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5-Sulfanylidene-2*H*,5*H*-1,3-dithiolo-[4,5-*d*][1,3]dithiol-2-one

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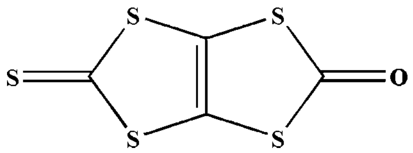
Key indicators: single-crystal X-ray study; *T* = 294 K; mean σ(C–C) = 0.009 Å; *R* factor = 0.044; *wR* factor = 0.130; data-to-parameter ratio = 18.3.

The title molecule, C_4OS_5, is essentially planar, with an r.m.s. deviation of 0.032 (3) Å. All the C—S single bonds are shorter than the standard Csp^3—S single-bond length, showing the π-conjugated nature of the molecule. In the crystal, molecules lie parallel to one another and pack in columns along the *a* axis. Short intermolecular S⋯S contacts [3.314 (3), 3.482 (2) and 3.501 (2) Å] are observed between the columns. The angle between the two molecular dipole moments in the unit cell is 39.3 (1)° and the macro-polarization vector is along the [1 0 − 1.41] direction. As a result of the high polarization and π-conjugation of the structure, the crystalline powder exhibits a second harmonic generating intensity, which is as strong as that of the urea standard powder crystals, when irradiated by a 1053 nm laser beam. The diffraction space of the crystal showed a nonmerohedral twinning.

Related literature

For details of *GAUSSIAN03* software, see: Frisch *et al.* (2003). For the synthesis, see: Schumaker & Engler (1977); Wang *et al.* (1998).



Experimental

Crystal data

C_4OS_5
M_r = 224.34
Monoclinic, *Pn*
a = 3.9638 (2) Å
b = 11.0211 (8) Å
c = 8.7110 (7) Å
β = 101.344 (5)°
V = 373.11 (4) Å^3
Z = 2
Mo *Kα* radiation
μ = 1.47 mm^{-1}
T = 294 K
0.27 × 0.07 × 0.05 mm

Data collection

Bruker APEXII CCD diffractometer
Absorption correction: multi-scan (*TWINABS*; Bruker, 2005) T_{min} = 0.697, T_{max} = 0.928
8524 measured reflections
1683 independent reflections
1487 reflections with $I > 2\sigma(I)$
R_{int} = 0.039

Refinement

$R[F^2 > 2\sigma(F^2)]$ = 0.044
$wR(F^2)$ = 0.130
S = 1.12
1683 reflections
92 parameters
2 restraints
$\Delta\rho_{max}$ = 0.41 e Å^{-3}
$\Delta\rho_{min}$ = −0.45 e Å^{-3}
Absolute structure: Flack (1983), 815 Friedel pairs
Flack parameter: 0.1 (3)

Data collection: *APEX2* (Bruker, 2005); cell refinement: *SAINT* (Bruker, 2005); data reduction: *SAINT*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 2008); program(s) used to refine structure: *SHELXL97* (Sheldrick, 2008); molecular graphics: *SHELXTL* (Sheldrick, 2008); software used to prepare material for publication: *SHELXTL*.

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Supplementary data and figures for this paper are available from the IUCr electronic archives (Reference: IS5027).

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supplementary materials

Acta Cryst. (2012). E**68**, o721   [doi:10.1107/S1600536812005703]

5-Sulfanylidene-2*H*,5*H*-1,3-dithiolo[4,5-*d*][1,3]dithiol-2-one

Hua-Wen Wen, Li-Xia Fan, Li Liu, Ao Li and Qi Fang

Comment

Sulfur-rich compounds are well known as electronic donors in the field of organic molecular conductors, while their non-linear optical (NLO) properties are seldom reported. The synthesis of the title sulfur-rich compounds was reported by Schumaker and Engler (1977). Recently, we have re-synthesized the title compound by a new synthetic route and determined its X-ray structure.

The molecule adopts a planar conformation. All the C—S bond lengths are shorter than the length of C(sp^3)—S single bond, showing the π-conjugated nature of the molecule. The molecules are parallel packed into columns along the *a* axis with a uniform spacing being 3.57 (1) Å. In addition to the above longitudinal π–π interactions, there are plenty of transverse short intermolecular S···S contacts. For example, S1···S2 [1/2 + *x*, 2 - *y*, -1/2 + *z*], S1···S3 [*x*, *y*, -1 + *z*], and S4···S5 [1/2 + *x*, 1 - *y*, -1/2 + *z*] distances are 3.314 (3), 3.482 (2) and 3.501 (2) Å, respectively.

