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5,6-Dihydro-1,4-dithiine-2,3-dicarboxylic anhydride

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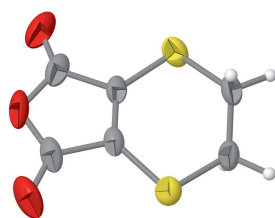
Keywords: crystal structure; fused ring; heterocycle; dithiine; anhydride.

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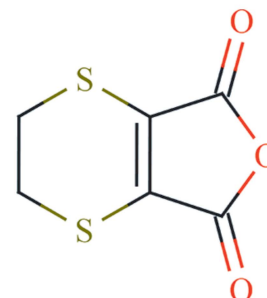
Structural data: full structural data are available from iucrdata.iucr.org

In the title compound (systematic name: 2,3-dihydro-1,4-dithiino[2,3-*c*]furan-5,7-dione), C₆H₄O₃S₂, the observed geometry agrees well with those of its phthalamide, thieno and hydroxy analogs, and with a calculated geometry obtained by density functional theory (DFT) calculations. Specific structural features are an S—C—C—S torsion angle of -70.39 (17)° and S—C bonds to *sp*²-hybridized C atoms approximately 0.1 Å shorter than those to *sp*³-hybridized C atoms. Unlike the extended structures of the analogs, there are no directed intermolecular interactions and the head-to-tail rows of molecules that are a prominent structural motif of the packing can be rationalized in terms of optimized dipole–dipole interactions.

3D view



Chemical scheme



Structure description

The unit-cell parameters for the title compound have been reported previously [Grabowski, 1968; Cambridge Structural Database (CSD; Groom *et al.*, 2016) refcode QQDIA], but atomic coordinates are not available. Related compounds with reported three-dimensional atomic coordinates are the phthalamide (DTHPIM; Kirfel *et al.*, 1975), the thieno (ZUHQUQ; Skabara *et al.*, 2003) and the monohydroxy (USUMOL; Kurbangalieva *et al.*, 2010) analogs, all of which are reported to crystallize in the monoclinic space groups *P*₂₁/*c* or *P*₂₁/*n*. We report here the three-dimensional structure of 5,6-dihydro-1,4-dithiine-2,3-dicarboxylic anhydride, which crystallizes in the triclinic space group *P* $\bar{1}$ with unit-cell parameters in agreement with those reported by Grabowski.

The molecule (Fig. 1) consists of furandione and dihydro-1,4-dithiine rings fused by a common carbon–carbon double bond (atoms C3 and C4) and is largely planar (r.m.s. deviation of 0.044 Å from the mean plane for all atoms except the CH₂ groups). The CH₂ groups are twisted about the molecular plane in order to reduce angle strain, with C1



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Table 1

Selected geometric parameters (Å, °).

S1—C1	1.805 (2)	C3—C5	1.469 (3)
S1—C3	1.7136 (19)	C4—C6	1.472 (3)
S2—C2	1.817 (2)	O1—C5	1.193 (3)
S2—C4	1.7160 (19)	O2—C5	1.376 (3)
C1—C2	1.510 (3)	O2—C6	1.386 (3)
C3—C4	1.345 (3)	O3—C6	1.186 (3)
C1—S1—C3	99.54 (10)	C3—C4—C6	107.44 (17)
C2—S2—C4	98.30 (10)	O1—C5—C3	129.7 (2)
S1—C1—C2	114.41 (15)	O2—C5—C3	108.36 (18)
C1—C2—S2	115.01 (15)	O1—C5—O2	121.98 (19)
S1—C3—C4	131.57 (14)	O2—C6—C4	108.13 (18)
S1—C3—C5	120.60 (16)	O3—C6—C4	130.7 (2)
C4—C3—C5	107.83 (17)	O2—C6—O3	121.2 (2)
C3—C4—S2	129.27 (14)	C5—O2—C6	108.14 (15)
C6—C4—S2	123.28 (16)		

0.323 (3) Å above and C2 0.528 (3) Å below, and an S1—C1—C2—S2 torsion angle of $-70.39 (17)^\circ$. The S—C bond lengths are 0.096 (7) Å shorter for bonds to sp^2 -hybridized C atoms than to those with sp^3 -hybridization (Table 1). The interior bond angles within the furandione ring are close to idealized values for a uniform pentagon, ranging from 107.44 (17) to 108.36 (18)°. The O=C—O angles have expected values of 121–122° for an sp^2 -hybridized center, while the external O=C—C angles average 130.2 (7)° in order to accommodate the geometry of the planar ring. These details agree well with the geometrical parameters for maleic anhydride [MLEICA (Marsh *et al.*, 1962) and MLEICA01 (Lutz, 2001)].

