

Ethyl 3-(6-phenyl-4λ⁴-1,2-dithiolo-[1,5-*b*][1,2,4]dithiazol-2-yl)propanoate

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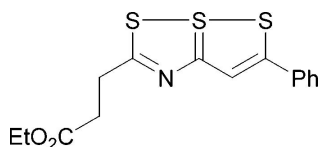
Received 19 November 2007; accepted 26 November 2007

Key indicators: single-crystal X-ray study; $T = 168$ K; mean $\sigma(\text{C}—\text{C}) = 0.003$ Å; R factor = 0.028; wR factor = 0.081; data-to-parameter ratio = 16.6.

The title compound, $\text{C}_{15}\text{H}_{15}\text{NO}_2\text{S}_3$, exists in a bicyclic form, with resonance contributions from two monocyclic forms, each without a second S—S bond. The trithiapentalene heterocyclic ring system is planar, with a mean deviation of 0.014 (2) Å from the mean plane, and is inclined to the plane of the attached phenyl ring at an angle of 17.24 (7)°.

Related literature

For related compounds, see: Rašović *et al.* (2007); Yokoyama *et al.* (1985). For related literature, see: Lozac'h (1984); Marković *et al.* (2004); Terem (1996); Allen (2002).



Experimental

Crystal data

$\text{C}_{15}\text{H}_{15}\text{NO}_2\text{S}_3$
 $M_r = 337.46$

Monoclinic, $P2_1/c$
 $a = 4.5830$ (8) Å

$b = 15.550$ (3) Å
 $c = 21.858$ (4) Å
 $\beta = 91.579$ (2)°
 $V = 1557.1$ (5) Å³
 $Z = 4$

Mo $K\alpha$ radiation
 $\mu = 0.48$ mm⁻¹
 $T = 168$ (2) K
 $0.56 \times 0.15 \times 0.14$ mm

Data collection

Bruker SMART CCD area-detector diffractometer
Absorption correction: multi-scan (*SADABS*; Sheldrick, 2002)
 $T_{\min} = 0.776$, $T_{\max} = 0.936$

18585 measured reflections
3154 independent reflections
2496 reflections with $I > 2\sigma(I)$
 $R_{\text{int}} = 0.024$

Refinement

$R[F^2 > 2\sigma(F^2)] = 0.028$
 $wR(F^2) = 0.081$
 $S = 1.04$
3154 reflections

190 parameters
H-atom parameters constrained
 $\Delta\rho_{\text{max}} = 0.22$ e Å⁻³
 $\Delta\rho_{\text{min}} = -0.18$ e Å⁻³

Data collection: *SMART* (Bruker, 1997); cell refinement: *SAINT* (Bruker, 1997); data reduction: *SAINT*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 1990); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *SHELXTL* (Bruker, 1997); software used to prepare material for publication: *SHELXTL*.

PJS thanks the Royal Society of New Zealand for the award of a James Cook Research Fellowship.

Supplementary data and figures for this paper are available from the IUCr electronic archives (Reference: GA2023).

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supporting information

Acta Cryst. (2008). E64, o179 [https://doi.org/10.1107/S1600536807063209]

Ethyl 3-(6-phenyl-4 λ^4 -1,2-dithiolo[1,5-*b*][1,2,4]dithiazol-2-yl)propanoate

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S1. Comment

The title compound (1) was prepared in the course of a study of the thionation of thiazolidine enaminones (Marković *et al.*, 2004). It could potentially exist in any of three forms (1 A - 1 C) as shown in Scheme 1. The X-ray structure reveals that it exists in the bicyclic form (1 A). However, comparison of the S—S bond lengths (Table 1) with the average value (2.07 Å) for the 31 1,2-dithiolanes and the 11 3-imino-3*H*-1,2-dithioles (as in 1B) in the Cambridge Structural Database (Allen, 2002) along with consideration of the S—C bond lengths suggests that resonance forms (1B) and (1 C) make some contribution to the overall structure. These results are consistent with two structurally related compounds that have been published previously (Rašović *et al.*, 2007; Yokoyama *et al.*, 1985) and with the known resonance behaviour of 1,6,6a-trithiapentalenes (Lozac'h, 1984; Terem, 1996; Rašović *et al.*, 2007).

