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## Structure Reports

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## 3,3-Bis(methylsulfanyl)-1-(4-nitrophenyl)-prop-2-en-1-one

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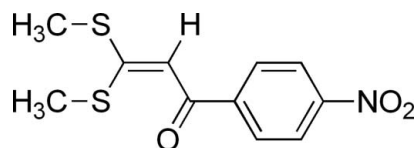
Received 16 March 2013; accepted 27 May 2013

Key indicators: single-crystal X-ray study;  $T = 173$  K; mean  $\sigma(\text{C}-\text{C}) = 0.004$  Å;  $R$  factor = 0.055;  $wR$  factor = 0.115; data-to-parameter ratio = 17.4.

In the title compound,  $\text{C}_{11}\text{H}_{11}\text{NO}_3\text{S}_2$ , the  $\text{S}-\text{C}_{\text{sp}^2}$  bonds are shorter [1.746 (3) and 1.750 (2) Å] than the  $\text{S}-\text{CH}_3$  bonds [1.794 (3) and 1.806 (3) Å], which we attribute to  $d-\pi$  interactions between the S atoms and the  $\text{C}=\text{C}$  bond. The 1,1-bis(methylsulfanyl)-3-oxopropylene fragment and the 4-nitrophenyl group are both almost planar, with the largest deviations from their mean planes being 0.053 (1) and 0.017 (2) Å, respectively. The dihedral angle between the two planes is 35.07 (7)°. Molecules in the crystal are linked into a three-dimensional network by  $\text{C}-\text{H}\cdots\text{S}$  and  $\text{C}-\text{H}\cdots\text{O}$  hydrogen bonds.

## Related literature

For the synthesis of the title compound, see: Huang & Liu (1989). For applications, see: Barun *et al.* (2000); Kuettel *et al.* (2007). For general background on ketene animals, see: Huang & Wang (1994).



## Experimental

## Crystal data

 $\text{C}_{11}\text{H}_{11}\text{NO}_3\text{S}_2$  $M_r = 269.33$ 

Triclinic,  $P\bar{1}$   
 $a = 7.917$  (2) Å  
 $b = 8.739$  (2) Å  
 $c = 9.574$  (3) Å  
 $\alpha = 70.415$  (13)°  
 $\beta = 81.985$  (14)°  
 $\gamma = 73.283$  (13)°

$V = 597.0$  (3) Å<sup>3</sup>  
 $Z = 2$   
Mo  $K\alpha$  radiation  
 $\mu = 0.44$  mm<sup>-1</sup>  
 $T = 173$  K  
 $0.27 \times 0.24 \times 0.05$  mm

## Data collection

Rigaku Saturn724+ CCD diffractometer  
Absorption correction: multi-scan (*CrystalClear*; Rigaku, 2007)  
 $T_{\text{min}} = 0.581$ ,  $T_{\text{max}} = 1.000$

7843 measured reflections  
2719 independent reflections  
2394 reflections with  $I > 2\sigma(I)$   
 $R_{\text{int}} = 0.053$

## Refinement

$R[F^2 > 2\sigma(F^2)] = 0.055$   
 $wR(F^2) = 0.115$   
 $S = 1.15$   
2719 reflections

156 parameters  
H-atom parameters constrained  
 $\Delta\rho_{\text{max}} = 0.29$  e Å<sup>-3</sup>  
 $\Delta\rho_{\text{min}} = -0.23$  e Å<sup>-3</sup>

Table 1

Hydrogen-bond geometry (Å, °).

$D-\text{H}\cdots A$	$D-\text{H}$	$\text{H}\cdots A$	$D\cdots A$	$D-\text{H}\cdots A$
$\text{C11}-\text{H11}\cdots\text{S2}^{\text{i}}$	0.95	2.93	3.614 (3)	130
$\text{C8}-\text{H8}\cdots\text{O3}^{\text{ii}}$	0.95	2.63	3.204 (3)	119
$\text{C2}-\text{H2B}\cdots\text{O3}^{\text{iii}}$	0.98	2.68	3.297 (4)	122
$\text{C10}-\text{H10}\cdots\text{O1}^{\text{iv}}$	0.95	2.66	3.602 (3)	171
$\text{C1}-\text{H1C}\cdots\text{O1}^{\text{v}}$	0.98	2.59	3.551 (3)	167
$\text{C7}-\text{H7}\cdots\text{O2}^{\text{vi}}$	0.95	2.55	3.499 (3)	179

Symmetry codes: (i)  $-x + 2, -y + 1, -z$ ; (ii)  $-x + 1, -y + 2, -z + 1$ ; (iii)  $-x + 2, -y + 1, -z + 1$ ; (iv)  $x - 1, y, z$ ; (v)  $x, y - 1, z$ ; (vi)  $x + 1, y, z$ .