The geometrical details for the related compounds listed above agree closely with those of the title compound. In particular, the S—C—C—S torsion-angle magnitudes range from 68.10 to 70.75° and the S—C bond lengths to sp^2 -hybridized C atoms average 0.087 (14) Å shorter than those to sp^3 -hybridized C atoms, with the phthalamide analog providing the closest agreement [average sp^3 – sp^2 bond length difference = 0.0995 (7) Å]. A DFT geometry optimization *in vacuo* [B3LYP functional, cc-pTVZ basis set; GAMESS (Schmidt *et al.*, 1993)] yields similar results, with an S—C—C—S torsion angle of -69.6° and S—C bond lengths of 1.730 and 1.829 Å to sp^2 - and sp^3 -hybridized C atoms, respectively. An electrostatic potential plot with the optimized molecule visible is presented in Fig. 2.

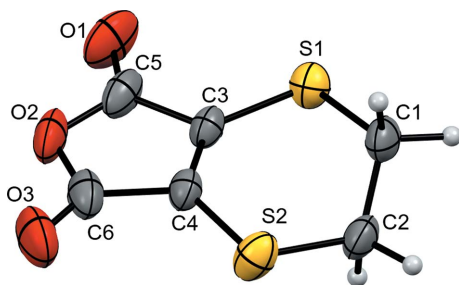


Figure 1

Displacement ellipsoid plot at the 50% probability level of the formula unit of the title compound, showing labels for non-H atoms.

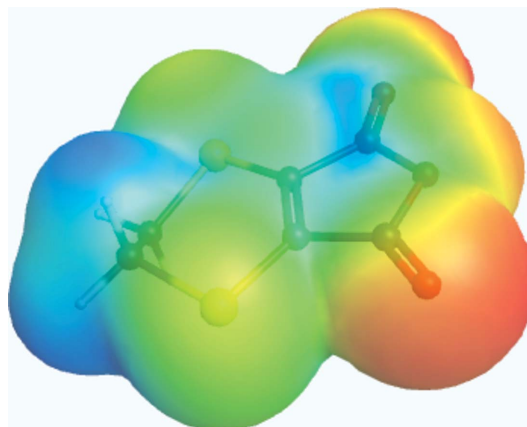


Figure 2

Electrostatic potential plot of the title molecule with the optimized geometry visible. Red represents the most negatively charged regions, while blue represents the most positively charged.

The unit-cell packing of the title compound consists of sheets of molecules lying parallel to $(11\bar{2})$, with neighboring sheets related by inversion. The molecular planes are approximately coplanar with the sheet, with molecules forming head-to-tail rows parallel to $[1\bar{1}0]$ within the sheet. Neighboring rows within the sheet have opposite orientations, while rows on neighboring sheets straddle each other. This packing differs from that of similar molecules, where directed hydrogen bonding or short S...O contacts feature prominently, with the head-to-tail rows of molecules in the title compound rationalized in terms of optimized dipole–dipole interactions. A ball-and-stick diagram of a sheet is presented in Fig. 3 and a unit-cell packing diagram viewed edge on to the sheets is presented in Fig. 4.

Synthesis and crystallization

5,6-Dihydro-1,4-dithiin-2,3-dicarboxylic anhydride (98+%) was purchased from Fisher Scientific and recrystallized by slow evaporation at room temperature from tetrahydrofuran solution to yield yellow block-like crystals.

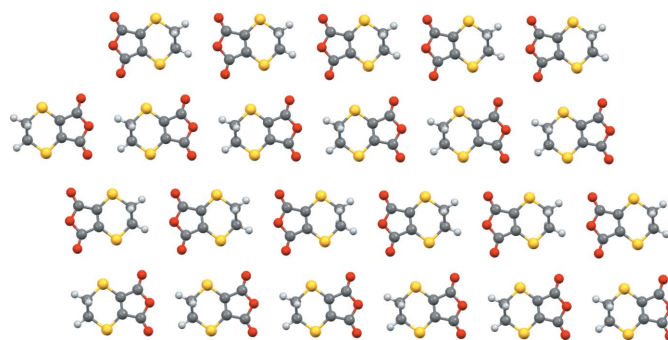


Figure 3

Ball-and-stick diagram of the sheet structure viewed perpendicular to $(11\bar{2})$.