The whole molecule is remarkably close to being planar with both substituents lying in the same plane as the trithiaazapentalene ring system. This bicyclic system is planar [mean deviation = 0.014 (3) Å] and the attached phenyl ring is inclined to this plane at an angle of 17.4 (1) °. Inspection of the packing shows that there are short intermolecular contacts [3.491 (1) Å] between sulfur atoms of molecules related by a crystallographic centre of inversion, as well as other weak C—H $\cdots$ O and C—H $\cdots$ π interactions.

S2. Experimental

The title compound was prepared as previously described (Marković *et al.*, 2004).

S3. Refinement

All H atoms were introduced in calculated positions as riding atoms, with $U_{\text{iso}}(\text{H}) = 1.5U_{\text{eq}}(\text{C})$ for the methyl group and $U_{\text{iso}}(\text{H}) = 1.2U_{\text{eq}}(\text{C})$ for other carbons.

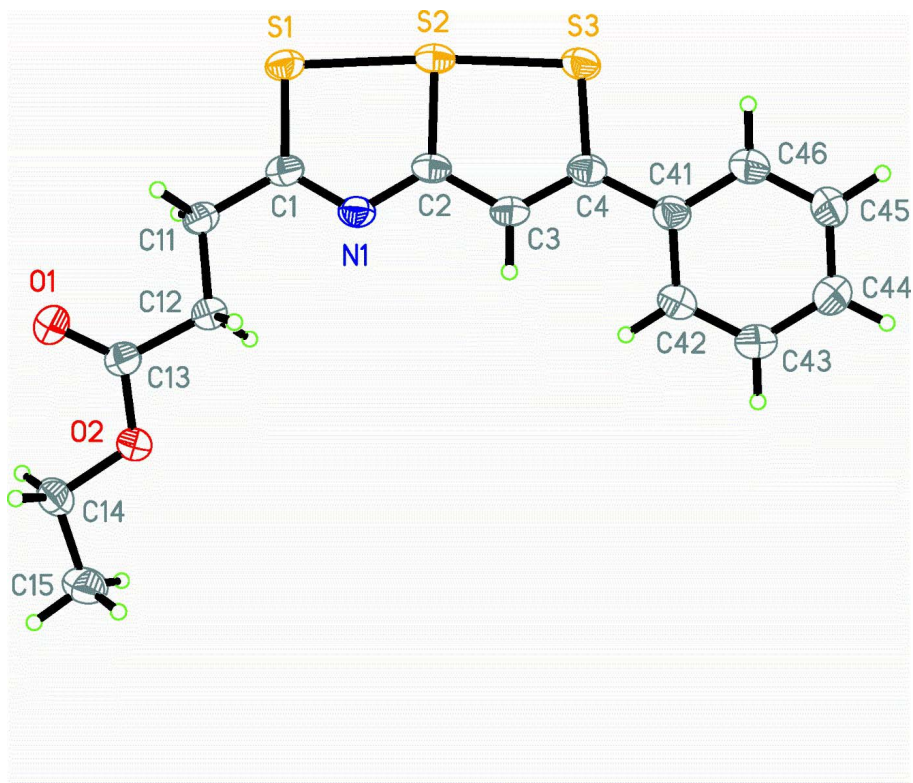


Figure 1

The molecular structure of (1), showing displacement ellipsoids at the 50% probability level.

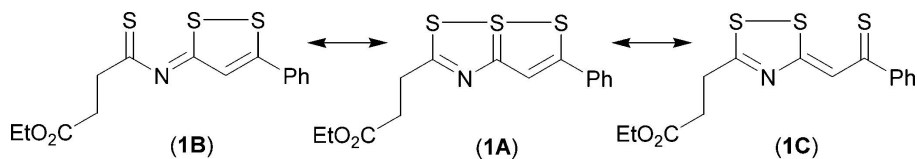


Figure 2

Forms of the title compound.