Data collection: *CrystalClear* (Rigaku, 2007); cell refinement: *CrystalClear*; data reduction: *CrystalClear*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 2008); program(s) used to refine structure: *SHELXL97* (Sheldrick, 2008); molecular graphics: *OLEX2* (Dolomanov *et al.*, 2009); software used to prepare material for publication: *SHELXL97*.

We thank Tongling Liang at the Chinese Academy of Sciences for the X-ray crystallographic structure determination.

Supplementary data and figures for this paper are available from the IUCr electronic archives (Reference: FY2092).

## References

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## supplementary materials

*Acta Cryst.* (2013). E69, o1036 [doi:10.1107/S1600536813014542]

**3,3-Bis(methylsulfanyl)-1-(4-nitrophenyl)prop-2-en-1-one**

Guan-Neng Yu, Jian-Hui Xia, Zhao-Hui Xu, Li-Ben Wang and Chu-Yi Yu

**Comment**

Heterocyclic ketene amins are important and versatile starting materials for the synthesis of a wide variety of fused heterocycles (Huang & Wang, 1994). In this paper, we report the crystal structure of the title compound, which is a precursor of heterocyclic ketene amins. The shortening of bonds C3—S1 [1.746 (3) Å] and C3—S2 [1.750 (2) Å] with respect to bonds C1—S1 [1.794 (3) Å] and C2—S2 [1.806 (3) Å] is attributed to *d*- $\pi$  interactions between sulfur and the C=C bond. The dihedral angle between 4-nitrophenyl group and (C1, C2, S1, S2, C3, C4, C5, O1) is 35.07 (7)°. In the structure of the title compound, molecules are connected through intermolecular C—H $\cdots$ S and C—H $\cdots$ O hydrogen bonding (Table 1) into a three-dimensional network.

**Experimental**

The title compound was prepared according to the method of Huang & Liu (1989). m.p. 435–437 K. MS:  $m/z = 269$  ( $M^+$ ). IR: 1615 (C=O), 1590 (C=C), 1512, 1345 (NO<sub>2</sub>) cm<sup>-1</sup>. <sup>1</sup>H-NMR:  $\delta = 8.33$  (d, 2H), 8.07 (d, 2H), 6.73 (s, 1H), 2.60 (s, 3H), 2.57 (s, 3H) p.p.m.. <sup>13</sup>C-NMR:  $\delta = 183.5, 170.6, 149.9, 144.9, 129.0, 124.1, 109.0, 17.9, 15.6$  p.p.m.. Anal. Calc. for C<sub>11</sub>H<sub>11</sub>N<sub>0</sub>S<sub>2</sub>: C, 49.05; H, 4.12; N, 5.20. Found C, 49.29; H, 4.23; N, 5.36. Single crystals of the title compound suitable for X-ray diffraction analysis were obtained from ethanol solution by slow evaporation after a week.

**Refinement**

H atoms were positioned geometrically and refined using a riding model, with C—H = 0.98 (C1, C3) or 0.95 Å (C6) and with  $U_{\text{iso}}(\text{H}) = 1.5$  times  $U_{\text{eq}}(\text{C})$  (methyl groups) or with  $U_{\text{iso}}(\text{H}) = 1.2$  times  $U_{\text{eq}}(\text{C})$  (benzene ring).

**Computing details**

Data collection: *CrystalClear* (Rigaku, 2007); cell refinement: *CrystalClear* (Rigaku, 2007); data reduction: *CrystalClear* (Rigaku, 2007); program(s) used to solve structure: *SHELXS97* (Sheldrick, 2008); program(s) used to refine structure: *SHELXL97* (Sheldrick, 2008); molecular graphics: *OLEX2* (Dolomanov *et al.*, 2009); software used to prepare material for publication: *SHELXL97* (Sheldrick, 2008).

