organic compounds

5,7-Di-2-pyridyl-2,3-dihydrothieno-[3,4-b][1,4]dioxine

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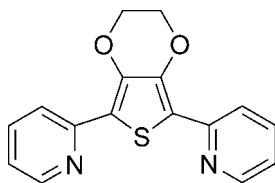Correspondence e-mail: mlemaire@brocku.ca

The title compound, $C_{16}H_{12}N_2O_2S$, was prepared by a Neigishi cross-coupling reaction to investigate the coordination chemistry of thiophene-containing ligands. In the molecule, the pyridine rings are twisted from the thiophene ring by 20.6 (1) and 4.1 (2)°. The six-membered dihydrodioxine ring is in a half-chair conformation.

Related literature

For the structures of other 2,5-disubstituted 3,4-ethylene-dioxythiophene (EDOT) derivatives, see: Lomas *et al.* (2007); and Sato *et al.* (2006). For related literature, see: Ghosh & Simonsen (1993); Han & Choi (2000); Roncali *et al.* (2005); Sotzing *et al.* (1996).

Experimental

Crystal data

$C_{16}H_{12}N_2O_2S$	V = 1358.2 (3) Å^3
M_r = 296.34	Z = 4
Monoclinic, $P2_1/n$	Mo $K\alpha$ radiation
a = 10.5189 (12) Å	μ = 0.24 mm^{-1}
b = 9.8752 (12) Å	T = 173 (2) K
c = 13.1961 (18) Å	0.38 × 0.30 × 0.20 mm
β = 97.752 (3)°	

Data collection

Bruker APEXII diffractometer	22945 measured reflections
Absorption correction: multi-scan (*SADABS*; Sheldrick, 1996)	5134 independent reflections
T_{min} = 0.864, T_{max} = 1.000	4316 reflections with $I > 2\sigma(I)$
(expected range = 0.823–0.952)	R_{int} = 0.026

Refinement

$R[F^2 > 2\sigma(F^2)]$ = 0.037	238 parameters
$wR(F^2)$ = 0.108	All H-atom parameters refined
S = 1.04	$\Delta\rho_{max}$ = 0.47 e Å^{-3}
5134 reflections	$\Delta\rho_{min}$ = −0.21 e Å^{-3}

Data collection: *APEX2* (Bruker, 2006); cell refinement: *APEX2*; data reduction: *APEX2*; program(s) used to solve structure: *SHELXTL* (Sheldrick, 2008); program(s) used to refine structure: *SHELXTL*; molecular graphics: *ORTEP-3 for Windows* (Farrugia, 1997); software used to prepare material for publication: *SHELXTL*.

Supplementary data and figures for this paper are available from the IUCr electronic archives (Reference: LH2589).

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supplementary materials

5,7-Di-2-pyridyl-2,3-dihydrothieno[3,4-*b*][1,4]dioxine

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Comment

Derivatives of 3,4-ethylenedioxythiophene (EDOT) have been actively pursued primarily as precursors to polymers with interesting electronic and optical properties (Roncali *et al.*, 2005). The presence of the ethylenedioxy substituent greatly enhances the stability of these materials relative to unsubstituted polythiophenes. As part of our efforts toward new molecule-based materials, we are investigating the propensity for 3,4-ethylenedioxythiophene derivatives to function as ligands for transition metal ions. We have prepared the title compound (I) featuring 2-pyridyl substituents appended to the 2,5-positions of the 3,4-ethylenedioxythiophene ring and are investigating the coordination chemistry of this potentially chelating ligand. We report herein the crystal structure of (I).

In the molecular structure of (I) bond lengths and angles within the EDOT moiety are within normal ranges (Han & Choi, 2000; Sotzing *et al.*, 1996). As is typical in the structures of other EDOT derivatives, the six-membered dioxane-type ring in (I) is in a half-chair conformation, with the H atoms on the ethylene C atoms in a nearly *gauche* configuration. Each pyridine ring is tilted out of the plane of the EDOT moiety, with torsion angles of 19.39 (12) and −0.78 (12)° for S1—C11—C12—N2 and N1—C5—C6—S1, respectively and is likely the result of short intramolecular contacts between N and S atoms (2.923 (1) and 2.965 (1)Å for S1···N1 and S1···N2, respectively). Bond lengths between the EDOT group and the pyridine rings are 1.4626 (13) and 1.4609 (13) Å for C5—C6 and C11—C12, respectively. These lengths are the same (within experimental error) as those observed for the related bonds in the structure of 2-pyridylthiophene [1.469 (3) Å] (Ghosh & Simonsen, 1993).