Ethyl 3-(6-phenyl-4 λ^4 -1,2-dithiolo[1,5-*b*][1,2,4]dithiazol-2-yl)propanoate

Crystal data

$C_{15}H_{15}NO_2S_3$

$M_r = 337.46$

Monoclinic, $P2_1/c$

Hall symbol: -P 2ybc

$a = 4.5830$ (8) Å

$b = 15.550$ (3) Å

$c = 21.858$ (4) Å

$\beta = 91.579$ (2)°

$V = 1557.1$ (5) Å³

$Z = 4$

$F(000) = 704$

$D_x = 1.440$ Mg m⁻³

Mo $K\alpha$ radiation, $\lambda = 0.71073$ Å

Cell parameters from 4889 reflections

$\theta = 2.3$ – 26.3 °

$\mu = 0.48$ mm⁻¹

$T = 168$ K

Block, red

$0.56 \times 0.15 \times 0.14$ mm

Data collection

Bruker SMART CCD area-detector
diffractometer
Radiation source: fine-focus sealed tube
Graphite monochromator
 ϕ and ω scans
Absorption correction: multi-scan
(*SADABS*; Sheldrick, 2002)
 $T_{\min} = 0.776$, $T_{\max} = 0.936$

18585 measured reflections
3154 independent reflections
2496 reflections with $I > 2\sigma(I)$
 $R_{\text{int}} = 0.024$
 $\theta_{\max} = 26.4^\circ$, $\theta_{\min} = 1.6^\circ$
 $h = -5 \rightarrow 3$
 $k = -19 \rightarrow 19$
 $l = -27 \rightarrow 27$

Refinement

Refinement on F^2
Least-squares matrix: full
 $R[F^2 > 2\sigma(F^2)] = 0.028$
 $wR(F^2) = 0.081$
 $S = 1.04$
3154 reflections
190 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
 $w = 1/[\sigma^2(F_o^2) + (0.040P)^2 + 0.6P]$
where $P = (F_o^2 + 2F_c^2)/3$
 $(\Delta/\sigma)_{\max} = 0.001$
 $\Delta\rho_{\max} = 0.22 \text{ e } \text{\AA}^{-3}$
 $\Delta\rho_{\min} = -0.18 \text{ e } \text{\AA}^{-3}$

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 ($\text{\AA}^2$)

	<i>x</i>	<i>y</i>	<i>z</i>	$U_{\text{iso}}^*/U_{\text{eq}}$
S1	0.14659 (10)	0.93968 (3)	−0.06460 (2)	0.03515 (13)
S2	0.45583 (10)	0.88164 (3)	0.01317 (2)	0.03275 (13)
S3	0.75628 (10)	0.81544 (3)	0.08417 (2)	0.03547 (13)
N1	0.1422 (3)	0.77027 (9)	−0.05925 (6)	0.0310 (3)
O1	−0.6255 (3)	0.78860 (8)	−0.22517 (6)	0.0469 (4)
O2	−0.4823 (3)	0.65138 (8)	−0.22943 (6)	0.0374 (3)
C1	0.0397 (4)	0.83948 (10)	−0.08685 (8)	0.0301 (4)
C2	0.3385 (4)	0.77998 (10)	−0.01248 (8)	0.0299 (4)
C3	0.4558 (4)	0.70707 (11)	0.01639 (8)	0.0323 (4)
H3A	0.3916	0.6517	0.0034	0.039*
C4	0.6610 (4)	0.71354 (11)	0.06291 (8)	0.0310 (4)
C11	−0.1756 (4)	0.83021 (10)	−0.13943 (8)	0.0321 (4)
H11A	−0.0930	0.8571	−0.1762	0.039*
H11B	−0.3559	0.8619	−0.1297	0.039*
C12	−0.2545 (4)	0.73746 (10)	−0.15426 (8)	0.0320 (4)
H12A	−0.0756	0.7057	−0.1648	0.038*