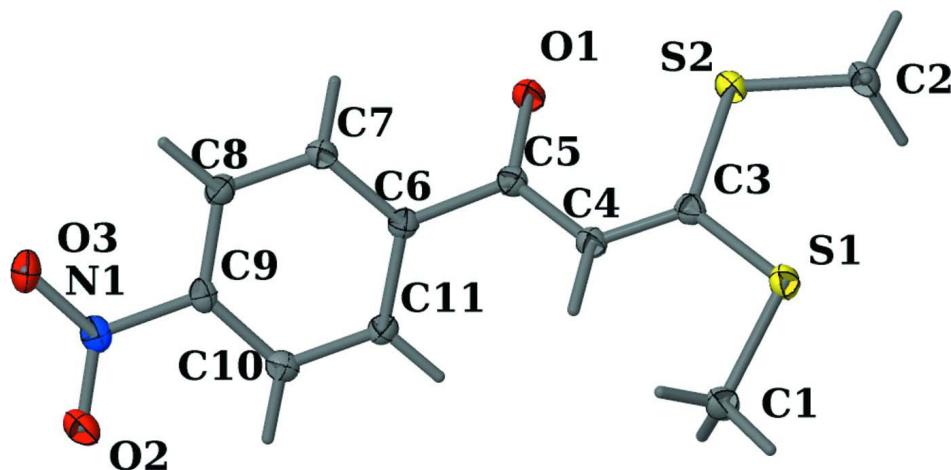


Figure 1

The molecular structure of (I). Displacement ellipsoids are drawn at the 30% probability level.

### 3,3-Bis(methylsulfanyl)-1-(4-nitrophenyl)prop-2-en-1-one

#### Crystal data

$C_{11}H_{11}NO_3S_2$

$M_r = 269.33$

Triclinic,  $P\bar{1}$

$a = 7.917(2) \text{ \AA}$

$b = 8.739(2) \text{ \AA}$

$c = 9.574(3) \text{ \AA}$

$\alpha = 70.415(13)^\circ$

$\beta = 81.985(14)^\circ$

$\gamma = 73.283(13)^\circ$

$V = 597.0(3) \text{ \AA}^3$

$Z = 2$

$F(000) = 280$

$D_x = 1.498 \text{ Mg m}^{-3}$

Mo  $K\alpha$  radiation,  $\lambda = 0.71073 \text{ \AA}$

Cell parameters from 2392 reflections

$\theta = 2.3\text{--}32.6^\circ$

$\mu = 0.44 \text{ mm}^{-1}$

$T = 173 \text{ K}$

Plate, yellow

$0.27 \times 0.24 \times 0.05 \text{ mm}$

#### Data collection

Saturn724+ CCD

diffractometer

Radiation source: sealed tube

Graphite monochromator

$\omega$  scans at fixed  $\chi = 45^\circ$

Absorption correction: multi-scan

(*CrystalClear*; Rigaku, 2007)

