

2-(Ethoxycarbonothioylthio)propanoic acid

Lukas N. Eyer, C. John McAdam and Jim Simpson*

Department of Chemistry, University of Otago, PO Box 56, Dunedin, New Zealand. *Correspondence e-mail: jsimpson@alkali.otago.ac.nz

Received 12 July 2017

Accepted 13 July 2017

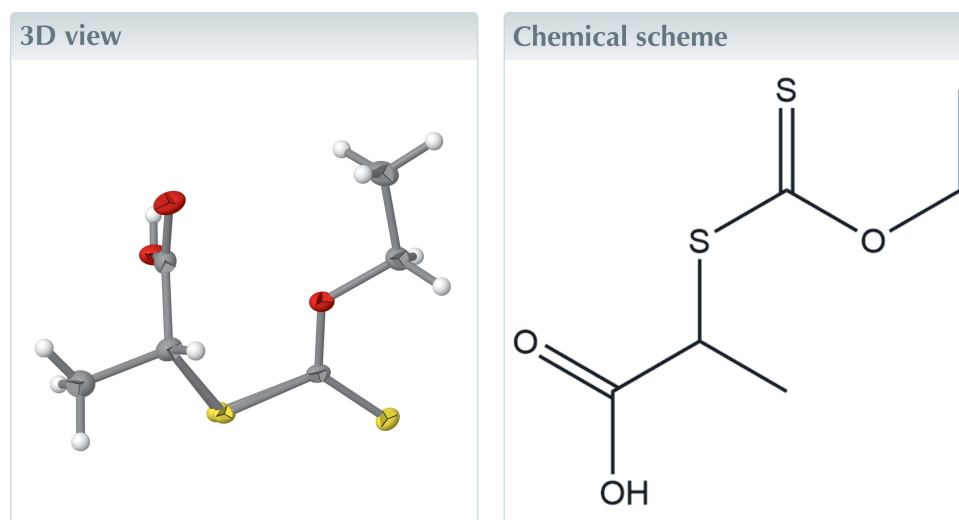
Edited by P. C. Healy, Griffith University, Australia

Keywords: crystal structure; 2-(ethoxycarbonothioylthio)propanoic acid; inversion dimers; hydrogen bonds.

CCDC reference: 1561912

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

In the title compound, $C_6H_{10}O_3S_2$, the *O,S*-diethyl carbonodithioate segment of the molecule is almost planar and is inclined to the carboxylic acid substituent by $82.31(8)^\circ$. In the crystal, $O-H\cdots O$, $C-H\cdots O$ and $C-H\cdots S$ hydrogen bonds each form inversion dimers and combine with a short $O\cdots S$ contact of $3.2394(16)$ Å to generate a three-dimensional network of molecules stacked along all three axial directions.



Structure description

The title compound is a commonly used reversible addition–fragmentation chain-transfer (RAFT) polymerization agent (Nakabayashi *et al.*, 2016; Peng *et al.*, 2016). The Cambridge Structural Database (Version 5.38 with three updates; Groom *et al.*, 2016) reveals only four closely related compounds with the $H-O-C(=O)-C-S-C(=S)-O$ skeleton of the title compound. Only two of these, namely 2-[(ethoxycarbonothioyl)sulfanyl]acetic acid (CSD refcode EROTAH; Xiao *et al.*, 2011) and 2-(*O*-ethyl dithiocarbonato)succinic acid (JAPHEN; Duarte *et al.*, 1989) have ethoxy substituents on the dithiocarbonyl unit. The other two analogues have methoxy (ULEHAV; Xiao & Charpentier, 2011) and isopropoxy (WACQOI; Xiao & Charpentier, 2010) substituents in these positions.

The $C3-C2-S2-C4(=S1)-O3-C5-C6$ segment of the title molecule (Fig. 1) is almost planar, with an r.m.s. deviation of 0.0859 Å from the best-fit plane through all eight non-H atoms. The $C2-C1(=O1)-O2$ carboxylic acid unit is also close to planar, with an r.m.s. deviation of 0.0106 Å, and is almost orthogonal to the previous plane, with a dihedral angle of $82.31(8)^\circ$ between them. In the crystal, classical $O2-H2O\cdots O1^i$ and nonclassical $C2-H2\cdots O1^{ii}$ and $C6-H6A\cdots S1^{iii}$ hydrogen bonds (Table 1) each form inversion dimers, enclosing $R_2^2(8)$, $R_2^2(8)$ and $R_2^2(12)$ ring motifs, respectively (Bernstein *et al.*, 1995). In addition, short $O1\cdots S1^{iv}$ contacts [$3.2394(16)$ Å; symmetry code: (iv) $x, y, 1 + z$] link adjacent molecules into rows along the c -axis direction. These contacts combine to stack the molecules along all three axial directions (Figs. 2, 3 and 4).

