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Benzo[1,2-*b*:4,5-*b'*]dithiophene-4,8-dioneAmanda L. Ramirez,^a Benny C. Chan^b and Daniel T. de Lill^{a*}^aDepartment of Chemistry & Biochemistry, Florida Atlantic University, 777 Glades Road, Boca Raton, FL 33431, USA, and ^bDepartment of Chemistry, The College of New Jersey, Ewing, NJ 08628, USA

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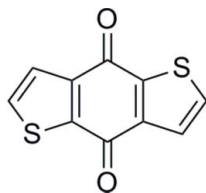
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Key indicators: single-crystal X-ray study; $T = 296$ K; mean $\sigma(\text{C}-\text{C}) = 0.004$ Å; R factor = 0.068; wR factor = 0.238; data-to-parameter ratio = 16.6.

The title molecule, $\text{C}_{10}\text{H}_4\text{O}_2\text{S}_2$, is situated on a crystallographic center of inversion. In the crystal, weak hydrogen bonding contributes to the packing of the molecules.

Related literature

This dione was synthesized according to modified literature procedures, see: Beilung & Kossmehl (1986); Slocum & Gierer (1976). It is a precursor to many different semi-conducting polymeric compounds and the structure is important in that it appears as crystalline products in poorly purified materials, see: Hundt *et al.* (2009); Subramaniyan *et al.* (2011); Yamamoto *et al.* (2011). For weak intermolecular interactions, see: Janiak (2000); Sinnokrot *et al.* (2002).



Experimental

Crystal data

 $\text{C}_{10}\text{H}_4\text{O}_2\text{S}_2$
 $M_r = 220.25$
 Monoclinic, $P2_1/n$
 $a = 5.6402$ (5) Å

 $b = 5.7745$ (5) Å
 $c = 13.6223$ (12) Å
 $\beta = 97.371$ (1)°
 $V = 440.00$ (7) Å³
 $Z = 2$
 Mo $K\alpha$ radiation
 $\mu = 0.57$ mm⁻¹
 $T = 296$ K
 $0.08 \times 0.06 \times 0.04$ mm

Data collection

 Bruker APEXII diffractometer
 Absorption correction: multi-scan
 (SADABS; Sheldrick, 2001)
 $T_{\min} = 0.955$, $T_{\max} = 0.978$

 4888 measured reflections
 1062 independent reflections
 815 reflections with $I > 2\sigma(I)$
 $R_{\text{int}} = 0.072$

Refinement

 $R[F^2 > 2\sigma(F^2)] = 0.068$
 $wR(F^2) = 0.238$
 $S = 1.09$
 1062 reflections

 64 parameters
 H-atom parameters constrained
 $\Delta\rho_{\max} = 0.78$ e Å⁻³
 $\Delta\rho_{\min} = -0.57$ e Å⁻³

Table 1

Hydrogen-bond geometry (Å, °).

$D-H\cdots A$	$D-H$	$H\cdots A$	$D\cdots A$	$D-H\cdots A$
$\text{C5}-\text{H5}\cdots\text{O1}^i$	0.93	2.44	3.319 (4)	158

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

Data collection: APEX2 (Bruker, 2010); cell refinement: SAINT (Bruker, 2009); data reduction: SAINT; program(s) used to solve structure: SHELXS97 (Sheldrick, 2008); program(s) used to refine structure: SHELXL97 (Sheldrick, 2008); molecular graphics: CrystalMaker (Palmer, 2009); software used to prepare material for publication: SHELXTL (Sheldrick, 2008).

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Supplementary data and figures for this paper are available from the IUCr electronic archives (Reference: RN2094).

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supporting information

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Benzo[1,2-*b*:4,5-*b'*]dithiophene-4,8-dione

Amanda L. Ramirez, Benny C. Chan and Daniel T. de Lill

S1. Comment

Benzodithiophene-4,8-dione (BDTD) is a common precursor for the construction of semiconducting organic monomers. Given our interest in this field, we have isolated single crystals of this compound for structural determination. This structure is important in that it appears as crystalline products in poorly purified materials.

