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3,4-Dibutoxy-N^2,$N^{2'}$-bis(propan-2-ylidene)thiophene-2,5-dicarbohydrazide

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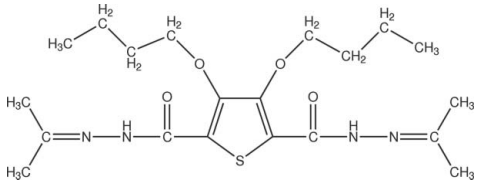
Key indicators: single-crystal X-ray study; T = 294 K; mean σ(C–C) = 0.005 Å; R factor = 0.061; wR factor = 0.189; data-to-parameter ratio = 17.3.

The asymmetric unit of the title compound, $C_{20}H_{32}N_4O_4S$, contains one half-molecule; a twofold rotation axis passes through the thiophene ring. Intramolecular N—H···O hydrogen bonding results in the formation of a nearly planar six-membered ring, which is oriented at a dihedral angle of 4.60 (3)° with respect to the thiophene ring. In the crystal structure, intermolecular C—H···N and C—H···O hydrogen bonds link the molecules.

Related literature

For related literature, see: Udayakumara & Adhikari (2006); Brault *et al.* (2005). For bond-length data, see: Allen *et al.* (1987).



Experimental

Crystal data

$C_{20}H_{32}N_4O_4S$
M_r = 424.57
Monoclinic, $C2/c$
a = 20.891 (4) Å
b = 10.526 (2) Å
c = 13.581 (3) Å
β = 128.24 (3)°
V = 2345.6 (13) Å^3
Z = 4
Mo $K\alpha$ radiation
μ = 0.17 mm^{-1}
T = 294 (2) K
0.30 × 0.10 × 0.10 mm

Data collection

Enraf–Nonius CAD-4 diffractometer
Absorption correction: ψ scan (North *et al.*, 1968)
T_{min} = 0.951, T_{max} = 0.983
2360 measured reflections
2297 independent reflections
1583 reflections with $I > 2\sigma(I)$
R_{int} = 0.041
3 standard reflections
frequency: 120 min
intensity decay: none

Refinement

$R[F^2 > 2\sigma(F^2)]$ = 0.061
$wR(F^2)$ = 0.189
S = 1.02
2297 reflections
133 parameters
H-atom parameters constrained
$\Delta\rho_{max}$ = 0.21 e Å^{-3}
$\Delta\rho_{min}$ = −0.40 e Å^{-3}

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

D—H···A	D—H	H···A	D···A	D—H···A
N1—H1A···O1	0.86	2.10	2.797 (3)	138
C4—H4A···O1^{i}	0.97	2.54	3.175 (5)	123
C4—H4B···N2^{ii}	0.97	2.58	3.480 (5)	154

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

Data collection: *CAD-4 Software* (Enraf–Nonius,1989); cell refinement: *CAD-4 Software*; data reduction: *XCAD4* (Harms & Wocadlo,1995); program(s) used to solve structure: *SHELXS97* (Sheldrick, 1997); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *SHELXTL* (Siemens,1996); software used to prepare material for publication: *SHELXTL*.

Supplementary data and figures for this paper are available from the IUCr electronic archives (Reference: HK2384).

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supplementary materials

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3,4-Dibutoxy-N^2,$N^{2'}$-bis(propan-2-ylidene)thiophene-2,5-dicarbohydrazide

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Comment

Thiophene derivatives possess electroluminescence (Udayakumara & Adhikari, 2006) and biological (Brault *et al.*, 2005) properties. As part of our studies in this area, we report herein the synthesis and crystal structure of the title compound, (I).

The asymmetric unit of the title compound, (I), (Fig. 1) contains one half -molecule, in which the bond lengths and angles are within normal ranges (Allen *et al.*, 1987). The intramolecular N—H···O hydrogen bond (Table 1) causes to the formation of a nearly planar six-membered ring; A (O1/C5—C7/N1/H1A), in which it is oriented with respect to ring B (S/C5/C6/C5A/C6A) [symmetry code A: −*x*, *y*, 1/2 − *z*] at a dihedral angle of 4.60 (3)°.

In the crystal structure, intermolecular C—H···N and C—H···O hydrogen bonds (Table 1) link the molecules, in which they seem to be effective in the stabilization of the structure.

Experimental

For the preparation of the title compound, 4,5-dibutoxycyclopenta-1,3-diene −1,3-dicarbohydrazide (10 mmol) was dissolved in acetone (30 ml). The resulting mixture was refluxed for 8 h. After cooling and filtering, the crude title compound was obtained and purified by recrystalization from ethyl acetate (yield; 72%, m.p. 443 K). Crystals of (I) suitable for X-ray analysis were obtained by slow evaporation of an acetone solution.

