Acta Crystallographica Section E
Structure Reports
Online
ISSN 1600-5368

A tripodal tris(thiophene) derivative of hexahydropyrimidine and its ladder-like extended structure

Deogratius Jaganyi, Allen Mambanda and Orde Q. Munro*

School of Chemistry, University of KwaZulu-Natal, Pietermaritzburg, Private Bag X01, Scottsville 3209, South Africa

Correspondence e-mail: munroo@ukzn.ac.za

Received 20 March 2007
Accepted 31 March 2007

Key indicators

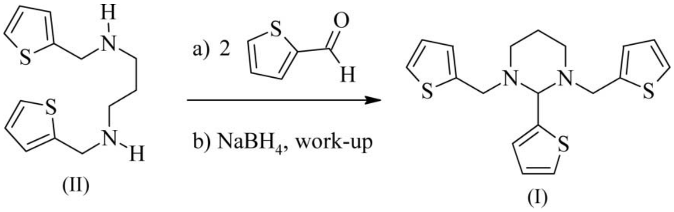
Single-crystal X-ray study
T = 110 K
Mean σ(C–C) = 0.002 Å
R factor = 0.029
wR factor = 0.082
Data-to-parameter ratio = 27.2

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

In the title compound, 2-(2-thienyl)-1,3-bis(2-thienylmethyl)-perhydropyrimidine, $C_{18}H_{20}N_2S_3$, a new hexahydropyrimidine derivative with no formal crystallographic symmetry (but approximate C_s molecular symmetry), the thiophene rings are approximately orthogonal to the mean plane of the saturated pyrimidine 'core' of the molecule, with the three S atoms positioned on one side of the six-atom mean plane. The S atom of the directly attached thiophene ring is involved in an unconventional (alkyl)C—H···S hydrogen bond (H···S = 2.87 Å) with a thiophene CH group of the closest neighbouring molecule, leading to a ladder-like one-dimensional chain as the extended structure. The crystal specimen used for data collection was an inversion twin [twin fraction x = 0.41 (4)].

Comment

Sato *et al.* (1992) have described a method for the synthesis of N,N'-bis(2-pyridylmethyl)-N,N'-bis(2-thienylmethyl)-1,2-ethanediamine. Our goal was to synthesize the tetra(thiophene) analogue with a propyldiamine core for binding two Pt^{II} ions. Contrary to expectation, addition of two equivalents of thiophene-2-carbaldehyde to N,N'-bis(2-thienylmethyl)-1,2-propanediamine, (II), followed by $NaBH_4$ reduction afforded the title compound, (I), the Mannich cyclization product (Buchen *et al.*, 1997).



Compound (I) is a hexahydropyrimidine derivative, and the six-membered ring core adopts a chair conformation (Fig. 1). This was confirmed quantitatively by Cremer–Pople ring puckering (CPRP) analysis (Cremer & Pople, 1975), which gave a θ value closer to 0° (chair) than 50.8° (half-chair). [The CPRP amplitudes were Q = 0.594 (2) Å, θ = 4.1 (1)° and φ = 89 (2)°.] Each atom of the six-membered ring thus deviates systematically from the six-atom mean plane: atom N1 by 0.243 (1), C6 by −0.263 (1), N2 by 0.263 (1), C16 by −0.241 (2), C17 by 0.221 (2) and C18 by −0.221 (2) Å. The weighted average absolute torsion angle for the six-membered ring is 59 (6)° and reflects a near-ideal (+)-synclinal conformation.

The thiophene rings are oriented with the three S atoms lying within the same plane. The dihedral angles of each

doi:10.1107/S1600536807016017

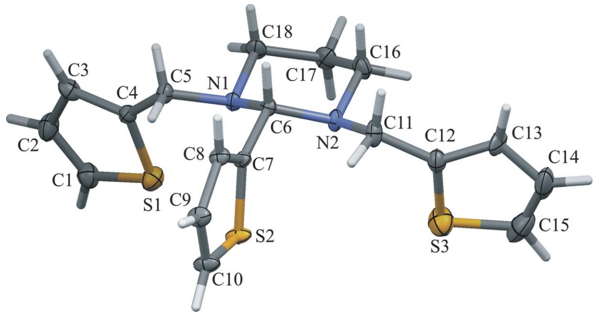


Figure 1
The molecular structure of (I), with 60% probability displacement ellipsoids. H atoms are shown only as the end-points of bonds represented as cylinders.