$T_{\min} = 0.581$ ,  $T_{\max} = 1.000$

7843 measured reflections

2719 independent reflections

2394 reflections with  $I > 2\sigma(I)$

$R_{\text{int}} = 0.053$

$\theta_{\max} = 27.5^\circ$ ,  $\theta_{\min} = 2.3^\circ$

$h = -10 \rightarrow 10$

$k = -11 \rightarrow 11$

$l = -12 \rightarrow 12$

#### Refinement

Refinement on  $F^2$

Least-squares matrix: full

$R[F^2 > 2\sigma(F^2)] = 0.055$

$wR(F^2) = 0.115$

$S = 1.15$

2719 reflections

156 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

$w = 1/[\sigma^2(F_o^2) + (0.0306P)^2 + 0.3933P]$

where  $P = (F_o^2 + 2F_c^2)/3$

$(\Delta/\sigma)_{\max} < 0.001$

$\Delta\rho_{\max} = 0.29 \text{ e \AA}^{-3}$

$\Delta\rho_{\min} = -0.23 \text{ e \AA}^{-3}$

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

	$x$	$y$	$z$	$U_{\text{iso}}^*/U_{\text{eq}}$
S1	1.24009 (8)	0.08728 (8)	0.14324 (8)	0.03498 (19)
S2	1.38394 (8)	0.37041 (8)	0.12260 (7)	0.03303 (18)
O1	1.1193 (2)	0.6171 (2)	0.1933 (2)	0.0386 (4)
O2	0.2086 (2)	0.7642 (3)	0.4617 (2)	0.0429 (5)
O3	0.3377 (3)	0.8672 (3)	0.5789 (2)	0.0518 (6)
N1	0.3402 (3)	0.7914 (3)	0.4916 (2)	0.0338 (5)
C1	1.0268 (3)	0.0451 (3)	0.1766 (3)	0.0404 (6)
H1A	0.9467	0.1298	0.1022	0.061*
H1B	0.9799	0.0492	0.2759	0.061*
H1C	1.0375	-0.0668	0.1698	0.061*
C2	1.5600 (3)	0.2069 (4)	0.0782 (3)	0.0398 (6)
H2A	1.5239	0.1753	0.0001	0.060*
H2B	1.5857	0.1086	0.1670	0.060*
H2C	1.6660	0.2481	0.0434	0.060*
C3	1.2001 (3)	0.2871 (3)	0.1613 (3)	0.0280 (5)
C4	1.0404 (3)	0.3722 (3)	0.2043 (3)	0.0297 (5)
H4	0.9447	0.3218	0.2225	0.036*
C5	1.0078 (3)	0.5353 (3)	0.2239 (3)	0.0299 (5)
C6	0.8303 (3)	0.6031 (3)	0.2912 (3)	0.0273 (5)
C7	0.8213 (3)	0.6942 (3)	0.3879 (3)	0.0309 (5)
H7	0.9257	0.7142	0.4083	0.037*
C8	0.6607 (3)	0.7558 (3)	0.4548 (3)	0.0321 (5)
H8	0.6540	0.8155	0.5229	0.038*
C9	0.5109 (3)	0.7280 (3)	0.4199 (3)	0.0280 (5)
C10	0.5143 (3)	0.6403 (3)	0.3229 (3)	0.0300 (5)
H10	0.4088	0.6243	0.3002	0.036*
C11	0.6762 (3)	0.5765 (3)	0.2597 (3)	0.0292 (5)
H11	0.6823	0.5139	0.1941	0.035*

*Atomic displacement parameters ( $\text{\AA}^2$ )*

	$U^{11}$	$U^{22}$	$U^{33}$	$U^{12}$	$U^{13}$	$U^{23}$
S1	0.0283 (3)	0.0309 (3)	0.0462 (4)	-0.0060 (3)	0.0047 (3)	-0.0165 (3)
S2	0.0256 (3)	0.0382 (4)	0.0383 (4)	-0.0103 (3)	0.0037 (3)	-0.0160 (3)
O1	0.0320 (10)	0.0386 (10)	0.0522 (12)	-0.0155 (8)	0.0104 (8)	-0.0227 (9)
O2	0.0277 (10)	0.0525 (12)	0.0472 (12)	-0.0118 (9)	0.0037 (8)	-0.0150 (10)
O3	0.0423 (12)	0.0650 (14)	0.0573 (13)	-0.0078 (10)	0.0109 (10)	-0.0411 (12)

N1	0.0305 (11)	0.0329 (11)	0.0342 (12)	-0.0064 (9)	0.0031 (9)	-0.0090 (10)
C1	0.0329 (14)	0.0321 (13)	0.0599 (18)	-0.0101 (12)	0.0026 (13)	-0.0194 (13)
C2	0.0242 (13)	0.0458 (16)	0.0479 (16)	-0.0069 (12)	0.0054 (11)	-0.0174 (13)
C3	0.0272 (12)	0.0304 (12)	0.0264 (12)	-0.0082 (10)	-0.0004 (9)	-0.0088 (10)
C4	0.0274 (12)	0.0296 (12)	0.0332 (13)	-0.0093 (10)	0.0022 (10)	-0.0108 (11)
C5	0.0295 (12)	0.0326 (13)	0.0303 (13)	-0.0114 (11)	0.0019 (10)	-0.0118 (10)
C6	0.0293 (12)	0.0252 (11)	0.0271 (12)	-0.0077 (10)	0.0005 (9)	-0.0077 (10)
C7	0.0270 (12)	0.0320 (13)	0.0371 (14)	-0.0109 (10)	0.0023 (10)	-0.0139 (11)
C8	0.0357 (14)	0.0327 (13)	0.0323 (13)	-0.0111 (11)	0.0010 (10)	-0.0150 (11)
C9	0.0271 (12)	0.0268 (12)	0.0265 (12)	-0.0052 (10)	0.0027 (9)	-0.0067 (10)
C10	0.0275 (12)	0.0292 (12)	0.0326 (13)	-0.0086 (10)	-0.0031 (10)	-0.0070 (10)
C11	0.0304 (12)	0.0306 (12)	0.0295 (12)	-0.0073 (10)	-0.0016 (10)	-0.0136 (10)

Geometric parameters (Å, °)