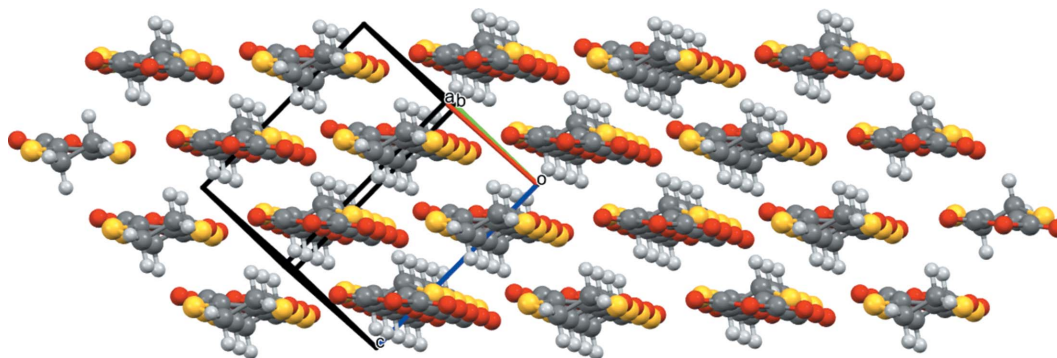


Figure 4

Ball-and-stick packing diagram of a unit cell, with axis labels viewed along $[1\bar{1}0]$, showing the stacking of four sheets to generate the three-dimensional structure.

Table 2

Experimental details.

Crystal data	
Chemical formula	$C_6H_4O_3S_2$
M_r	188.23
Crystal system, space group	Triclinic, $P\bar{1}$
Temperature (K)	295
a, b, c (Å)	5.398 (1), 7.5537 (15), 9.2566 (18)
α, β, γ (°)	89.273 (6), 87.361 (6), 75.701 (5)
V (Å ³)	365.36 (12)
Z	2
Radiation type	Mo $K\alpha$
μ (mm ⁻¹)	0.68
Crystal size (mm)	0.42 × 0.38 × 0.17
Data collection	
Diffractometer	Bruker D8 Quest Eco
Absorption correction	Multi-scan (SADABS; Bruker, 2016)
T_{\min}, T_{\max}	0.648, 0.746
No. of measured, independent and observed [$I \geq 2\sigma(I)$] reflections	16978, 1669, 1338
R_{int}	0.046
$(\sin \theta/\lambda)_{\text{max}}$ (Å ⁻¹)	0.651
Refinement	
$R[F^2 > 2\sigma(F^2)], wR(F^2), S$	0.033, 0.074, 1.11
No. of reflections	1669
No. of parameters	136
H-atom treatment	All H-atom parameters refined
$\Delta\rho_{\text{max}}, \Delta\rho_{\text{min}}$ (e Å ⁻³)	0.45, -0.25

Computer programs: APEX3 and SAINT (Bruker, 2018), SHELXT2014 (Sheldrick, 2015a), SHELXL2016 (Sheldrick, 2015b), olex2.refine (Bourhis *et al.*, 2015), OLEX2 (Dolomanov *et al.*, 2009), Mercury (Macrae *et al.*, 2020), WebMO (Schmidt & Polik, 2016), and publCIF (Westrip, 2010).

Refinement

Crystal data, data collection, and structure refinement details are listed in Table 2. The final structure refinement was carried out within the OLEX2 system via Hirshfeld atom refinement with nonspherical atomic form factors using NoSpherA2 (Kleemiss *et al.*, 2021; Midgley *et al.*, 2021) derived from electron density from DFT calculations using ORCA (B3LYP functional, def2-SVP basis set; Neese, 2022). All atoms were refined anisotropically.