A thermal ellipsoid plot (Fig. 1) displays the molecular structure of the title compound.

Figure 2 shows a packing diagram of the crystal structure. Weak intermolecular interactions attribute to the packing of this compound, see: Sinnokrot *et al.* (2002); Janiak (2000). The closest CH $\cdots$ centroid distance is C1—H1 $\cdots$ Cg1 at 3.715 (4) Å between a hydrogen atom and the center of a neighboring thiophene ring. No classic hydrogen bonds were found, but a weak hydrogen bond from C5—H5 $\cdots$ O1 is present at 3.319 (4) Å D—A distance.

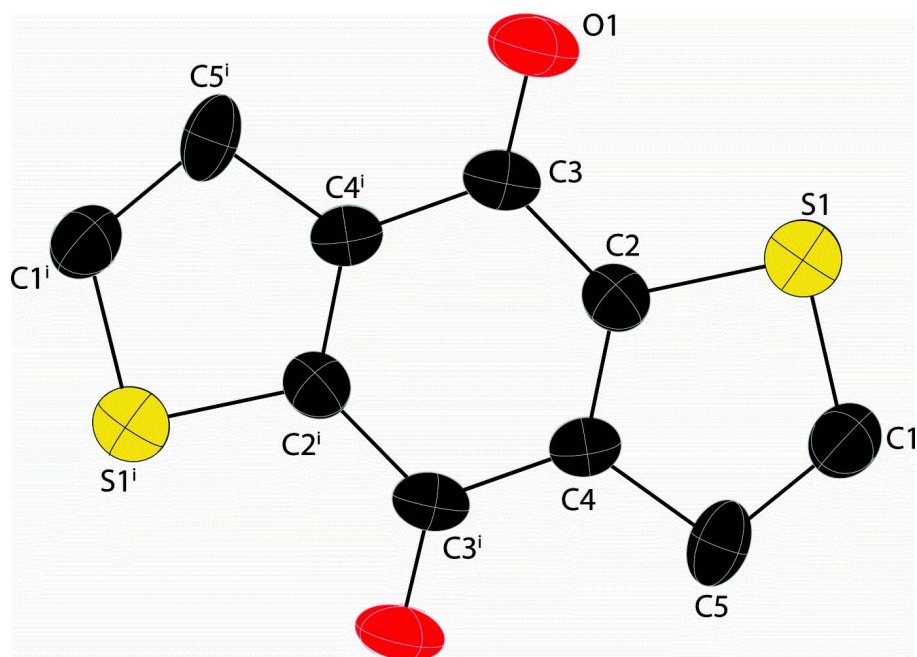
S2. Experimental

The title compound was prepared according to a modified literature procedure (Beimlung & Kossmehl, 1986). In a typical reaction, 2 g of 3-theonic acid was reacted with excess thionyl chloride (50 ml) at reflux temperature overnight to produce the resulting acid chloride. Upon removal of the thionyl chloride, the acid chloride was dissolved in toluene (minimum amount). The acid chloride was then added to excess diethylamine (approximately 42 ml) to produce the thiophene amide. The product was isolated in diethyl ether, concentrated, and then re-dissolved in ether (30 ml). The amide was then cyclized with excess *n*-butyl lithium (1.6 *M* in hexane, approximately 7 ml) added dropwise and allowed to stir overnight. The reaction was quenched with water, filtered, and recrystallized from glacial acetic acid in a 31–45% yield depending on reaction.