S1—C3	1.746 (3)	C3—C4	1.357 (3)
S1—C1	1.794 (3)	C4—C5	1.444 (3)
S2—C3	1.750 (2)	C4—H4	0.9500
S2—C2	1.806 (3)	C5—C6	1.505 (3)
O1—C5	1.236 (3)	C6—C7	1.392 (3)
O2—N1	1.223 (3)	C6—C11	1.395 (3)
O3—N1	1.223 (3)	C7—C8	1.389 (3)
N1—C9	1.473 (3)	C7—H7	0.9500
C1—H1A	0.9800	C8—C9	1.381 (3)
C1—H1B	0.9800	C8—H8	0.9500
C1—H1C	0.9800	C9—C10	1.381 (3)
C2—H2A	0.9800	C10—C11	1.385 (3)
C2—H2B	0.9800	C10—H10	0.9500
C2—H2C	0.9800	C11—H11	0.9500
C3—S1—C1	104.01 (12)	C5—C4—H4	118.2
C3—S2—C2	103.83 (12)	O1—C5—C4	123.4 (2)
O2—N1—O3	123.4 (2)	O1—C5—C6	119.3 (2)
O2—N1—C9	118.3 (2)	C4—C5—C6	117.2 (2)
O3—N1—C9	118.3 (2)	C7—C6—C11	119.6 (2)
S1—C1—H1A	109.5	C7—C6—C5	118.6 (2)
S1—C1—H1B	109.5	C11—C6—C5	121.8 (2)
H1A—C1—H1B	109.5	C8—C7—C6	120.4 (2)
S1—C1—H1C	109.5	C8—C7—H7	119.8
H1A—C1—H1C	109.5	C6—C7—H7	119.8
H1B—C1—H1C	109.5	C9—C8—C7	118.3 (2)
S2—C2—H2A	109.5	C9—C8—H8	120.9
S2—C2—H2B	109.5	C7—C8—H8	120.9
H2A—C2—H2B	109.5	C10—C9—C8	123.0 (2)
S2—C2—H2C	109.5	C10—C9—N1	118.4 (2)
H2A—C2—H2C	109.5	C8—C9—N1	118.6 (2)
H2B—C2—H2C	109.5	C9—C10—C11	118.0 (2)
C4—C3—S1	123.37 (19)	C9—C10—H10	121.0
C4—C3—S2	121.71 (19)	C11—C10—H10	121.0
S1—C3—S2	114.92 (14)	C10—C11—C6	120.8 (2)

C3—C4—C5	123.6 (2)	C10—C11—H11	119.6
C3—C4—H4	118.2	C6—C11—H11	119.6
C1—S1—C3—C4	5.0 (3)	C5—C6—C7—C8	-178.6 (2)
C1—S1—C3—S2	-176.01 (14)	C6—C7—C8—C9	-1.6 (4)
C2—S2—C3—C4	178.0 (2)	C7—C8—C9—C10	0.7 (4)
C2—S2—C3—S1	-0.99 (17)	C7—C8—C9—N1	179.4 (2)
S1—C3—C4—C5	178.02 (19)	O2—N1—C9—C10	-0.3 (3)
S2—C3—C4—C5	-0.9 (4)	O3—N1—C9—C10	179.1 (2)
C3—C4—C5—O1	5.3 (4)	O2—N1—C9—C8	-179.0 (2)
C3—C4—C5—C6	-172.2 (2)	O3—N1—C9—C8	0.4 (3)
O1—C5—C6—C7	-34.5 (3)	C8—C9—C10—C11	0.7 (4)
C4—C5—C6—C7	143.0 (2)	N1—C9—C10—C11	-178.0 (2)
O1—C5—C6—C11	145.8 (2)	C9—C10—C11—C6	-1.2 (4)
C4—C5—C6—C11	-36.7 (3)	C7—C6—C11—C10	0.4 (4)
C11—C6—C7—C8	1.1 (4)	C5—C6—C11—C10	-180.0 (2)

Hydrogen-bond geometry (Å, °)

<i>D</i> —H... <i>A</i>	<i>D</i> —H	H... <i>A</i>	<i>D</i> ... <i>A</i>	<i>D</i> —H... <i>A</i>
C11—H11...S2 <sup>i</sup>	0.95	2.93	3.614 (3)	130
C8—H8...O3 <sup>ii</sup>	0.95	2.63	3.204 (3)	119
C2—H2B...O3 <sup>iii</sup>	0.98	2.68	3.297 (4)	122
C10—H10...O1 <sup>iv</sup>	0.95	2.66	3.602 (3)	171
C1—H1C...O1 <sup>v</sup>	0.98	2.59	3.551 (3)	167
C7—H7...O2 <sup>vi</sup>	0.95	2.55	3.499 (3)	179

Symmetry codes: (i)  $-x+2, -y+1, -z$ ; (ii)  $-x+1, -y+2, -z+1$ ; (iii)  $-x+2, -y+1, -z+1$ ; (iv)  $x-1, y, z$ ; (v)  $x, y-1, z$ ; (vi)  $x+1, y, z$ .