



Crystal structures of 4,4'-(disulfane-1,2-diyl)bis(5-methyl-2*H*-1,3-dithiol-2-one) and 4,4'-(diselenane-1,2-diyl)bis(5-methyl-2*H*-1,3-dithiol-2-one)

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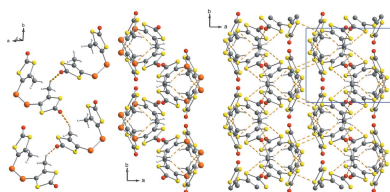
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Technology, Austria**Keywords:** crystal structure; catenation; 1,3-ene-dithiol-2-ones; disulfide; diselenide.**CCDC references:** 1843766; 1843765**Supporting information:** this article has
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The two title compounds, $C_8H_6O_2S_6$ and $C_8H_6O_2S_4Se_2$, are isotypic with very similar cell parameters. The complete molecules constitute the asymmetric units, despite being chemically perfectly symmetric. The most prominent differences in the metrical parameters arise from the distinct sizes of sulfur and selenium in the dichalcogenide bridges, with C—S—S—C and C—Se—Se—C torsion angles of 70.70 (5) and 68.88 (3)°, respectively. The crystal packing is determined by weak non-classical hydrogen-bonding interactions. One carbonyl oxygen but not the other participates in C—H...O interactions zigzagging along the *b* axis, forming infinite chains. This is complemented by an intramolecular C—H...S interaction and further intermolecular C—H...S (C—H...Se) interactions, resulting in a three-dimensional network. The interactions involving the bridging chalcogenides form chains protruding along the *c* axis.

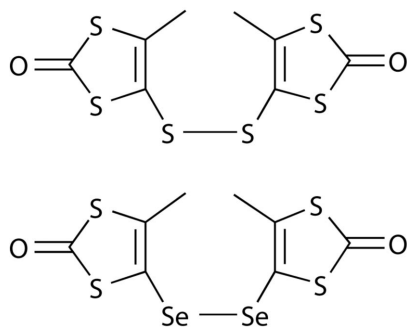
1. Chemical context

Selenium- and sulfur-containing compounds play an important role in nature. Sulfur-rich compounds, in particular derivatives of tetrathiafulvalene and dithiolene, comprise chemically interesting compounds with exceptional electronic structural characteristics. Selenium is an essential trace element in the active sites of several enzymes and plays *inter alia* an important role in antioxidant selenoproteins for protection against oxidative stress such as in thioredoxin reductase (Lee *et al.*, 1999; Lescure *et al.*, 1999; Mustacich & Powis, 2000; Watabe *et al.*, 1999; Williams *et al.*, 2000). In the disulfide isomerase protein family, thioredoxin-like domains are rich in cysteine residues. A diselenide from selenocysteins was shown to be structurally very similar to the respective disulfide from two cysteines (Görbitz *et al.*, 2015). As a consequence, disulfide and diselenide compounds were developed as catalysts for oxidative protein folding and refolding reactions (Arai *et al.*, 2018). Here we report the serendipitous synthesis and structural characterization of bis[3-methyl-1,3-ene-dithiol-2-one] disulfide and bis[3-methyl-1,3-ene-dithiol-2-one] diselenide *via* unprecedented routes. Instead of the targeted products, the applied order of reactions yielded the novel disulfide and its diselenide analogue, which have potential applications in redox chemistry and as biologically interesting compounds. By *in situ* oxidation, S—S or Se—Se moieties are formed, replacing the nBu_3Sn substituents of alkene carbon atoms of two distinct and consequently linked 1,3-ene-dithiol-2-one units. As this constitutes a substitution of a nBu_3Sn functional



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group, it is quite likely that this method can be applied to a variety of respective different precursors.



2. Structural commentary

The two title compounds are isotopic. One complete molecule constitutes the asymmetric unit despite being chemically perfectly symmetric: *i.e.* no symmetry operation is used to generate the whole molecular structure. In both compounds, two 3-methyl-1,3-ene-dithiol-2-one moieties are linked by a dichalcogenide bridge (S_2^{2-} or Se_2^{2-}), which is attached to one of the ene carbon atoms, while the other ene carbon is bound to a methyl group (Figs. 1 and 2). Both structures constitute the first examples of crystallographically characterized disulfides and diselenides in which two 1,3-ene-dithiol-2-one moieties are linked by a dichalcogenide bridge. While related bridged 1,3-ene-dithiol-2-thione moieties are reported for disulfides and also one compound in which the disulfide is part of a heterocycle with the 1,3-ene-dithiol-2-one moiety (Chou *et al.*, 1998), no such analogues are known in the case of the diselenide bridge.