H12B	−0.3361	0.7100	−0.1176	0.038*
C13	−0.4727 (4)	0.73123 (11)	−0.20648 (8)	0.0310 (4)
C14	−0.6901 (4)	0.63594 (12)	−0.27984 (9)	0.0386 (4)
H14A	−0.6579	0.6772	−0.3135	0.046*
H14B	−0.8924	0.6429	−0.2659	0.046*
C15	−0.6416 (5)	0.54575 (13)	−0.30130 (10)	0.0502 (5)
H15A	−0.7748	0.5333	−0.3360	0.075*
H15B	−0.6788	0.5056	−0.2679	0.075*
H15C	−0.4394	0.5394	−0.3141	0.075*
C41	0.8042 (4)	0.63919 (11)	0.09330 (8)	0.0336 (4)
C42	0.7975 (5)	0.55824 (13)	0.06601 (10)	0.0565 (6)
H42A	0.6956	0.5504	0.0280	0.068*
C43	0.9372 (6)	0.48925 (14)	0.09362 (12)	0.0697 (8)
H43A	0.9286	0.4343	0.0747	0.084*
C44	1.0889 (5)	0.49931 (13)	0.14834 (11)	0.0559 (6)
H44A	1.1855	0.4517	0.1672	0.067*
C45	1.0989 (5)	0.57867 (13)	0.17530 (10)	0.0531 (6)
H45A	1.2040	0.5862	0.2130	0.064*
C46	0.9578 (5)	0.64779 (12)	0.14830 (9)	0.0451 (5)
H46A	0.9662	0.7023	0.1678	0.054*

Atomic displacement parameters (Å²)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
S1	0.0389 (3)	0.0220 (2)	0.0444 (3)	−0.00255 (17)	−0.0017 (2)	−0.00393 (17)
S2	0.0358 (3)	0.0245 (2)	0.0379 (2)	−0.00752 (17)	0.00185 (19)	−0.00651 (17)
S3	0.0410 (3)	0.0291 (2)	0.0361 (2)	−0.00723 (18)	−0.0037 (2)	−0.00541 (18)
N1	0.0316 (8)	0.0253 (7)	0.0359 (8)	−0.0035 (6)	−0.0013 (6)	−0.0045 (6)
O1	0.0529 (9)	0.0353 (7)	0.0514 (8)	0.0115 (6)	−0.0168 (7)	−0.0040 (6)
O2	0.0415 (7)	0.0292 (6)	0.0406 (7)	0.0029 (5)	−0.0119 (6)	−0.0066 (5)
C1	0.0290 (9)	0.0251 (8)	0.0364 (9)	−0.0006 (7)	0.0045 (7)	−0.0045 (7)
C2	0.0301 (9)	0.0251 (8)	0.0347 (9)	−0.0071 (7)	0.0029 (7)	−0.0053 (7)
C3	0.0362 (10)	0.0234 (8)	0.0372 (9)	−0.0059 (7)	−0.0003 (8)	−0.0043 (7)
C4	0.0336 (9)	0.0281 (8)	0.0315 (9)	−0.0060 (7)	0.0049 (7)	−0.0026 (7)
C11	0.0335 (10)	0.0243 (8)	0.0384 (9)	0.0020 (7)	−0.0004 (7)	−0.0025 (7)
C12	0.0349 (10)	0.0257 (8)	0.0351 (9)	0.0015 (7)	−0.0026 (7)	−0.0022 (7)
C13	0.0316 (9)	0.0278 (9)	0.0336 (9)	0.0006 (7)	0.0022 (7)	−0.0012 (7)
C14	0.0375 (11)	0.0418 (10)	0.0359 (10)	0.0002 (8)	−0.0071 (8)	−0.0068 (8)
C15	0.0638 (14)	0.0408 (11)	0.0453 (11)	−0.0062 (10)	−0.0109 (10)	−0.0088 (9)
C41	0.0365 (10)	0.0306 (9)	0.0337 (9)	−0.0070 (7)	−0.0014 (8)	−0.0004 (7)
C42	0.0761 (17)	0.0369 (11)	0.0547 (13)	0.0049 (10)	−0.0300 (12)	−0.0110 (9)
C43	0.103 (2)	0.0333 (11)	0.0707 (15)	0.0070 (12)	−0.0400 (15)	−0.0110 (11)
C44	0.0726 (16)	0.0341 (10)	0.0596 (13)	0.0006 (10)	−0.0232 (12)	0.0036 (9)
C45	0.0711 (15)	0.0404 (11)	0.0464 (12)	−0.0049 (10)	−0.0244 (11)	0.0019 (9)
C46	0.0589 (13)	0.0323 (10)	0.0433 (11)	−0.0069 (9)	−0.0117 (10)	−0.0036 (8)