Refinement

H atoms were positioned geometrically, with N—H = 0.86 Å (for NH) and C—H = 0.97 and 0.96 Å for methylene and methyl H, and constrained to ride on their parent atoms, with U_{iso}(H) = xU_{eq}(C,*N*), where x = 1.5 for methyl H, and x = 1.2 for all other H atoms.

Figures

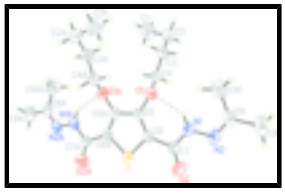


Fig. 1. The molecular structure of the title molecule, with the atom-numbering scheme. Displacement ellipsoids are drawn at the 30% probability level [symmetry code A: −*x*, *y*, 1/2 − *z*]. Hydrogen bonds are shown as dashed lines.

3,4-Dibutoxy-N^2,$N^{2'}$-bis(propan-2-ylidene)thiophene-2,5- dicarbohydrazide

Crystal data

$C_{20}H_{32}N_4O_4S$	F_{000} = 912
M_r = 424.57	D_x = 1.202 Mg m^{-3}
Monoclinic, *C*2/*c*	Melting point: 443 K
Hall symbol: -C 2yc	Mo *K*α radiation λ = 0.71073 Å
a = 20.891 (4) Å	Cell parameters from 25 reflections
b = 10.526 (2) Å	θ = 9–13º
c = 13.581 (3) Å	μ = 0.17 mm^{-1}
β = 128.24 (3)º	*T* = 294 (2) K
V = 2345.6 (13) Å^3	Block, colorless
Z = 4	0.30 × 0.10 × 0.10 mm

Data collection

Enraf–Nonius CAD-4 diffractometer	R_{int} = 0.041
Radiation source: fine-focus sealed tube	θ_{max} = 26.0º
Monochromator: graphite	θ_{min} = 2.3º
T = 294(2) K	*h* = −25→20
ω/2θ scans	*k* = 0→12
Absorption correction: ψ scan (North *et al.*, 1968)	*l* = 0→16
T_{min} = 0.951, T_{max} = 0.983	3 standard reflections
2360 measured reflections	every 120 min
2297 independent reflections	intensity decay: none
1583 reflections with $I > 2\sigma(I)$	

Refinement

Refinement on F^2	Secondary atom site location: difference Fourier map
Least-squares matrix: full	Hydrogen site location: inferred from neighbouring sites
$R[F^2 > 2\sigma(F^2)]$ = 0.061	H-atom parameters constrained
$wR(F^2)$ = 0.189	$w = 1/[\sigma^2(F_o^2) + (0.1P)^2 + 2.P]$ where $P = (F_o^2 + 2F_c^2)/3$
S = 1.02	$(\Delta/\sigma)_{max} < 0.001$
2297 reflections	$\Delta\rho_{max}$ = 0.21 e Å^{-3}
133 parameters	$\Delta\rho_{min}$ = −0.39 e Å^{-3}
Primary atom site location: structure-invariant direct methods	Extinction correction: none

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 $F^2 > 2\text{sigma}(F^2)$ 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}
S	0.0000	0.08050 (10)	0.2500	0.0466 (3)
O1	0.08170 (12)	0.42142 (18)	0.37436 (18)	0.0483 (5)
O2	0.16503 (15)	0.0362 (2)	0.4897 (2)	0.0667 (7)
N1	0.19373 (14)	0.2437 (2)	0.5525 (2)	0.0468 (6)
H1A	0.1784	0.3213	0.5310	0.056*
N2	0.26579 (14)	0.2169 (2)	0.6707 (2)	0.0480 (6)
C1	0.0866 (3)	0.7585 (4)	0.1859 (4)	0.0863 (13)
H1B	0.1073	0.8175	0.1580	0.129*
H1C	0.0420	0.7967	0.1783	0.129*
H1D	0.0680	0.6832	0.1353	0.129*
C2	0.1533 (2)	0.7242 (4)	0.3214 (4)	0.0708 (11)
H2B	0.1724	0.8013	0.3712	0.085*
H2C	0.1987	0.6884	0.3283	0.085*
C3	0.1273 (2)	0.6305 (3)	0.3754 (3)	0.0551 (8)
H3A	0.1717	0.6197	0.4641	0.066*
H3B	0.0813	0.6656	0.3673	0.066*
C4	0.10415 (19)	0.5041 (3)	0.3133 (3)	0.0495 (8)
H4A	0.0585	0.5128	0.2250	0.059*
H4B	0.1496	0.4675	0.3206	0.059*
C5	0.04004 (17)	0.3141 (3)	0.3090 (2)	0.0417 (7)
C6	0.06878 (16)	0.1940 (3)	0.3526 (2)	0.0412 (7)
C7	0.14743 (17)	0.1492 (3)	0.4708 (3)	0.0424 (7)
C8	0.30294 (19)	0.3120 (3)	0.7437 (3)	0.0508 (8)
C9	0.3805 (2)	0.2835 (4)	0.8705 (3)	0.0719 (11)
H9A	0.3906	0.1937	0.8784	0.108*
H9B	0.3760	0.3109	0.9335	0.108*
H9C	0.4247	0.3276	0.8813	0.108*
C10	0.2756 (3)	0.4475 (4)	0.7121 (3)	0.0788 (12)
H10A	0.2172	0.4510	0.6596	0.118*
H10B	0.2938	0.4842	0.6685	0.118*
H10C	0.2983	0.4943	0.7878	0.118*