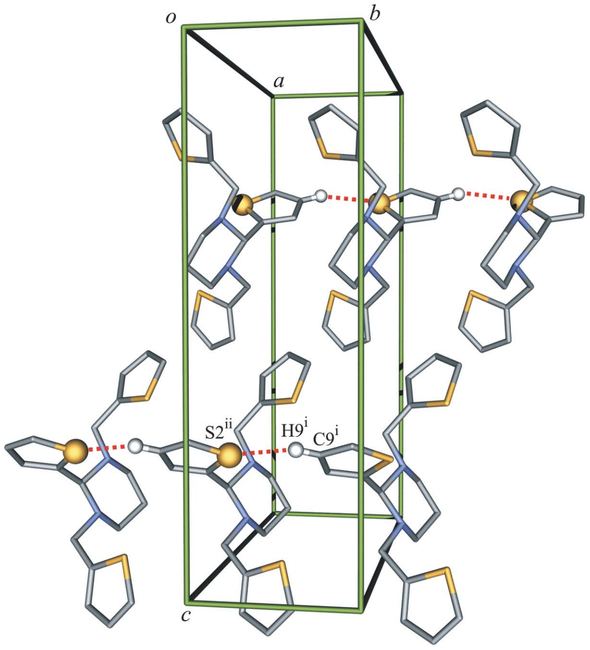


Figure 2
A partial packing diagram for (I), showing two chains of interacting molecules with an interaction axis collinear with the unit-cell *b* axis. Dashed lines indicate hydrogen bonds. Interacting H and S atoms are represented as spheres of arbitrary radii. Non-interacting H atoms have been omitted for clarity. All other atoms are shown only as the intersections of bonds represented as cylinders. [Symmetry codes: (i) $\frac{1}{2} - x$, $\frac{1}{2} + y$, $\frac{3}{2} + z$; (ii) $\frac{1}{2} - x$, $-\frac{1}{2} + y$, $\frac{3}{2} + z$.]

thiophene ring relative to the mean plane of the hexahydropyrimidine ring are 81.6 (1)° (S1/C1–C4 ring), 87.9 (1)° (S2/C7–C10 ring) and 82.0 (1)° (S3/C12–C15 ring). The three thiophene rings exhibit significant in-plane libration, even at 110 K (*cf.* the displacements for atoms C14 and C15). However, the C—S bonds average 1.712 (6) Å (Table 1) and their precision is thus not overly affected by this thermal motion.

A significant attractive intermolecular interaction (Fig. 2, Table 2) exists between atom H9 and atom $S2^{i}$ of a neighbouring molecule [symmetry code: (i) x, $y - 1$, z]. The $H9\cdots S2^{i}$ distance (2.87 Å) is shorter than the sum of the van der Waals radii of S and H by 0.13 Å (Bondi, 1964). The geometry is consistent with an unconventional hydrogen bond between sp^2-hybridized S and a π-type C—H donor (Steiner, 2002). Molecules of (I) are thus held together (probably only weakly and in the condensed phase) to form a one-dimensional hydrogen-bonded stack whose axis is collinear with the *b* axis of the unit cell. Each molecule within the stack is translated by 1 along the *b*-axis direction [$(x, y - 1, z)$, (x, y, z), $(x, y + 1, z)$ *etc.*] to give a molecular sequence reminiscent of the steps in a conventional ladder (Fig. 3).