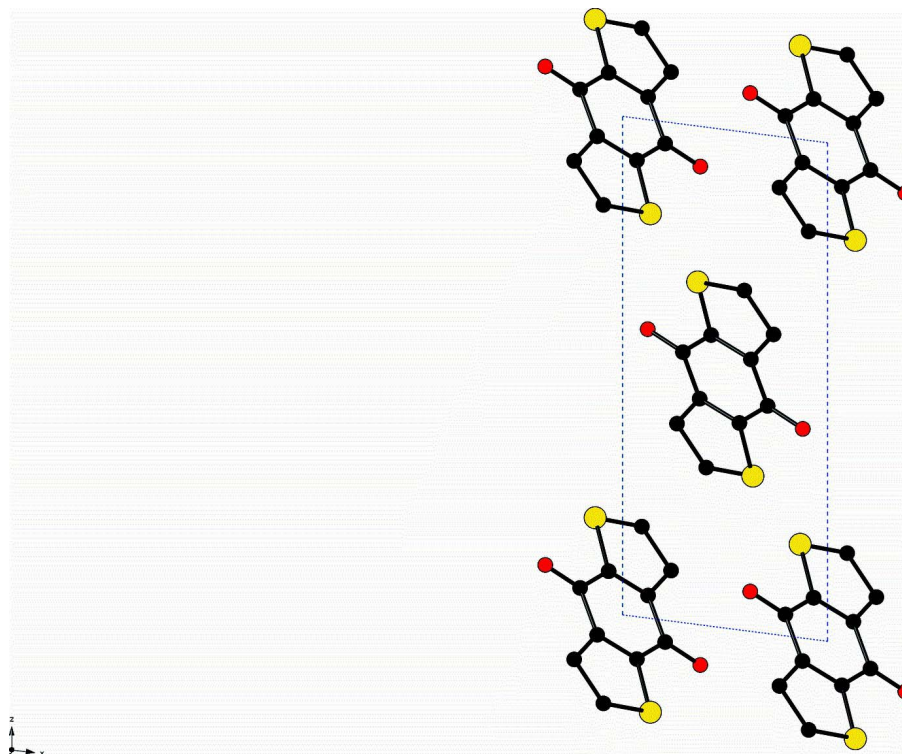
Upon isolation of the final compound, crystals suitable for X-ray diffraction were obtained from slow evaporation of approximately 20 mg of product in approximately 5 ml of chloroform. Clear, yellow block crystals formed overnight.

S3. Refinement

Crystallography. Hydrogen atom positions were placed in calculated positions and allowed to ride on the coordinates of the parent atom [C—H distances at 0.93 Å and $U_{\text{iso}}(\text{H})=1.2U_{\text{iso}}(\text{C})$].

**Figure 1**

Thermal ellipsoid plot (50% probability) of title compound. Hydrogen atoms are omitted. Symmetry operator: $i = -x + 2, -y + 1, -z + 2$.

**Figure 2**

Packing diagram of title compound down [010]. Hydrogen atoms were removed for clarity.

Benzo[1,2-*b*:4,5-*b'*]dithiophene-4,8-dione

Crystal data

C₁₀H₄O₂S₂
 $M_r = 220.25$
 Monoclinic, $P2_1/n$
 $a = 5.6402$ (5) Å
 $b = 5.7745$ (5) Å
 $c = 13.6223$ (12) Å
 $\beta = 97.371$ (1)°
 $V = 440.00$ (7) Å³
 $Z = 2$

$F(000) = 224$
 $D_x = 1.662$ Mg m⁻³
 Mo $K\alpha$ radiation, $\lambda = 0.71073$ Å
 Cell parameters from 2545 reflections
 $\theta = 6.0$ – 55.2°
 $\mu = 0.57$ mm⁻¹
 $T = 296$ K
 Prismatic block, clear yellow
 $0.08 \times 0.06 \times 0.04$ mm

Data collection

Bruker APEXII
 diffractometer
 Radiation source: fine-focus sealed tube
 Graphite monochromator
 Fixed Chi scans
 Absorption correction: multi-scan
 (SADABS; Sheldrick, 2001)
 $T_{\min} = 0.955$, $T_{\max} = 0.978$

4888 measured reflections
 1062 independent reflections
 815 reflections with $I > 2\sigma(I)$
 $R_{\text{int}} = 0.072$
 $\theta_{\max} = 28.6^\circ$, $\theta_{\min} = 3.0^\circ$
 $h = -7 \rightarrow 7$
 $k = -7 \rightarrow 7$
 $l = -18 \rightarrow 17$

