.7

S1—C4—H4A	123.9	S2—C9—H9A	124.7
O1—C5—C6	107.58 (16)	C9—C10—O3	128.5 (2)
O1—C5—H5B	110.2	C9—C10—C11	112.9 (2)
C6—C5—H5B	110.2	O3—C10—C11	118.64 (18)
O1—C5—H5A	110.2	C12—C11—C10	112.3 (2)
C6—C5—H5A	110.2	C12—C11—H11A	123.8
H5B—C5—H5A	108.5	C10—C11—H11A	123.8
O2—C6—C5	108.33 (17)	C11—C12—S2	112.15 (18)
O2—C6—H6A	110.0	C11—C12—H12A	123.9
C5—C6—H6A	110.0	S2—C12—H12A	123.9
O2—C6—H6B	110.0		

C4—S1—C1—C2	0.16 (17)	C6—O2—C7—C8	−179.31 (17)
S1—C1—C2—O1	−179.53 (17)	C10—O3—C8—C7	−176.48 (16)
S1—C1—C2—C3	0.3 (2)	O2—C7—C8—O3	−65.7 (2)
C5—O1—C2—C1	4.9 (3)	C12—S2—C9—C10	0.02 (15)
C5—O1—C2—C3	−174.89 (18)	S2—C9—C10—O3	−178.87 (15)
C1—C2—C3—C4	−0.7 (3)	S2—C9—C10—C11	0.5 (2)
O1—C2—C3—C4	179.13 (19)	C8—O3—C10—C9	2.4 (3)
C2—C3—C4—S1	0.8 (2)	C8—O3—C10—C11	−176.98 (16)
C1—S1—C4—C3	−0.55 (18)	C9—C10—C11—C12	−1.0 (2)
C2—O1—C5—C6	171.17 (17)	O3—C10—C11—C12	178.47 (17)
C7—O2—C6—C5	−172.63 (17)	C10—C11—C12—S2	1.0 (2)
O1—C5—C6—O2	−67.9 (2)	C9—S2—C12—C11	−0.60 (17)

Hydrogen-bond geometry (Å, º)

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
C9—H9*A*···O1^{i}	0.95	2.52	3.358 (2)	148
C12—H12*A*···S1^{ii}	0.95	2.86	3.787 (2)	164

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