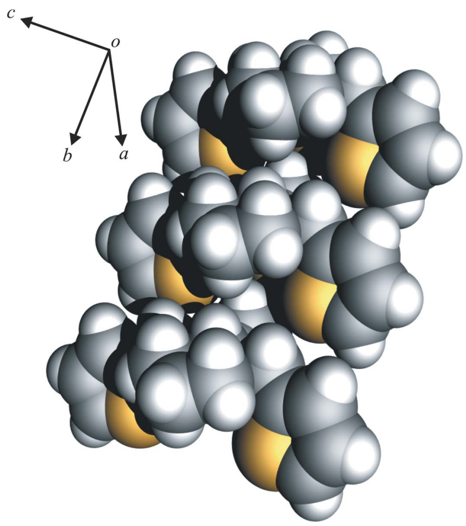


Figure 3
A space-filling model of three interacting molecules of (I), showing the ladder-like one-dimensional hydrogen-bonded extended structure. The axis of the stack is collinear with the *b* axis of the unit cell.

Experimental

Under a flow of nitrogen, a solution of 2-thiophenecarbaldehyde (4.45 ml, 47.6 mmol) in absolute ethanol (16 ml) was added to a vigorously stirred solution of 1,3-propanediamine (2.0 ml, 23.9 mmol) in a dropwise manner. The mixture was stirred at room temperature for a further 2 h to afford a bright-yellow solution of the diimine Schiff base. The solvent was removed under reduced pressure and the residue redissolved in fresh absolute ethanol (60 ml), an excess of $NaBH_4$ (1.52 g, 40 mmol) added and the mixture stirred for a further 24 h after effervescence of the gas had ceased. The mixture was extracted with CH_2Cl_2 (3 × 40 ml), washed thoroughly with deionized water (3 × 50 ml) and dried over Na_2SO_4. The extracting solvent was removed under reduced pressure to afford a light-yellow oil, (II).

The above imination-reduction step was repeated once, starting with the light-yellow oil of (II) as the amine source and 2-thiophenecarbaldehyde as the imination reagent. Slow addition of $NaBH_4$ in small portions is necessary as the second reduction step is highly exothermic. Colourless crystals of (I) were obtained by layering a concentrated CH_2Cl_2 solution of (I) with a 1:1 (*v*/*v*) mixture of hexane and cyclohexane (yield 74%).

Crystal data

$C_{18}H_{20}N_2S_3$
$M_r = 360.54$
Orthorhombic, $Pna2_1$
$a = 15.4391$ (6) Å
$b = 5.9873$ (2) Å
$c = 19.5007$ (7) Å

$V = 1802.62$ (11) Å^3
$Z = 4$
Mo $K\alpha$ radiation
$\mu = 0.41$ mm^{-1}
$T = 110$ (2) K
0.6 × 0.5 × 0.2 mm

Data collection

Oxford Diffraction Xcalibur2 CCD diffractometer
Absorption correction: multi-scan [*CrysAlis RED* (Oxford Diffraction, 2006; Blessing, 1995)]
$T_{\min} = 0.790$, $T_{\max} = 0.92$
17289 measured reflections
5679 independent reflections
5600 reflections with $I > 2\sigma(I)$
$R_{\rm int} = 0.011$

Refinement

$R[F^2 > 2\sigma(F^2)] = 0.029$
$wR(F^2) = 0.082$
$S = 1.12$
5679 reflections
209 parameters
95 restraints
H-atom parameters constrained
$\Delta\rho_{\max} = 0.46$ e Å^{-3}
$\Delta\rho_{\min} = -0.37$ e Å^{-3}
Absolute structure: Flack (1983), 2483 Friedel pairs
Flack parameter: 0.41 (4)

Table 1
Selected geometric parameters (Å, °).