The metrical parameters of both molecules are nearly identical (see Fig. 3 for an overlay of the molecules), with the largest differences found for the dichalcogenide bridge itself. The Se—Se distance [2.3397 (7) Å] is longer by *ca.* 0.27 Å than the S—S distance [2.0723 (7) Å], matching almost exactly the difference in the respective covalent radii (0.13 Å; Pyykkö &

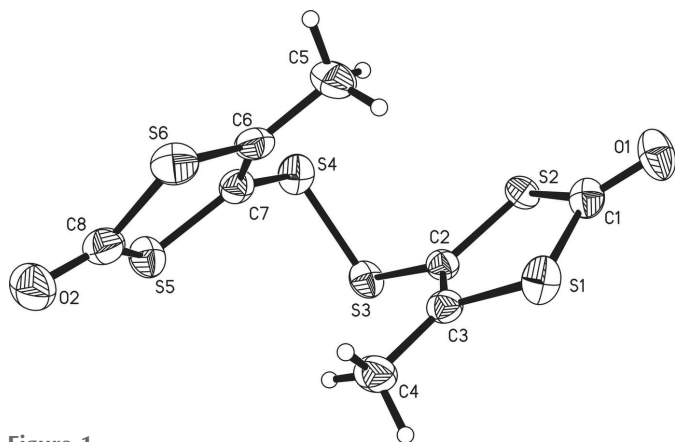


Figure 1
The molecular structure of bis[4-methyl-1,3-ene-dithiol-2-one] disulfide. Displacement ellipsoids are shown at the 50% probability level.

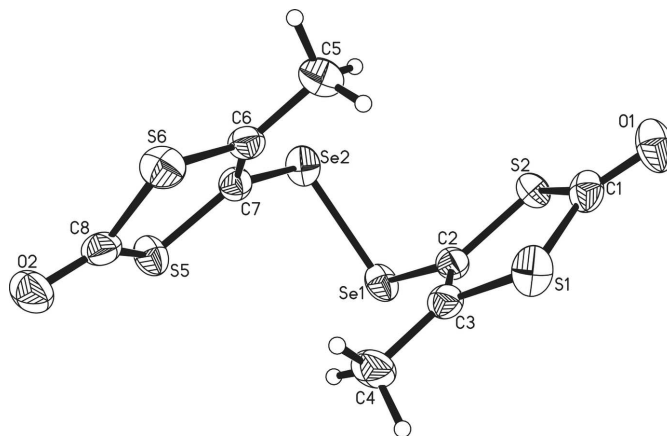


Figure 2
The molecular structure of [bis[4-methyl-1,3-ene-dithiol-2-one] diselenide. Displacement ellipsoids are shown at the 50% probability level.

Atsumi, 2009) multiplied by two. Similarly, the average C—Se distance [1.897 (4) Å] is longer by 0.15 Å than the average C—S distance [1.749 (2) Å]. Unusual electronic effects upon exchanging selenium for sulfur can, hence, be excluded. The average C—Se—Se angle [98.8 (6)°] is slightly more acute than the C—S—S angle [101.8 (6)°], which necessarily results from the longer distances involving the Se atom and the nearly identical atom positions of the 1,3-ene-dithiol-2-thione moieties. All other differences in the metrical parameters between the two molecular structures are marginal. All observed distances and angles also fall into or close to the expected/previously reported ranges. The S—S distances of the most closely related compounds range from 2.078 Å in an $Fe(CO)_2Cp$ -coordinating species (Matsubayashi *et al.*, 2002) to 2.160 Å in the $[C_6S_{10}]^{2-}$ dianion crystallized as an ammonium salt (Breitzer *et al.*, 2001). The observed S—S distance [S3—S4; 2.0723 (7) Å] here is slightly shorter than the former, though not shorter than the lower limit of *ca.* 2.00 Å when generally evaluating C—S—S—C linkages (Comerlato *et al.*, 2010; Aida & Nagata, 1986). Se—Se distances in compounds in which one Se_2^{2-} unit binds to alkene carbon atoms and bridges two identical ene-moieties range from 2.303 Å (Biswas