Experimental

2-pyridylzinc bromide solution (20.0 ml of a 0.5 *M* THF solution, 10.0 mmol) was added *via* syringe to a dry, nitrogen-purged Schlenk flask protected from light containing 2,5-dibromo-3,4-ethylenedioxythiophene (1.0 g, 3.3 mmol) and Pd(PPh$_3$)$_4$ (0.35 g, 0.3 mmol). The mixture was refluxed for 24 h, cooled to room temperature and stirred in basic edta solution (~0.2 *M*) for approximately 24 h. The edta solution was extracted with chloroform, concentrated to a small volume and poured into pentane to precipitate out the product as a pale yellow solid. Yield 0.48 g (49%). Crystals were grown by slow evaporation of an acetone solution of the product at 278 K. Anal.calcd (%) for C$_{16}$H$_{12}$N$_2$O$_2$S: C 64.85, H 4.09, N 9.46.Found: C 64.23, H 3.82, N 9.25. MS(EI+), *m/z* (%): 296 (100).

Refinement

H atoms were found using the difference map and all H parameters were refined.
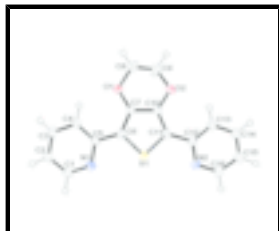
supplementary materials

Figures

Fig. 1. The molecular structure of the title compound with atom labels and 50% probability displacement ellipsoids for non-H atoms.

5,7-Di-2-pyridyl-2,3-dihydrothieno[3,4-*b*][1,4]dioxine

Crystal data

$C_{16}H_{12}N_2O_2S$	$F_{000} = 616$
$M_r = 296.34$	$D_x = 1.449$ Mg m^{-3}
Monoclinic, $P2_1/n$	Mo $K\alpha$ radiation $\lambda = 0.71073$ Å
Hall symbol: -P 2yn	Cell parameters from 8327 reflections
$a = 10.5189$ (12) Å	$\theta = 2.6–32.3°$
$b = 9.8752$ (12) Å	$\mu = 0.24$ mm^{-1}
$c = 13.1961$ (18) Å	$T = 173$ (2) K
$\beta = 97.752$ (3)°	Block, colourless
$V = 1358.2$ (3) Å^3	$0.38 \times 0.30 \times 0.20$ mm
$Z = 4$	

Data collection

Bruker APEXII diffractometer	5134 independent reflections
Radiation source: fine-focus sealed tube	4316 reflections with $I > 2\sigma(I)$
Monochromator: graphite	$R_{int} = 0.026$
$T = 173(2)$ K	$\theta_{max} = 33.3°$
φ and ω scans	$\theta_{min} = 2.3°$
Absorption correction: multi-scan (SADABS; Sheldrick, 1996)	$h = -16 \rightarrow 16$
$T_{min} = 0.864$, $T_{max} = 1.000$	$k = -8 \rightarrow 15$
22945 measured reflections	$l = -20 \rightarrow 18$

Refinement

Refinement on F^2	Secondary atom site location: difference Fourier map
Least-squares matrix: full	Hydrogen site location: difference Fourier map
$R[F^2 > 2\sigma(F^2)] = 0.037$	All H-atom parameters refined
$wR(F^2) = 0.109$	$w = 1/[\sigma^2(F_o^2) + (0.0623P)^2 + 0.2445P]$ where $P = (F_o^2 + 2F_c^2)/3$
$S = 1.05$	$(\Delta/\sigma)_{max} = 0.001$