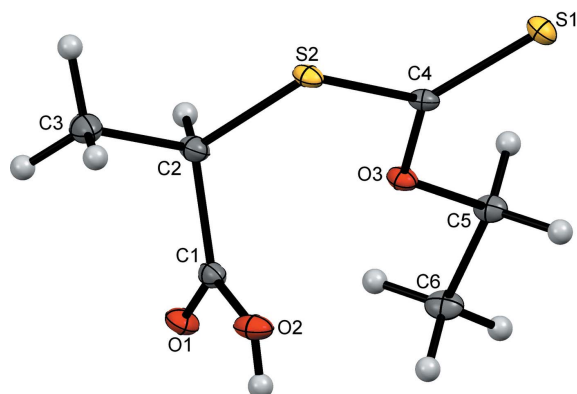


Figure 1
The structure of the title compound, with displacement ellipsoids drawn at the 50% probability level. Only the major-disorder component of the S2 atom is shown.

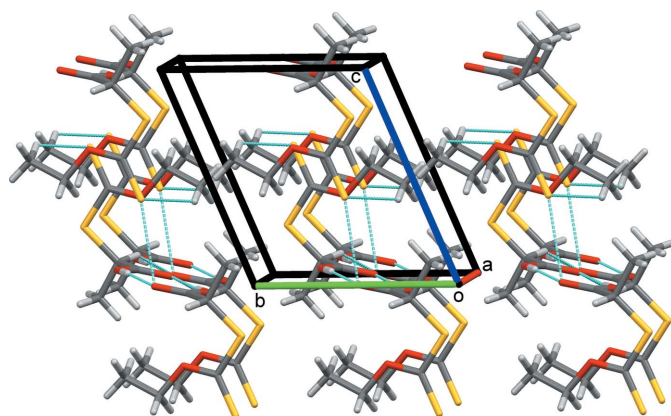


Figure 2
The overall packing of the title compound, viewed along the *a*-axis direction. In this and Figs. 3 and 4, only the major-disorder component of the S2 atom is shown in each case.

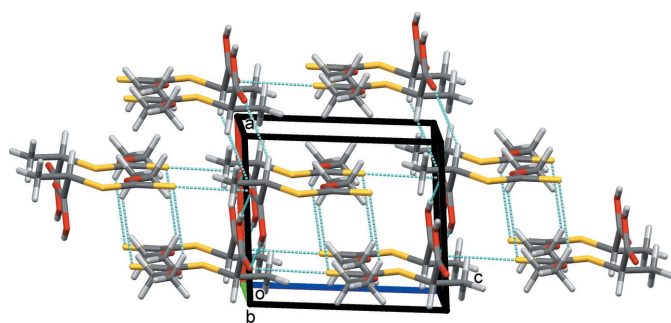


Figure 3
The overall packing of the title compound, viewed along the *b*-axis direction.

Table 1
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>
O2—H2O...O1 ⁱ	0.72 (4)	1.92 (4)	2.639 (2)	175 (4)
C2—H2...O1 ⁱⁱ	1.00	2.62	3.497 (3)	146
C6—H6A...S1 ⁱⁱⁱ	0.98	2.99	3.759 (2)	136

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

Table 2
Experimental details.