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full crystallographic data

IUCrData (2023). **8**, x230647 [https://doi.org/10.1107/S2414314623006478]

5,6-Dihydro-1,4-dithiine-2,3-dicarboxylic anhydride

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5,6-Dihydro-1,4-dithiine-2,3-dicarboxylic anhydride

Crystal data

$C_6H_4O_3S_2$	$Z = 2$
$M_r = 188.23$	$F(000) = 192.603$
Triclinic, $P\bar{1}$	$D_x = 1.711 \text{ Mg m}^{-3}$
$a = 5.398 (1) \text{ \AA}$	Mo $K\alpha$ radiation, $\lambda = 0.71073 \text{ \AA}$
$b = 7.5537 (15) \text{ \AA}$	Cell parameters from 7641 reflections
$c = 9.2566 (18) \text{ \AA}$	$\theta = 2.8\text{--}27.4^\circ$
$\alpha = 89.273 (6)^\circ$	$\mu = 0.68 \text{ mm}^{-1}$
$\beta = 87.361 (6)^\circ$	$T = 295 \text{ K}$
$\gamma = 75.701 (5)^\circ$	Plate, yellow
$V = 365.36 (12) \text{ \AA}^3$	$0.42 \times 0.38 \times 0.17 \text{ mm}$

Data collection

Bruker D8 Quest Eco diffractometer	1669 independent reflections
φ and ω scans	1338 reflections with $I \geq 2\sigma(I)$
Absorption correction: multi-scan (SADABS; Bruker, 2016)	$R_{\text{int}} = 0.046$
$T_{\text{min}} = 0.648$, $T_{\text{max}} = 0.746$	$\theta_{\text{max}} = 27.6^\circ$, $\theta_{\text{min}} = 3.6^\circ$
16978 measured reflections	$h = -7 \rightarrow 7$
	$k = -9 \rightarrow 9$
	$l = -12 \rightarrow 12$

Refinement

Refinement on F^2	0 constraints
Least-squares matrix: full	Primary atom site location: dual
$R[F^2 > 2\sigma(F^2)] = 0.033$	All H-atom parameters refined
$wR(F^2) = 0.074$	$w = 1/[\sigma^2(F_o^2) + (0.0229P)^2 + 0.1706P]$
$S = 1.11$	where $P = (F_o^2 + 2F_c^2)/3$
1669 reflections	$(\Delta/\sigma)_{\text{max}} = 0.0002$
136 parameters	$\Delta\rho_{\text{max}} = 0.45 \text{ e \AA}^{-3}$
0 restraints	$\Delta\rho_{\text{min}} = -0.25 \text{ e \AA}^{-3}$

Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (\AA^2)

	x	y	z	$U_{\text{iso}}^*/U_{\text{eq}}$
S1	0.87227 (9)	0.35661 (7)	0.38382 (6)	0.04127 (16)
S2	0.45568 (10)	0.23942 (8)	0.13318 (6)	0.04824 (17)
C1	0.8444 (5)	0.1333 (3)	0.3315 (2)	0.0440 (5)
H1a	1.028 (5)	0.039 (4)	0.347 (3)	0.091 (10)
H1b	0.700 (5)	0.098 (3)	0.400 (3)	0.072 (8)
C2	0.7794 (4)	0.1195 (3)	0.1758 (2)	0.0440 (5)

H2a	0.793 (6)	-0.019 (4)	0.152 (3)	0.086 (9)
H2b	0.909 (5)	0.169 (4)	0.102 (3)	0.064 (8)
C3	0.6129 (3)	0.4890 (2)	0.3010 (2)	0.0338 (4)
C4	0.4505 (3)	0.4463 (2)	0.2093 (2)	0.0347 (4)
C5	0.5328 (4)	0.6869 (3)	0.3268 (2)	0.0457 (5)
C6	0.2545 (4)	0.6150 (3)	0.1802 (2)	0.0478 (5)
O1	0.6268 (4)	0.7808 (2)	0.3987 (2)	0.0682 (5)
O2	0.3162 (3)	0.75751 (18)	0.25156 (17)	0.0558 (4)
O3	0.0695 (3)	0.6399 (2)	0.11090 (19)	0.0695 (5)