5134 reflections	$\Delta\rho_{max} = 0.47$ e Å^{-3}
238 parameters	$\Delta\rho_{min} = -0.21$ 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 > 2sigma(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}
S1	0.52108 (2)	0.40887 (2)	0.128549 (18)	0.02244 (7)
O1	0.21374 (7)	0.28139 (9)	−0.04158 (6)	0.03008 (17)
N1	0.32131 (9)	0.54483 (9)	0.22458 (7)	0.02895 (18)
C1	0.24126 (12)	0.61030 (12)	0.27867 (9)	0.0343 (2)
H1	0.2820 (16)	0.6590 (17)	0.3407 (13)	0.046 (4)*
O2	0.44345 (8)	0.16437 (8)	−0.10327 (6)	0.02944 (16)
N2	0.76947 (9)	0.27018 (10)	0.12037 (8)	0.03112 (19)
C2	0.10899 (12)	0.60791 (12)	0.25650 (10)	0.0343 (2)
H2	0.0574 (15)	0.6560 (17)	0.2998 (12)	0.043 (4)*
C3	0.05533 (11)	0.53586 (12)	0.17120 (10)	0.0338 (2)
H3	−0.0338 (17)	0.5319 (17)	0.1520 (13)	0.044 (4)*
C4	0.13538 (11)	0.46837 (11)	0.11278 (9)	0.0294 (2)
H4	0.0956 (16)	0.4152 (16)	0.0528 (13)	0.043 (4)*
C5	0.26776 (9)	0.47352 (9)	0.14214 (7)	0.02228 (17)
C6	0.35800 (9)	0.39961 (9)	0.08746 (7)	0.02107 (17)
C7	0.33364 (9)	0.31265 (9)	0.00561 (7)	0.02180 (17)
C8	0.21613 (12)	0.21560 (15)	−0.13906 (9)	0.0373 (3)
H8B	0.1311 (17)	0.1762 (17)	−0.1607 (13)	0.045 (4)*
H8A	0.2400 (17)	0.2820 (17)	−0.1874 (14)	0.048 (4)*
C9	0.31708 (12)	0.10680 (12)	−0.13079 (10)	0.0343 (2)
H9B	0.3068 (16)	0.0402 (16)	−0.0763 (13)	0.042 (4)*
H9A	0.3192 (16)	0.0601 (16)	−0.1964 (13)	0.040 (4)*
C10	0.44657 (9)	0.25377 (9)	−0.02383 (7)	0.02233 (17)
C11	0.55669 (9)	0.29531 (9)	0.03618 (7)	0.02234 (17)
C12	0.68890 (10)	0.25174 (10)	0.03345 (8)	0.02406 (18)
C13	0.72798 (11)	0.19200 (11)	−0.05374 (9)	0.0289 (2)
H13	0.6694 (17)	0.1792 (18)	−0.1144 (13)	0.049 (5)*
C14	0.85394 (11)	0.14936 (13)	−0.04938 (10)	0.0341 (2)

H14	0.8846 (18)	0.1135 (18)	−0.1082 (14)	0.051 (5)*
C15	0.93616 (11)	0.16398 (14)	0.04084 (11)	0.0389 (3)
H15	1.0276 (17)	0.1367 (18)	0.0466 (13)	0.050 (5)*
C16	0.89017 (11)	0.22521 (14)	0.12321 (10)	0.0375 (3)
H16	0.9492 (17)	0.2418 (17)	0.1890 (14)	0.051 (5)*