The polar molecules crystallized into polar *Pn* space group. The angle [39.3 (1)°] between the two molecular dipole moments in the unit cell is not large, meaning that the crystal is well auto-polarized. The projection of both the molecular moments on the (010) plane is along the [1 0 -1.41] direction, which is also the direction of the macro polarization vector.

By the way, the molecular dipole moment has been calculated to be 0.8862 Bebye by using the Gaussian-03 programs (Frisch *et al.*, 2003), by the DFT method at the B3LYP/6–311(*d*) level. Meantime, the theoretical optimization for the molecular conformation by using the same Gaussian-03 programs indicates that the "free" molecule indeed adopts a perfect planar conformation with a strict C_{2v} symmetry.

The highly polar structure prompted us to carry out a frequency doubling experiment. When irradiated by the 1053 nm of laser pulses, the powder sample of the title crystal can emit 526.5 nm of green light, which is as strong as that of the urea powder crystals (as reference) and therefore has a remarkable 2-nd NLO effect.

Experimental

We firstly synthesized bis(tetrabutylammonium)bis(1,3-dithiole-2-thione-4,5-dithiol) zincate precursor by the method reported by Wang *et al.* (1998). For the synthesis of the title compound, the above zincate precursor (2.3 g, 2.5 mmol) was dissolved in THF (50 ml). And then the triphosgen (1.40 g, 5.0 mmol) at 195 K was added in presence of N_2. The solution was stirred overnight. An orange precipitate was obtained and dried *in vacuo*. And the final compound was purified by column chromatography using carbon disulfide as eluent, giving 0.46 g (86.7% yield) orange crystalline product. MS (EI): m/*z* 224.

Refinement

There is no hydrogen atom in this structure. The reciprocal space showed a non-merohedral twin for the crystal used. All diffraction spots, except those of (0*kl*) kind, appeared in pairs. The diffraction spots on the (0*kl*) layer were supposed to be overlapped in pairs. By using the editing tools in RLATT, two reciprocal lattices corresponding to the two domains have been successfully separated and two P4P files been produced separately. After merging two P4P files into a new P4P file, data integration and absorption correction have been carried out. All the programs used are in the *APEX2* Software Suite (Bruker, 2005). The domain scale factor has been refined to be 0.293 for the second domain.

Computing details

Data collection: *APEX2* (Bruker, 2005); cell refinement: *SAINT* (Bruker, 2005); data reduction: *SAINT* (Bruker, 2005); program(s) used to solve structure: *SHELXS97* (Sheldrick, 2008); program(s) used to refine structure: *SHELXL97* (Sheldrick, 2008); molecular graphics: *SHELXTL* (Sheldrick, 2008); software used to prepare material for publication: *SHELXTL* (Sheldrick, 2008).

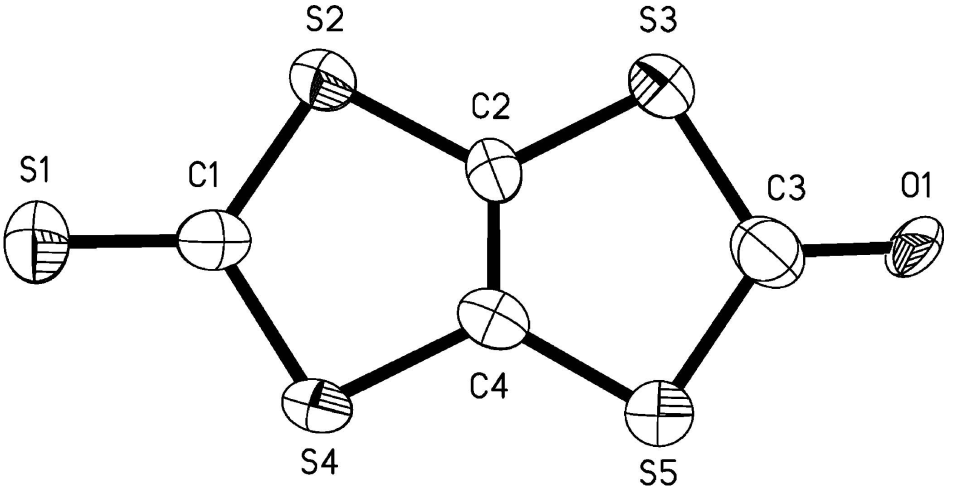

Figure 1

Molecular structure of the title compound. Displacement ellipsoids are drawn at 50% probability level.