Crystal data	
Chemical formula	C ₆ H ₁₀ O ₃ S ₂
<i>M_r</i>	194.26
Crystal system, space group	Triclinic, <i>P</i> $\bar{1}$
Temperature (K)	100
<i>a</i> , <i>b</i> , <i>c</i> (Å)	7.4093 (4), 7.9779 (3), 8.6250 (3)
α , β , γ (°)	67.300 (4), 85.900 (4), 74.068 (4)
<i>V</i> (Å ³)	451.93 (4)
<i>Z</i>	2
Radiation type	Cu <i>K</i> α
μ (mm ⁻¹)	5.04
Crystal size (mm)	0.30 × 0.13 × 0.10
Data collection	
Diffractometer	Agilent SuperNova Dual Source diffractometer with an Atlas detector
Absorption correction	Multi-scan (<i>CrysAlis PRO</i> ; Agilent, 2014)
<i>T_{min}</i> , <i>T_{max}</i>	0.637, 1.000
No. of measured, independent and observed [<i>I</i> > 2σ(<i>I</i>)] reflections	6643, 1875, 1766
<i>R_{int}</i>	0.064
(sin θ/λ) _{max} (Å ⁻¹)	0.630
Refinement	
<i>R</i> [<i>F</i> ² > 2σ(<i>F</i> ²)], <i>wR</i> (<i>F</i> ²), <i>S</i>	0.047, 0.128, 1.06
No. of reflections	1875
No. of parameters	115
No. of restraints	7
H-atom treatment	H atoms treated by a mixture of independent and constrained refinement
$\Delta\rho_{\max}$, $\Delta\rho_{\min}$ (e Å ⁻³)	0.62, -0.60

Computer programs: *CrysAlis PRO* (Agilent, 2014), *SHELXT* (Sheldrick, 2015a), *SHELXL2014* (Sheldrick, 2015b), *TITAN* (Hunter & Simpson, 1999), *Mercury* (Macrae *et al.*, 2008), *enCIFer* (Allen *et al.*, 2004), *PLATON* (Spek, 2009), *pubCIF* (Westrip, 2010) and *WinGX* (Farrugia, 2012).

Synthesis and crystallization

The title compound was prepared according to the literature procedure of Nguyen *et al.* (2015) and X-ray-quality crystals were obtained by recrystallization from mixed solvents of diethyl ether layered with hexane.

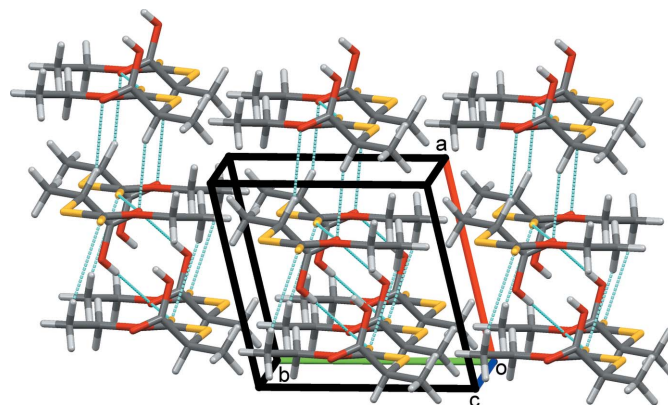


Figure 4
The overall packing of the title compound, viewed along the *c*-axis direction.

Refinement

Crystal data, data collection and structure refinement details are summarized in Table 2. Once all of the atoms in the structure had been found, a high peak remained in the difference Fourier map close to the S2 atom, suggesting possible disorder. Refinement of the two locations of the S2 atom converged with an occupancy ratio of 0.861 (18):0.139 (18).

Funding information

Funding for this research was provided by: NZ Ministry of Business Innovation and Employment Science Investment Fund (grant No. UOO-X1206); University of Otago for the purchase of the diffractometer.