Atomic displacement parameters (Å^2)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
S1	0.02221 (12)	0.02250 (11)	0.02233 (12)	−0.00056 (7)	0.00197 (8)	0.00032 (7)
O1	0.0229 (3)	0.0409 (4)	0.0257 (3)	0.0009 (3)	0.0004 (3)	−0.0099 (3)
N1	0.0312 (4)	0.0294 (4)	0.0248 (4)	0.0052 (3)	−0.0010 (3)	−0.0057 (3)
C1	0.0382 (6)	0.0349 (5)	0.0283 (5)	0.0088 (4)	−0.0005 (4)	−0.0098 (4)
O2	0.0285 (4)	0.0329 (4)	0.0275 (4)	0.0003 (3)	0.0059 (3)	−0.0082 (3)
N2	0.0230 (4)	0.0383 (5)	0.0318 (5)	−0.0004 (3)	0.0027 (3)	−0.0059 (4)
C2	0.0367 (6)	0.0331 (5)	0.0335 (5)	0.0105 (4)	0.0055 (5)	−0.0073 (4)
C3	0.0270 (5)	0.0353 (5)	0.0388 (6)	0.0064 (4)	0.0036 (4)	−0.0084 (4)
C4	0.0257 (5)	0.0314 (5)	0.0305 (5)	0.0039 (4)	0.0020 (4)	−0.0075 (4)
C5	0.0258 (4)	0.0203 (4)	0.0207 (4)	0.0025 (3)	0.0028 (3)	0.0007 (3)
C6	0.0225 (4)	0.0212 (4)	0.0195 (4)	0.0012 (3)	0.0029 (3)	0.0017 (3)
C7	0.0216 (4)	0.0240 (4)	0.0197 (4)	0.0003 (3)	0.0022 (3)	0.0010 (3)
C8	0.0320 (6)	0.0513 (7)	0.0267 (5)	0.0050 (5)	−0.0027 (4)	−0.0137 (5)
C9	0.0323 (5)	0.0360 (5)	0.0343 (6)	−0.0025 (4)	0.0032 (4)	−0.0125 (4)
C10	0.0247 (4)	0.0224 (4)	0.0203 (4)	0.0011 (3)	0.0047 (3)	0.0009 (3)
C11	0.0224 (4)	0.0222 (4)	0.0229 (4)	0.0014 (3)	0.0051 (3)	0.0030 (3)
C12	0.0228 (4)	0.0237 (4)	0.0263 (4)	−0.0003 (3)	0.0058 (3)	0.0024 (3)
C13	0.0273 (5)	0.0318 (5)	0.0287 (5)	0.0001 (4)	0.0074 (4)	−0.0011 (4)
C14	0.0281 (5)	0.0376 (6)	0.0385 (6)	0.0003 (4)	0.0117 (4)	−0.0067 (4)
C15	0.0220 (5)	0.0447 (6)	0.0500 (7)	0.0011 (4)	0.0051 (5)	−0.0107 (5)
C16	0.0235 (5)	0.0471 (7)	0.0406 (6)	−0.0005 (4)	−0.0004 (4)	−0.0091 (5)

Geometric parameters (Å, °)

S1—C6	1.7303 (10)	C5—C6	1.4626 (13)
S1—C11	1.7340 (10)	C6—C7	1.3767 (13)
O1—C7	1.3644 (12)	C7—C10	1.4229 (13)
O1—C8	1.4444 (13)	C8—C9	1.5042 (18)
N1—C1	1.3412 (14)	C8—H8B	0.982 (17)
N1—C5	1.3533 (13)	C8—H8A	0.971 (18)
C1—C2	1.3828 (18)	C9—H9B	0.991 (16)
C1—H1	0.996 (18)	C9—H9A	0.984 (16)
O2—C10	1.3674 (12)	C10—C11	1.3747 (14)
O2—C9	1.4463 (14)	C11—C12	1.4609 (13)
N2—C16	1.3408 (15)	C12—C13	1.4029 (14)
N2—C12	1.3435 (14)	C13—C14	1.3841 (16)
C2—C3	1.3857 (17)	C13—H13	0.950 (18)
C2—H2	0.965 (16)	C14—C15	1.3814 (19)
C3—C4	1.3867 (15)	C14—H14	0.948 (18)
C3—H3	0.938 (17)	C15—C16	1.3868 (18)