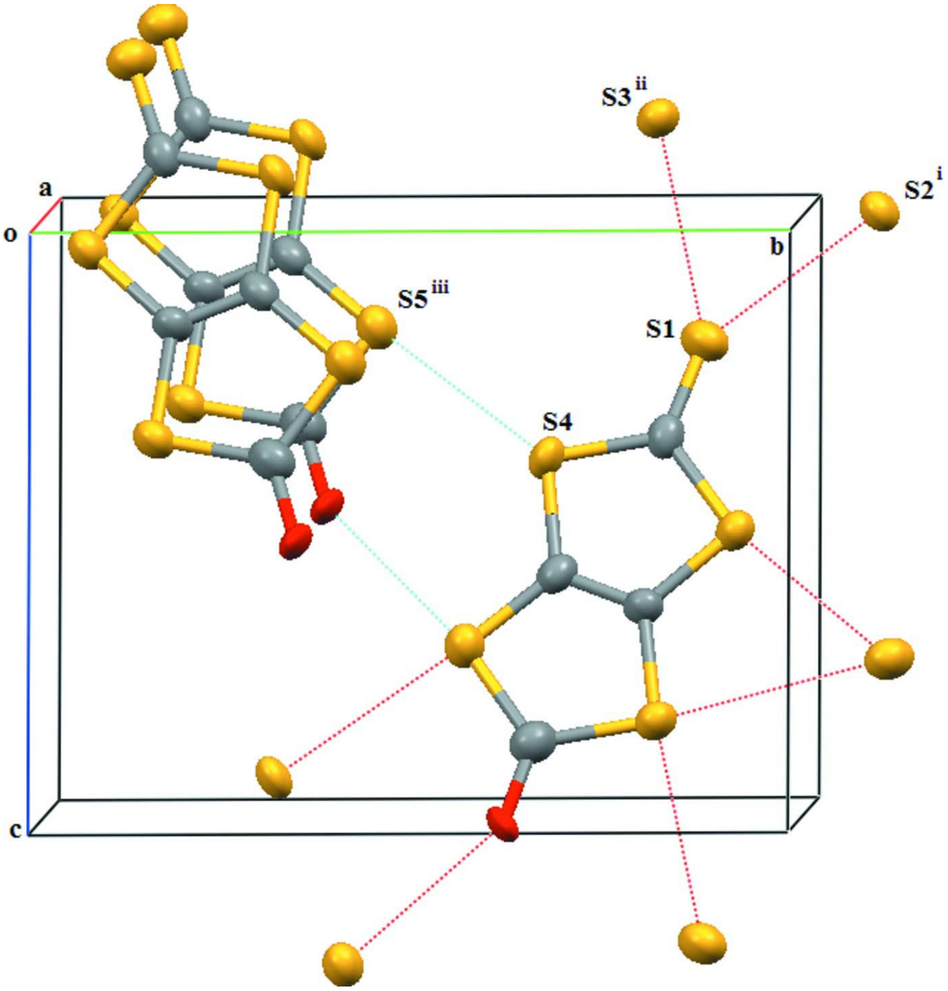

Figure 2

The packing pattern of the title molecules in crystal viewed down the *a*- axis, showing S···S and other intermolecular short contacts. [Symmetry codes: (i) 1/2 + *x*,-*y* + 2,-1/2 + *z*; (ii) *x*, *y*, -1 + *z*; (iii) 1/2 + *x* 1 - *y* -1/2 + *z*].

5-Sulfanylidene-2*H*,5*H*-1,3-dithiolo[4,5-*d*][1,3]dithiol-2-one

Crystal data

C_4OS_5	$F(000) = 224$
$M_r = 224.34$	$D_x = 1.997$ Mg m^{-3}
Monoclinic, *Pn*	Mo $K\alpha$ radiation, $\lambda = 0.71073$ Å
Hall symbol: P -2yac	Cell parameters from 1431 reflections
$a = 3.9638$ (2) Å	$\theta = 3.0$–26.0°
$b = 11.0211$ (8) Å	$\mu = 1.47$ mm^{-1}
$c = 8.7110$ (7) Å	$T = 294$ K
$\beta = 101.344$ (5)°	Bar, orange
$V = 373.11$ (4) Å^3	0.27 × 0.07 × 0.05 mm
$Z = 2$	

Data collection

Bruker APEXII CCD diffractometer
Radiation source: fine-focus sealed tube
Graphite monochromator
Detector resolution: 8.3 pixels mm^{-1}
ω scans
Absorption correction: multi-scan (*TWINABS*; Bruker, 2005)
$T_{min} = 0.697$, $T_{max} = 0.928$
8524 measured reflections
1683 independent reflections
1487 reflections with $I > 2\sigma(I)$
$R_{int} = 0.039$
$\theta_{max} = 27.5°$, $\theta_{min} = 1.9°$
$h = -5 \rightarrow 5$
$k = -14 \rightarrow 14$
$l = -11 \rightarrow 11$