References

- Agilent (2014). *CrysAlis PRO*. Agilent Technologies, Yarnton, Oxfordshire, England.
- Allen, F. H., Johnson, O., Shields, G. P., Smith, B. R. & Towler, M. (2004). *J. Appl. Cryst.* **37**, 335–338.
- Bernstein, J., Davis, R. E., Shimon, L. & Chang, N.-L. (1995). *Angew. Chem. Int. Ed. Engl.* **34**, 1555–1573.
- Duarte, M., Frampton, C., Howard-Lock, H. E., Lock, C. J. L. & Wu, H. (1989). *Acta Cryst.* **C45**, 1028–1031.
- Farrugia, L. J. (2012). *J. Appl. Cryst.* **45**, 849–854.
- Groom, C. R., Bruno, I. J., Lightfoot, M. P. & Ward, S. C. (2016). *Acta Cryst.* **B72**, 171–179.
- Hunter, K. A. & Simpson, J. (1999). *TITAN2000*. University of Otago, New Zealand.
- Macrae, C. F., Bruno, I. J., Chisholm, J. A., Edgington, P. R., McCabe, P., Pidcock, E., Rodriguez-Monge, L., Taylor, R., van de Streek, J. & Wood, P. A. (2008). *J. Appl. Cryst.* **41**, 466–470.
- Nakabayashi, K., Umeda, A., Sato, Y. & Mori, H. (2016). *Polymer*, **96**, 81–93.
- Nguyen, T. H., Paluck, S. J., McGahran, A. J. & Maynard, H. D. (2015). *Biomacromolecules*, **16**, 2684–2692.
- Peng, H., Ruebsam, K., Huang, X., Jakob, F., Karperien, M., Schwaneberg, U. & Pich, A. (2016). *Macromolecules*, **49**, 7141–7154.
- Sheldrick, G. M. (2015a). *Acta Cryst.* **A71**, 3–8.
- Sheldrick, G. M. (2015b). *Acta Cryst.* **C71**, 3–8.
- Spek, A. L. (2009). *Acta Cryst.* **D65**, 148–155.
- Westrip, S. P. (2010). *J. Appl. Cryst.* **43**, 920–925.
- Xiao, S. & Charpentier, P. A. (2010). *Acta Cryst.* **E66**, o3103.
- Xiao, S. & Charpentier, P. A. (2011). *Acta Cryst.* **E67**, o575.
- Xiao, S., Gu, R. & Charpentier, P. A. (2011). *Acta Cryst.* **E67**, o1442.

full crystallographic data

IUCrData (2017). 2, x171035 [https://doi.org/10.1107/S2414314617010355]

2-(Ethoxycarbonothioylthio)propanoic acid

Lukas N. Eyer, C. John McAdam and Jim Simpson

2-(Ethoxycarbonothioylthio)propanoic acid

Crystal data

$C_6H_{10}O_3S_2$	$Z = 2$
$M_r = 194.26$	$F(000) = 204$
Triclinic, $P\bar{1}$	$D_x = 1.428 \text{ Mg m}^{-3}$
$a = 7.4093 (4) \text{ \AA}$	Cu $K\alpha$ radiation, $\lambda = 1.54184 \text{ \AA}$
$b = 7.9779 (3) \text{ \AA}$	Cell parameters from 4826 reflections
$c = 8.6250 (3) \text{ \AA}$	$\theta = 5.5\text{--}75.3^\circ$
$\alpha = 67.300 (4)^\circ$	$\mu = 5.04 \text{ mm}^{-1}$
$\beta = 85.900 (4)^\circ$	$T = 100 \text{ K}$
$\gamma = 74.068 (4)^\circ$	Rectangular block, colourless
$V = 451.93 (4) \text{ \AA}^3$	$0.30 \times 0.13 \times 0.10 \text{ mm}$

Data collection

Agilent SuperNova Dual Source diffractometer with an Atlas detector	6643 measured reflections
Radiation source: SuperNova (Cu) X-ray Source	1875 independent reflections
Detector resolution: $5.1725 \text{ pixels mm}^{-1}$	1766 reflections with $I > 2\sigma(I)$
ω scans	$R_{\text{int}} = 0.064$
Absorption correction: multi-scan (CrysAlis PRO; Agilent, 2014)	$\theta_{\text{max}} = 76.3^\circ$, $\theta_{\text{min}} = 5.6^\circ$
$T_{\text{min}} = 0.637$, $T_{\text{max}} = 1.000$	$h = -9 \rightarrow 9$
	$k = -9 \rightarrow 10$
	$l = -10 \rightarrow 10$

Refinement

Refinement on F^2	Hydrogen site location: mixed
Least-squares matrix: full	H atoms treated by a mixture of independent and constrained refinement
$R[F^2 > 2\sigma(F^2)] = 0.047$	$w = 1/[\sigma^2(F_o^2) + (0.0828P)^2 + 0.2987P]$
$wR(F^2) = 0.128$	where $P = (F_o^2 + 2F_c^2)/3$
$S = 1.06$	$(\Delta/\sigma)_{\text{max}} < 0.001$
1875 reflections	$\Delta\rho_{\text{max}} = 0.62 \text{ e \AA}^{-3}$
115 parameters	$\Delta\rho_{\text{min}} = -0.60 \text{ e \AA}^{-3}$
7 restraints	

Special details

Geometry. All esds (except the esd in the dihedral angle between two l.s. planes) are estimated using the full covariance matrix. The cell esds are taken into account individually in the estimation of esds in distances, angles and torsion angles; correlations between esds in cell parameters are only used when they are defined by crystal symmetry. An approximate (isotropic) treatment of cell esds is used for estimating esds involving l.s. planes.