Refinement

Refinement on F^2
 Least-squares matrix: full
 $R[F^2 > 2\sigma(F^2)] = 0.068$
 $wR(F^2) = 0.238$
 $S = 1.09$
 1062 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
 $w = 1/[\sigma^2(F_o^2) + (0.1499P)^2 + 0.2282P]$
 where $P = (F_o^2 + 2F_c^2)/3$
 $(\Delta/\sigma)_{\max} < 0.001$
 $\Delta\rho_{\max} = 0.78$ e Å⁻³
 $\Delta\rho_{\min} = -0.57$ 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)

	<i>x</i>	<i>y</i>	<i>z</i>	$U_{\text{iso}}^*/U_{\text{eq}}$
S1	0.13427 (18)	0.25931 (18)	0.81226 (8)	0.0558 (5)
O1	0.3782 (5)	0.6780 (5)	0.9199 (2)	0.0540 (8)
C1	-0.0936 (7)	0.0712 (6)	0.8176 (3)	0.0517 (9)
H1	-0.1261	-0.0467	0.7714	0.062*
C2	0.0689 (6)	0.3977 (5)	0.9156 (2)	0.0379 (7)

C3	0.2074 (6)	0.5981 (5)	0.9569 (2)	0.0390 (8)
C4	−0.1243 (5)	0.3053 (5)	0.9539 (2)	0.0366 (7)
C5	−0.2363 (6)	0.1035 (5)	0.8983 (2)	0.0421 (8)
H5	−0.3675	0.0174	0.9120	0.050*

Atomic displacement parameters (Å²)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
S1	0.0531 (8)	0.0612 (8)	0.0549 (8)	−0.0008 (4)	0.0137 (5)	−0.0091 (4)
O1	0.0442 (14)	0.0666 (17)	0.0540 (15)	−0.0147 (12)	0.0175 (11)	0.0106 (13)
C1	0.0493 (19)	0.0468 (19)	0.058 (2)	−0.0021 (15)	0.0037 (16)	−0.0143 (16)
C2	0.0371 (15)	0.0388 (16)	0.0384 (15)	0.0010 (12)	0.0079 (12)	0.0028 (12)
C3	0.0345 (15)	0.0416 (16)	0.0413 (16)	−0.0041 (13)	0.0066 (12)	0.0096 (13)
C4	0.0339 (16)	0.0348 (15)	0.0406 (17)	−0.0034 (12)	0.0037 (13)	0.0043 (12)
C5	0.0534 (19)	0.0295 (14)	0.0394 (16)	0.0089 (13)	−0.0091 (14)	−0.0053 (12)

Geometric parameters (Å, °)

S1—C1	1.691 (4)	C2—C3	1.467 (5)
S1—C2	1.700 (3)	C3—C4 ⁱ	1.468 (5)
O1—C3	1.232 (4)	C4—C3 ⁱ	1.468 (5)
C1—C5	1.455 (5)	C4—C5	1.486 (4)
C1—H1	0.9300	C5—H5	0.9300
C2—C4	1.374 (4)		
C1—S1—C2	91.10 (17)	O1—C3—C4 ⁱ	123.0 (3)
C5—C1—S1	116.6 (3)	C2—C3—C4 ⁱ	114.0 (3)
C5—C1—H1	121.7	C2—C4—C3 ⁱ	121.3 (3)
S1—C1—H1	121.7	C2—C4—C5	114.7 (3)
C4—C2—C3	124.7 (3)	C3 ⁱ —C4—C5	124.0 (3)
C4—C2—S1	113.5 (3)	C1—C5—C4	104.2 (3)
C3—C2—S1	121.8 (2)	C1—C5—H5	127.9
O1—C3—C2	123.0 (3)	C4—C5—H5	127.9

Symmetry code: (i) $-x, -y+1, -z+2$.*Hydrogen-bond geometry (Å, °)*

$D—H\cdots A$	$D—H$	$H\cdots A$	$D\cdots A$	$D—H\cdots A$
C5—H5 $\cdots$ O1 ⁱⁱ	0.93	2.44	3.319 (4)	158

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