Geometric parameters (Å, °)

S1—C1	1.7003 (16)	C12—H12A	0.9900
S1—S2	2.3623 (7)	C12—H12B	0.9900
S2—C2	1.7567 (16)	C14—C15	1.497 (3)
S2—S3	2.2905 (7)	C14—H14A	0.9900
S3—C4	1.7047 (17)	C14—H14B	0.9900
N1—C1	1.314 (2)	C15—H15A	0.9800
N1—C2	1.351 (2)	C15—H15B	0.9800
O1—C13	1.199 (2)	C15—H15C	0.9800
O2—C13	1.339 (2)	C41—C46	1.383 (3)
O2—C14	1.456 (2)	C41—C42	1.393 (3)
C1—C11	1.501 (2)	C42—C43	1.380 (3)
C2—C3	1.398 (2)	C42—H42A	0.9500
C3—C4	1.370 (2)	C43—C44	1.376 (3)
C3—H3A	0.9500	C43—H43A	0.9500
C4—C41	1.478 (3)	C44—C45	1.368 (3)
C11—C12	1.520 (2)	C44—H44A	0.9500
C11—H11A	0.9900	C45—C46	1.379 (3)
C11—H11B	0.9900	C45—H45A	0.9500
C12—C13	1.500 (2)	C46—H46A	0.9500
C1—S1—S2	91.04 (6)	O1—C13—C12	125.60 (16)
C2—S2—S3	89.13 (6)	O2—C13—C12	111.04 (14)
C2—S2—S1	86.66 (6)	O2—C14—C15	106.97 (15)
S3—S2—S1	175.44 (2)	O2—C14—H14A	110.3
C4—S3—S2	95.07 (6)	C15—C14—H14A	110.3
C1—N1—C2	118.55 (14)	O2—C14—H14B	110.3
C13—O2—C14	116.74 (14)	C15—C14—H14B	110.3
N1—C1—C11	119.47 (14)	H14A—C14—H14B	108.6
N1—C1—S1	121.50 (13)	C14—C15—H15A	109.5
C11—C1—S1	119.03 (12)	C14—C15—H15B	109.5
N1—C2—C3	119.38 (14)	H15A—C15—H15B	109.5
N1—C2—S2	122.25 (13)	C14—C15—H15C	109.5
C3—C2—S2	118.38 (13)	H15A—C15—H15C	109.5
C4—C3—C2	121.55 (15)	H15B—C15—H15C	109.5
C4—C3—H3A	119.2	C46—C41—C42	117.67 (18)
C2—C3—H3A	119.2	C46—C41—C4	121.61 (16)
C3—C4—C41	124.30 (16)	C42—C41—C4	120.68 (16)
C3—C4—S3	115.86 (13)	C43—C42—C41	120.72 (19)
C41—C4—S3	119.82 (13)	C43—C42—H42A	119.6
C1—C11—C12	113.71 (14)	C41—C42—H42A	119.6
C1—C11—H11A	108.8	C44—C43—C42	120.6 (2)
C12—C11—H11A	108.8	C44—C43—H43A	119.7
C1—C11—H11B	108.8	C42—C43—H43A	119.7
C12—C11—H11B	108.8	C45—C44—C43	119.2 (2)
H11A—C11—H11B	107.7	C45—C44—H44A	120.4
C13—C12—C11	111.93 (14)	C43—C44—H44A	120.4

C13—C12—H12A	109.2	C44—C45—C46	120.60 (19)
C11—C12—H12A	109.2	C44—C45—H45A	119.7
C13—C12—H12B	109.2	C46—C45—H45A	119.7
C11—C12—H12B	109.2	C45—C46—C41	121.23 (18)
H12A—C12—H12B	107.9	C45—C46—H46A	119.4
O1—C13—O2	123.33 (16)	C41—C46—H46A	119.4