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

	<i>x</i>	<i>y</i>	<i>z</i>	$U_{\text{iso}}^*/U_{\text{eq}}$	Occ. (<1)
O1	0.7282 (2)	0.4764 (2)	0.0116 (2)	0.0259 (4)	
O2	0.4935 (2)	0.6981 (3)	0.0545 (2)	0.0272 (4)	
H2O	0.433 (5)	0.647 (5)	0.042 (4)	0.041*	
C1	0.6695 (3)	0.6171 (3)	0.0468 (3)	0.0201 (4)	
C2	0.8089 (3)	0.7123 (3)	0.0736 (3)	0.0216 (5)	
H2	0.9359	0.6201	0.0989	0.026*	
C3	0.8165 (4)	0.8809 (4)	-0.0890 (3)	0.0305 (6)	
H3A	0.8454	0.8383	-0.1827	0.046*	
H3B	0.9143	0.9365	-0.0761	0.046*	
H3C	0.6947	0.9756	-0.1122	0.046*	
S2	0.7542 (6)	0.7994 (3)	0.24168 (12)	0.0156 (4)	0.861 (18)
S2A	0.704 (3)	0.829 (2)	0.2403 (9)	0.0171 (18)	0.139 (18)
C4	0.7572 (3)	0.5968 (3)	0.4189 (3)	0.0164 (4)	
S1	0.75397 (7)	0.59867 (7)	0.60794 (6)	0.0198 (2)	
O3	0.7618 (2)	0.4524 (2)	0.37763 (18)	0.0186 (3)	
C5	0.7683 (3)	0.2696 (3)	0.5119 (3)	0.0210 (5)	
H5A	0.6612	0.2809	0.5861	0.025*	
H5B	0.8866	0.2208	0.5806	0.025*	
C6	0.7573 (3)	0.1402 (3)	0.4260 (3)	0.0255 (5)	
H6A	0.6388	0.1896	0.3598	0.038*	
H6B	0.7633	0.0142	0.5108	0.038*	
H6C	0.8628	0.1326	0.3514	0.038*	

Atomic displacement parameters (\AA^2)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
O1	0.0334 (9)	0.0282 (10)	0.0246 (8)	-0.0125 (7)	-0.0001 (7)	-0.0159 (7)
O2	0.0306 (9)	0.0216 (9)	0.0329 (9)	-0.0108 (7)	-0.0083 (7)	-0.0100 (7)
C1	0.0253 (10)	0.0193 (11)	0.0158 (9)	-0.0089 (8)	-0.0033 (8)	-0.0041 (8)
C2	0.0251 (10)	0.0215 (11)	0.0206 (10)	-0.0084 (9)	-0.0035 (8)	-0.0083 (9)
C3	0.0420 (14)	0.0304 (14)	0.0237 (11)	-0.0202 (11)	-0.0006 (10)	-0.0078 (10)
S2	0.0174 (9)	0.0106 (5)	0.0188 (4)	-0.0019 (5)	-0.0058 (3)	-0.0058 (3)
S2A	0.019 (2)	0.018 (2)	0.0169 (19)	-0.0070 (11)	-0.0024 (9)	-0.0070 (11)
C4	0.0158 (8)	0.0147 (10)	0.0207 (9)	-0.0042 (7)	-0.0040 (7)	-0.0079 (8)
S1	0.0238 (3)	0.0186 (3)	0.0182 (3)	-0.0035 (2)	-0.0032 (2)	-0.0092 (2)
O3	0.0229 (7)	0.0147 (8)	0.0202 (7)	-0.0055 (6)	-0.0031 (6)	-0.0080 (6)
C5	0.0234 (10)	0.0144 (11)	0.0237 (10)	-0.0041 (8)	-0.0049 (8)	-0.0053 (8)
C6	0.0283 (11)	0.0153 (12)	0.0330 (12)	-0.0039 (9)	-0.0048 (9)	-0.0095 (9)