C4—C5	1.3950 (15)	C15—H15	0.992 (18)
C4—H4	0.994 (17)	C16—H16	1.010 (18)
C6—S1—C11	92.56 (5)	C9—C8—H8A	106.7 (10)
C7—O1—C8	112.47 (8)	H8B—C8—H8A	112.5 (15)
C1—N1—C5	117.10 (10)	O2—C9—C8	110.69 (10)
N1—C1—C2	124.42 (11)	O2—C9—H9B	105.4 (10)
N1—C1—H1	116.0 (9)	C8—C9—H9B	112.5 (10)
C2—C1—H1	119.5 (9)	O2—C9—H9A	106.0 (10)
C10—O2—C9	111.87 (8)	C8—C9—H9A	111.7 (9)
C16—N2—C12	117.70 (10)	H9B—C9—H9A	110.1 (13)
C1—C2—C3	117.94 (10)	O2—C10—C11	124.44 (9)
C1—C2—H2	119.8 (10)	O2—C10—C7	122.58 (9)
C3—C2—H2	122.3 (10)	C11—C10—C7	112.98 (8)
C2—C3—C4	119.15 (11)	C10—C11—C12	128.97 (9)
C2—C3—H3	121.6 (10)	C10—C11—S1	110.66 (7)
C4—C3—H3	119.3 (10)	C12—C11—S1	120.30 (7)
C3—C4—C5	119.10 (10)	N2—C12—C13	122.44 (10)
C3—C4—H4	118.4 (10)	N2—C12—C11	115.59 (9)
C5—C4—H4	122.5 (10)	C13—C12—C11	121.96 (9)
N1—C5—C4	122.27 (9)	C14—C13—C12	118.59 (11)
N1—C5—C6	115.39 (9)	C14—C13—H13	120.2 (10)
C4—C5—C6	122.32 (9)	C12—C13—H13	121.2 (10)
C7—C6—C5	129.33 (9)	C15—C14—C13	119.24 (11)
C7—C6—S1	110.53 (7)	C15—C14—H14	120.1 (12)
C5—C6—S1	120.07 (7)	C13—C14—H14	120.6 (12)
O1—C7—C6	124.20 (9)	C14—C15—C16	118.50 (11)
O1—C7—C10	122.50 (8)	C14—C15—H15	121.7 (10)
C6—C7—C10	113.28 (9)	C16—C15—H15	119.7 (10)
O1—C8—C9	110.71 (10)	N2—C16—C15	123.48 (12)
O1—C8—H8B	108.2 (10)	N2—C16—H16	116.1 (10)
C9—C8—H8B	110.2 (10)	C15—C16—H16	120.3 (10)
O1—C8—H8A	108.5 (10)		
C5—N1—C1—C2	0.93 (18)	C9—O2—C10—C7	−17.88 (13)
N1—C1—C2—C3	−1.7 (2)	O1—C7—C10—O2	1.80 (14)
C1—C2—C3—C4	0.77 (19)	C6—C7—C10—O2	179.87 (8)
C2—C3—C4—C5	0.74 (18)	O1—C7—C10—C11	−177.64 (9)
C1—N1—C5—C4	0.72 (15)	C6—C7—C10—C11	0.44 (12)
C1—N1—C5—C6	−177.85 (9)	O2—C10—C11—C12	−3.24 (16)
C3—C4—C5—N1	−1.55 (16)	C7—C10—C11—C12	176.18 (9)
C3—C4—C5—C6	176.92 (10)	O2—C10—C11—S1	179.96 (7)
N1—C5—C6—C7	175.73 (10)	C7—C10—C11—S1	−0.62 (10)
C4—C5—C6—C7	−2.84 (16)	C6—S1—C11—C10	0.51 (7)
N1—C5—C6—S1	−0.78 (12)	C6—S1—C11—C12	−176.61 (8)
C4—C5—C6—S1	−179.35 (8)	C16—N2—C12—C13	−2.13 (16)
C11—S1—C6—C7	−0.26 (7)	C16—N2—C12—C11	176.57 (10)
C11—S1—C6—C5	176.86 (8)	C10—C11—C12—N2	−157.14 (10)
C8—O1—C7—C6	165.76 (10)	S1—C11—C12—N2	19.39 (12)
C8—O1—C7—C10	−16.38 (14)	C10—C11—C12—C13	21.56 (15)

C5—C6—C7—O1	1.22 (16)	S1—C11—C12—C13	−161.91 (8)
S1—C6—C7—O1	177.99 (8)	N2—C12—C13—C14	0.69 (16)
C5—C6—C7—C10	−176.82 (9)	C11—C12—C13—C14	−177.93 (10)
S1—C6—C7—C10	−0.04 (10)	C12—C13—C14—C15	1.45 (17)
C7—O1—C8—C9	45.42 (14)	C13—C14—C15—C16	−2.0 (2)
C10—O2—C9—C8	46.89 (13)	C12—N2—C16—C15	1.51 (19)
O1—C8—C9—O2	−62.83 (14)	C14—C15—C16—N2	0.6 (2)
C9—O2—C10—C11	161.49 (10)		

Fig. 1