Refinement

Refinement on F^2
Least-squares matrix: full
$R[F^2 > 2\sigma(F^2)] = 0.044$
$wR(F^2) = 0.130$
$S = 1.12$
1683 reflections
92 parameters
2 restraints
Primary atom site location: structure-invariant direct methods
Secondary atom site location: difference Fourier map
$w = 1/[\sigma^2(F_o^2) + (0.0831P)^2 + 0.0664P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} < 0.001$
$\Delta\rho_{max} = 0.41$ e Å^{-3}
$\Delta\rho_{min} = -0.45$ e Å^{-3}
Absolute structure: Flack (1983), 815 Friedel pairs
Flack parameter: 0.1 (3)

Special details

Experimental. The twin operator is an 180° rotation about the c* axis and the twin law can be recognized as -1 0 0, 0 - 1 0, 0.873 0 1. The frequency doubling experiment indicates that it is impossible for the crystal to adopt the centrosymmetric $P2_1/c$ space group.

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 (Å^2)

	x	y	z	U_{iso}*/U_{eq}
S1	0.5018 (5)	0.86748 (19)	0.2126 (2)	0.0551 (5)
S2	0.3162 (4)	0.91619 (15)	0.51687 (18)	0.0415 (4)
S3	0.1270 (5)	0.82054 (14)	0.8209 (2)	0.0451 (4)
S4	0.3021 (4)	0.66835 (13)	0.39376 (17)	0.0427 (4)
S5	0.1178 (5)	0.56886 (16)	0.6947 (2)	0.0471 (4)
O1	−0.0459 (13)	0.6265 (3)	0.9824 (4)	0.0394 (10)
C1	0.3780 (16)	0.8219 (6)	0.3637 (8)	0.0373 (14)
C2	0.216 (2)	0.8000 (6)	0.6361 (8)	0.0372 (13)
C3	0.055 (2)	0.6625 (7)	0.8518 (8)	0.0487 (18)
C4	0.211 (2)	0.6863 (6)	0.5810 (7)	0.0386 (14)

Atomic displacement parameters (Å^2)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
S1	0.0732 (12)	0.0538 (10)	0.0417 (8)	−0.0058 (10)	0.0194 (8)	0.0051 (9)
S2	0.0544 (9)	0.0344 (7)	0.0386 (7)	−0.0034 (7)	0.0161 (7)	−0.0067 (6)
S3	0.0617 (10)	0.0400 (9)	0.0371 (7)	0.0003 (8)	0.0186 (8)	−0.0060 (7)
S4	0.0604 (10)	0.0291 (7)	0.0427 (8)	−0.0019 (7)	0.0205 (8)	−0.0101 (7)
S5	0.0614 (11)	0.0367 (8)	0.0478 (8)	−0.0023 (8)	0.0222 (8)	−0.0025 (7)
O1	0.066 (3)	0.0233 (18)	0.031 (2)	−0.004 (2)	0.015 (2)	0.0100 (16)
C1	0.034 (3)	0.032 (3)	0.046 (3)	0.000 (2)	0.009 (3)	−0.005 (2)
C2	0.046 (3)	0.038 (3)	0.032 (3)	−0.003 (3)	0.017 (3)	−0.002 (2)
C3	0.055 (4)	0.050 (4)	0.043 (4)	0.005 (3)	0.015 (3)	−0.006 (3)
C4	0.043 (3)	0.037 (3)	0.036 (3)	0.001 (3)	0.007 (3)	−0.009 (2)

Geometric parameters (Å, º)

S1—C1	1.575 (7)	S4—C4	1.750 (6)
S2—C1	1.746 (6)	S5—C4	1.713 (7)
S2—C2	1.743 (6)	S5—C3	1.770 (7)
S3—C2	1.730 (7)	O1—C3	1.338 (8)
S3—C3	1.794 (8)	C2—C4	1.340 (7)
S4—C1	1.747 (7)		
C1—S2—C2	95.8 (3)	C4—C2—S2	117.6 (4)
C2—S3—C3	94.6 (3)	S3—C2—S2	124.8 (4)
C1—S4—C4	95.9 (3)	O1—C3—S5	126.6 (5)
C4—S5—C3	94.9 (3)	O1—C3—S3	119.9 (5)
S1—C1—S2	124.2 (4)	S5—C3—S3	113.5 (4)
S1—C1—S4	121.7 (4)	C2—C4—S5	119.3 (4)
S2—C1—S4	114.1 (4)	C2—C4—S4	116.6 (4)
C4—C2—S3	117.6 (4)	S5—C4—S4	124.1 (4)