Geometric parameters (\AA , $^\circ$)

O1—C1	1.232 (3)	S2A—C4	1.856 (13)
O2—C1	1.296 (3)	C4—O3	1.322 (3)
O2—H2O	0.72 (4)	C4—S1	1.635 (2)
C1—C2	1.515 (3)	S1—O1 ⁱ	3.2394 (16)

C2—C3	1.535 (3)	O3—C5	1.462 (3)
C2—S2	1.813 (3)	C5—C6	1.505 (3)
C2—S2A	2.004 (13)	C5—H5A	0.9900
C2—H2	1.0000	C5—H5B	0.9900
C3—H3A	0.9800	C6—H6A	0.9800
C3—H3B	0.9800	C6—H6B	0.9800
C3—H3C	0.9800	C6—H6C	0.9800
S2—C4	1.740 (2)		
C1—O2—H2O	112 (3)	O3—C4—S1	127.40 (17)
O1—C1—O2	124.6 (2)	O3—C4—S2	111.49 (15)
O1—C1—C2	118.99 (19)	S1—C4—S2	121.11 (13)
O2—C1—C2	116.27 (19)	O3—C4—S2A	114.6 (3)
C1—C2—C3	108.95 (18)	S1—C4—S2A	116.9 (3)
C1—C2—S2	114.60 (17)	C4—S1—O1 ⁱ	162.49 (9)
C3—C2—S2	107.51 (16)	C4—O3—C5	118.71 (16)
C1—C2—S2A	108.0 (4)	O3—C5—C6	106.08 (17)
C3—C2—S2A	104.2 (4)	O3—C5—H5A	110.5
C1—C2—H2	108.5	C6—C5—H5A	110.5
C3—C2—H2	108.5	O3—C5—H5B	110.5
S2—C2—H2	108.5	C6—C5—H5B	110.5
C2—C3—H3A	109.5	H5A—C5—H5B	108.7
C2—C3—H3B	109.5	C5—C6—H6A	109.5
H3A—C3—H3B	109.5	C5—C6—H6B	109.5
C2—C3—H3C	109.5	H6A—C6—H6B	109.5
H3A—C3—H3C	109.5	C5—C6—H6C	109.5
H3B—C3—H3C	109.5	H6A—C6—H6C	109.5
C4—S2—C2	103.40 (14)	H6B—C6—H6C	109.5
C4—S2A—C2	92.4 (7)		
O1—C1—C2—C3	97.9 (2)	C2—S2A—C4—O3	-26.7 (7)
O2—C1—C2—C3	-78.7 (2)	C2—S2A—C4—S1	164.1 (2)
O1—C1—C2—S2	-141.7 (2)	O3—C4—S1—O1 ⁱ	-9.5 (4)
O2—C1—C2—S2	41.8 (3)	S2—C4—S1—O1 ⁱ	170.4 (2)
O1—C1—C2—S2A	-149.6 (5)	S2A—C4—S1—O1 ⁱ	158.1 (6)
O2—C1—C2—S2A	33.9 (5)	S1—C4—O3—C5	-1.2 (3)
C1—C2—S2—C4	60.7 (3)	S2—C4—O3—C5	178.92 (19)
C3—C2—S2—C4	-178.06 (19)	S2A—C4—O3—C5	-169.0 (6)
C2—S2—C4—O3	-11.7 (3)	C4—O3—C5—C6	175.74 (17)
C2—S2—C4—S1	168.43 (15)		

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

Hydrogen-bond geometry (\AA , $^\circ$)

<i>D</i> —H \cdots <i>A</i>	<i>D</i> —H	H \cdots <i>A</i>	<i>D</i> \cdots <i>A</i>	<i>D</i> —H \cdots <i>A</i>
O2—H2O \cdots O1 ⁱⁱ	0.72 (4)	1.92 (4)	2.639 (2)	175 (4)

C2—H2···O1 ⁱⁱⁱ	1.00	2.62	3.497 (3)	146
C6—H6A···S1 ^{iv}	0.98	2.99	3.759 (2)	136

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