C1—S1	1.7102 (16)	C10—S2	1.7181 (14)
C4—S1	1.7176 (14)	C12—S3	1.7035 (16)
C6—N1	1.4696 (16)	C15—S3	1.701 (2)
C6—N2	1.4779 (16)	C16—N2	1.4658 (17)
C7—S2	1.7228 (13)	C18—N1	1.4726 (16)
C16—N2—C11	109.80 (11)	C6—N1—C18	111.52 (10)
C16—N2—C6	110.33 (10)	C1—S1—C4	92.31 (7)
C11—N2—C6	112.23 (10)	C10—S2—C7	92.09 (6)
C5—N1—C6	112.44 (10)	C15—S3—C12	92.53 (9)
C5—N1—C18	109.00 (10)		

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

*Cg*1 is the centroid of the S1/C1–C4 ring.

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
C9—H9···S2$^{\rm i}$	0.95	2.87	3.5423 (12)	129
C10—H10···*Cg*1$^{\rm ii}$	0.95	2.78	3.643	151

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

Methylene and methine H atoms were positioned geometrically and refined using a riding model, with C—H = 0.97 and 0.98 Å, respectively, and with $U_{\rm iso}({\rm H}) = 1.2U_{\rm eq}({\rm C})$. Aromatic H atoms were positioned geometrically and refined using a riding model, with C—H = 0.93 Å and $U_{\rm iso}({\rm H}) = 1.2U_{\rm eq}({\rm C})$. Towards the end of the least-squares refinement process, it became clear that thermal libration of the two 'outer' thiophene rings was responsible for highly anisotropic displacement parameters for the C atoms of these rings. These atoms were therefore refined with a rigid bond restraint limiting the components of their anisotropic displacements in the bond directions to be equal within an s.u. of 0.01 Å.

The crystal was an inversion twin with a twin fraction of 0.41 (4). The idealized point group symmetry of (I) is C_s with a mirror plane passing through the plane of the central thiophene ring. However, this is not crystallographically observed because the thiophene rings S1/C1–C4 and S3/C12–C15 are positioned at different perpendicular distances from the plane passing through the central thiophene ring of the molecule. This conformational distortion or feature of (I) therefore precludes it from having mirror symmetry and hence the possibility of a structure solution in the centrosymmetric space group *Pnam*.

Data collection: *CrysAlis CCD* (Oxford Diffraction, 2006); cell refinement: *CrysAlis RED* (Oxford Diffraction, 2006); data reduction: *CrysAlis RED*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 1997); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *ORTEP-3* (Farrugia, 1997); software used to prepare material for publication: *WinGX* (Farrugia, 1999).

The authors gratefully acknowledge financial support from the University of KwaZulu-Natal and the National Research Foundation (NRF, Pretoria). Any opinion, findings and conclusions or recommendations expressed in this paper are those of the authors and therefore the NRF does not accept any liability in regard thereto. We thank Mr C. Grimmer for the NMR analysis of the samples.

References

Blessing, R. H. (1995). *Acta Cryst.* A**51**, 33–38.
Bondi, A. (1964). *J. Phys. Chem.* **68**, 441–451.
Buchen, T., Hazell, A., Jessen, L., McKenzie, C. J., Nielsen, L. P., Pedersen, J. Z. & Schollmeyer, D. (1997). *J. Chem. Soc. Dalton Trans.* pp. 2697–2704.
Cremer, D. & Pople, J. A. (1975). *J. Am. Chem. Soc.* **97**, 1354–1358.
Farrugia, L. J. (1997). *J. Appl. Cryst.* **30**, 565.
Farrugia, L. J. (1999). *J. Appl. Cryst.* **32**, 837–838.
Flack, H. D. (1983). *Acta Cryst.* A**39**, 876–881.
Oxford Diffraction (2006). *CrysAlis CCD* and *CrysAlis RED*. Versions 1.171.29.9 (Release 23-03-2006 CrysAlis 171 . Net). Oxford Diffraction Ltd., Abingdon, Oxfordshire, England.
Sato, M., Mori, Y. & Iida, T. (1992). *Synthesis*, pp. 539–540.
Sheldrick, G. M. (1997). *SHELXS97* and *SHELXL97*. University of Göttingen, Germany.
Steiner, T. (2002). *Angew. Chem. Int. Ed.* **41**, 48–76.