Atomic displacement parameters (Å^2)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
S	0.0408 (6)	0.0422 (6)	0.0458 (6)	0.000	0.0213 (5)	0.000
O1	0.0380 (11)	0.0468 (11)	0.0432 (11)	−0.0059 (9)	0.0167 (9)	−0.0035 (9)
O2	0.0624 (15)	0.0517 (13)	0.0532 (13)	0.0124 (11)	0.0194 (12)	0.0019 (11)
N1	0.0340 (13)	0.0470 (14)	0.0435 (14)	0.0073 (11)	0.0161 (12)	0.0055 (11)
N2	0.0321 (13)	0.0632 (16)	0.0386 (13)	0.0096 (12)	0.0170 (11)	0.0088 (12)
C1	0.083 (3)	0.092 (3)	0.078 (3)	−0.019 (2)	0.046 (3)	0.012 (2)
C2	0.055 (2)	0.062 (2)	0.084 (3)	−0.0159 (17)	0.037 (2)	−0.006 (2)
C3	0.0471 (18)	0.0499 (17)	0.0499 (17)	−0.0084 (14)	0.0208 (15)	0.0000 (15)
C4	0.0386 (15)	0.0445 (16)	0.0599 (18)	−0.0018 (13)	0.0278 (15)	−0.0001 (14)
C5	0.0342 (15)	0.0409 (15)	0.0395 (15)	−0.0040 (11)	0.0175 (13)	−0.0046 (12)
C6	0.0322 (15)	0.0457 (15)	0.0385 (15)	0.0017 (12)	0.0183 (13)	0.0011 (12)
C7	0.0397 (15)	0.0418 (15)	0.0416 (15)	0.0041 (12)	0.0231 (13)	0.0004 (13)
C8	0.0411 (17)	0.068 (2)	0.0405 (16)	−0.0038 (15)	0.0236 (14)	−0.0001 (15)
C9	0.0432 (19)	0.107 (3)	0.0432 (18)	−0.0018 (19)	0.0157 (16)	0.0012 (19)
C10	0.080 (3)	0.073 (2)	0.054 (2)	−0.015 (2)	0.027 (2)	−0.0097 (18)

Geometric parameters (Å, °)

S—C6	1.719 (3)	C3—C4	1.487 (4)
S—C6^{i}	1.719 (3)	C3—H3A	0.9700
O1—C5	1.366 (3)	C3—H3B	0.9700
O1—C4	1.465 (4)	C4—H4A	0.9700
N1—C7	1.352 (4)	C4—H4B	0.9700
N1—N2	1.390 (3)	C5—C6	1.367 (4)
N1—H1A	0.8600	C5—C5^{i}	1.432 (5)
C1—C2	1.511 (5)	C6—C7	1.495 (4)
C1—H1B	0.9600	C8—C9	1.492 (4)
C1—H1C	0.9600	C8—C10	1.498 (5)
C1—H1D	0.9600	C9—H9A	0.9600
O2—C7	1.224 (3)	C9—H9B	0.9600
N2—C8	1.278 (4)	C9—H9C	0.9600
C2—C3	1.517 (5)	C10—H10A	0.9600
C2—H2B	0.9700	C10—H10B	0.9600
C2—H2C	0.9700	C10—H10C	0.9600
C6—S—C6^{i}	91.93 (19)	O1—C4—H4B	110.0
C5—O1—C4	115.0 (2)	C3—C4—H4B	110.0
C7—N1—N2	120.8 (2)	H4A—C4—H4B	108.4
C7—N1—H1A	119.6	O1—C5—C6	123.4 (2)
N2—N1—H1A	119.6	O1—C5—C5^{i}	124.10 (14)
C2—C1—H1B	109.5	C6—C5—C5^{i}	112.37 (16)
C2—C1—H1C	109.5	C5—C6—C7	130.8 (3)
H1B—C1—H1C	109.5	C5—C6—S	111.7 (2)
C2—C1—H1D	109.5	C7—C6—S	117.5 (2)
H1B—C1—H1D	109.5	O2—C7—N1	125.0 (3)