Atomic displacement parameters (Å²)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
S1	0.0364 (3)	0.0389 (3)	0.0489 (3)	-0.0100 (2)	-0.0021 (2)	-0.0005 (2)
S2	0.0401 (3)	0.0441 (3)	0.0610 (4)	-0.0107 (2)	-0.0014 (2)	-0.0144 (3)
C1	0.0523 (14)	0.0263 (10)	0.0484 (13)	-0.0007 (10)	0.0016 (11)	0.0030 (9)
H1a	0.08 (2)	0.057 (19)	0.10 (2)	0.045 (17)	-0.031 (18)	0.019 (17)
H1b	0.09 (2)	0.033 (15)	0.10 (2)	-0.030 (15)	0.015 (18)	-0.009 (15)
C2	0.0464 (12)	0.0299 (11)	0.0496 (13)	0.0014 (9)	0.0061 (10)	-0.0076 (10)
H2a	0.13 (3)	0.038 (16)	0.09 (2)	-0.012 (17)	0.007 (18)	-0.021 (15)
H2b	0.053 (17)	0.076 (19)	0.060 (17)	-0.013 (15)	0.022 (13)	0.014 (15)
C3	0.0335 (9)	0.0236 (9)	0.0427 (10)	-0.0055 (7)	0.0074 (8)	-0.0008 (8)
C4	0.0306 (9)	0.0281 (9)	0.0415 (10)	-0.0011 (7)	0.0060 (8)	0.0003 (8)
C5	0.0551 (13)	0.0245 (10)	0.0556 (13)	-0.0096 (9)	0.0171 (10)	-0.0021 (9)
C6	0.0370 (11)	0.0442 (12)	0.0528 (12)	0.0054 (9)	0.0076 (10)	0.0118 (10)
O1	0.0867 (13)	0.0358 (9)	0.0862 (12)	-0.0262 (9)	0.0178 (10)	-0.0185 (9)
O2	0.0611 (10)	0.0270 (7)	0.0673 (10)	0.0084 (7)	0.0161 (8)	0.0070 (7)
O3	0.0467 (9)	0.0712 (12)	0.0784 (12)	0.0086 (8)	-0.0076 (9)	0.0218 (10)

Geometric parameters (Å, °)

S1—C1	1.805 (2)	C2—H2b	1.08 (2)
S1—C3	1.7136 (19)	C3—C4	1.345 (3)
S2—C2	1.817 (2)	C3—C5	1.469 (3)
S2—C4	1.7160 (19)	C4—C6	1.472 (3)
C1—H1a	1.08 (2)	O1—C5	1.193 (3)
C1—H1b	1.06 (2)	O2—C5	1.376 (3)
C1—C2	1.510 (3)	O2—C6	1.386 (3)
C2—H2a	1.06 (2)	O3—C6	1.186 (3)
C1—S1—C3	99.54 (10)	S1—C3—C4	131.57 (14)
C2—S2—C4	98.30 (10)	S1—C3—C5	120.60 (16)
S1—C1—H1a	107.2 (15)	C4—C3—C5	107.83 (17)
S1—C1—H1b	108.1 (12)	C3—C4—S2	129.27 (14)
H1a—C1—H1b	110 (2)	C6—C4—S2	123.28 (16)
S1—C1—C2	114.41 (15)	C3—C4—C6	107.44 (17)
C2—C1—H1a	107.8 (16)	O1—C5—C3	129.7 (2)
C2—C1—H1b	108.9 (15)	O2—C5—C3	108.36 (18)

C1—C2—S2	115.01 (15)	O1—C5—O2	121.98 (19)
S2—C2—H2a	105.1 (17)	O2—C6—C4	108.13 (18)
S2—C2—H2b	107.5 (13)	O3—C6—C4	130.7 (2)
C1—C2—H2a	108.8 (16)	O2—C6—O3	121.2 (2)
C1—C2—H2b	111.8 (14)	C5—O2—C6	108.14 (15)
H2a—C2—H2b	108 (2)		
S1—C1—C2—S2	-70.39 (17)	S2—C4—C6—O3	4.1 (2)
S1—C3—C4—S2	-3.9 (2)	C3—C4—C6—O2	3.05 (16)
S1—C3—C4—C6	176.69 (19)	C3—C4—C6—O3	-176.50 (17)
S1—C3—C5—O1	1.95 (19)	C3—C5—O2—C6	0.24 (18)
S1—C3—C5—O2	-177.86 (15)	C4—C6—O2—C5	-1.95 (18)
S2—C4—C3—C5	176.57 (18)	C5—O2—C6—O3	177.65 (17)
S2—C4—C6—O2	-176.39 (17)		