H1C—C1—H1D	109.5	O2—C7—C6	121.3 (3)
C8—N2—N1	116.2 (3)	N1—C7—C6	113.7 (2)
C1—C2—C3	114.0 (3)	N2—C8—C9	116.3 (3)
C1—C2—H2B	108.7	N2—C8—C10	125.6 (3)
C3—C2—H2B	108.7	C9—C8—C10	118.1 (3)
C1—C2—H2C	108.7	C8—C9—H9A	109.5
C3—C2—H2C	108.7	C8—C9—H9B	109.5
H2B—C2—H2C	107.6	H9A—C9—H9B	109.5
C4—C3—C2	113.3 (3)	C8—C9—H9C	109.5
C4—C3—H3A	108.9	H9A—C9—H9C	109.5
C2—C3—H3A	108.9	H9B—C9—H9C	109.5
C4—C3—H3B	108.9	C8—C10—H10A	109.5
C2—C3—H3B	108.9	C8—C10—H10B	109.5
H3A—C3—H3B	107.7	H10A—C10—H10B	109.5
O1—C4—C3	108.4 (3)	C8—C10—H10C	109.5
O1—C4—H4A	110.0	H10A—C10—H10C	109.5
C3—C4—H4A	110.0	H10B—C10—H10C	109.5
C7—N1—N2—C8	−176.2 (3)	C6^{i}—S—C6—C5	−0.39 (15)
C1—C2—C3—C4	63.9 (4)	C6^{i}—S—C6—C7	179.5 (3)
C5—O1—C4—C3	164.3 (2)	N2—N1—C7—O2	−3.1 (5)
C2—C3—C4—O1	179.0 (3)	N2—N1—C7—C6	175.1 (2)
C4—O1—C5—C6	117.8 (3)	C5—C6—C7—O2	−174.6 (3)
C4—O1—C5—C5^{i}	−65.7 (5)	S—C6—C7—O2	5.5 (4)
O1—C5—C6—C7	−2.0 (5)	C5—C6—C7—N1	7.1 (5)
C5^{i}—C5—C6—C7	−178.9 (3)	S—C6—C7—N1	−172.8 (2)
O1—C5—C6—S	177.9 (2)	N1—N2—C8—C9	−179.8 (2)
C5^{i}—C5—C6—S	1.0 (4)	N1—N2—C8—C10	−0.3 (5)

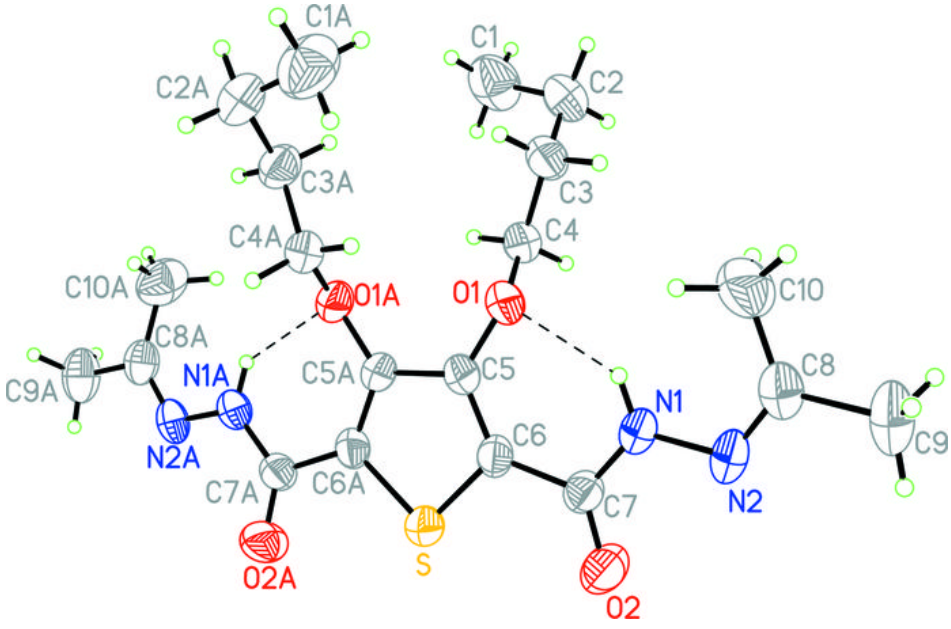
Symmetry codes: (i) −*x*, *y*, −*z*+1/2.

Hydrogen-bond geometry (Å, °)

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
N1—H1A···O1	0.86	2.10	2.797 (3)	138
C4—H4A···O1^{ii}	0.97	2.54	3.175 (5)	123
C4—H4B···N2^{iii}	0.97	2.58	3.480 (5)	154

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

Fig. 1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C2A
C3A
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C6A
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O2A
S
C1
C2
C3
C4
O1
C5
C6
C7
O2
N1
N2
C8
C10
C9