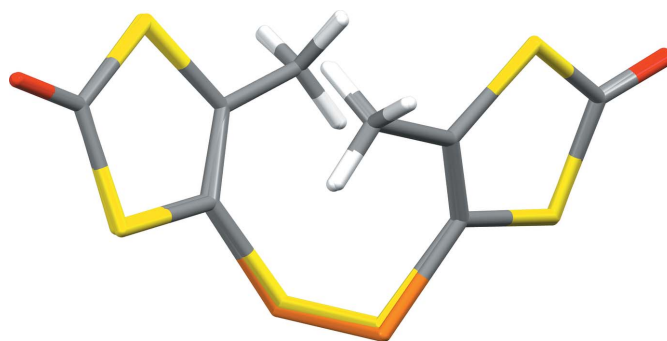


Figure 3
An overlay (*Mercury*; Macrae *et al.*, 2006) of the molecular structures of bis[4-methyl-1,3-ene-dithiol-2-one] disulfide (yellow bridge) and bis[4-methyl-1,3-ene-dithiol-2-one] diselenide (orange bridge). The root-mean-square deviation (r.m.s.d.) and the maximum distance between atom positions are 0.078 and 0.171 Å, respectively.

Table 1
Hydrogen-bond geometry (Å, °) for C₈H₆O₂S₆.

<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>
C4—H4 <i>A</i> ···S3	0.98	2.76	3.244 (2)	111
C5—H5 <i>A</i> ···S4	0.98	2.75	3.234 (2)	111
C4—H4 <i>B</i> ···O1 ⁱ	0.98	2.53	3.345 (2)	141
C5—H5 <i>C</i> ···S3 ⁱⁱ	0.98	3.14	3.8063 (19)	126
C5—H5 <i>C</i> ···S5 ⁱⁱⁱ	0.98	3.01	3.825 (2)	142
C4—H4 <i>C</i> ···S2 ^{iv}	0.98	3.12	4.021 (2)	153

Symmetry codes: (i) $-x+1, y-\frac{1}{2}, -z+\frac{1}{2}$; (ii) $x, -y+\frac{3}{2}, z-\frac{1}{2}$; (iii) $-x+2, -y+1, -z+1$; (iv) $-x+1, -y+2, -z+1$.

et al., 2017) to 2.389 Å (Ruban *et al.*, 1981), with the Se—Se distance observed here [2.3397 (7) Å] falling right in the center of this range.

The structurally most notable features are the C—S—C and C—Se—Se—C torsion angles [70.70 (5) and 68.86 (3)°, respectively] which bring the two 1,3-ene-dithiol-2-thione moieties in rather close proximity. In related disulfides they range from 52.08 to 109.82° (Breitzer *et al.*, 2001). C—S—C torsion angles near 90° were found *in silico* to stabilize structures by an overlap of one σ^*S-C orbital with the 3*p* lone pair of the other sulfur atom, which is maximized in such an arrangement (Aida & Nagata, 1986). The observed C—Se—Se—C torsion angles of diselenide-bridged alkenes as the closest relatives of the title diselenide range from 73.03° (Ruban *et al.*, 1981) to 92.04° (Biswas *et al.*, 2017). In the crystalline solid state, apparently packing effects, steric bulk, hydrogen-bonding interactions, and $\pi-\pi$ -stacking can influence the relative orientations of the two substituents on the disulfide unit significantly, whereas the values for alkene bridging diselenides observed to date are less varied.

Table 2
Hydrogen-bond geometry (Å, °) for C₈H₆O₂S₄Se₂.

<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>
C4—H4 <i>A</i> ···Se1	0.98	2.84	3.354 (4)	114
C5—H5 <i>A</i> ···Se2	0.98	2.83	3.341 (4)	114
C4—H4 <i>B</i> ···O1 ⁱ	0.98	2.55	3.369 (5)	141
C5—H5 <i>C</i> ···Se1 ⁱⁱ	0.98	3.14	3.801 (4)	126
C5—H5 <i>C</i> ···S5 ⁱⁱⁱ	0.98	3.04	3.850 (4)	141
C4—H4 <i>C</i> ···S2 ^{iv}	0.98	3.13	3.992 (4)	148

Symmetry codes: (i) $-x+1, y-\frac{1}{2}, -z+\frac{1}{2}$; (ii) $x, -y+\frac{3}{2}, z-\frac{1}{2}$; (iii) $-x+2, -y+1, -z+1$; (iv) $-x+1, -y+2, -z+1$.

The four 1,3-ene-dithiol-2-one moieties (two in each structure) are essentially planar, with maximum deviations from the least-squares plane of 0.028 and 0.022 Å for the disulfide and for the diselenide, respectively, corresponding to the distances from atom S1 to the O1—S1—S2—C1—C2—C3 plane in both cases. The dihedral angles between the O1—S1—S2—C1—C2—C3 and the O2—S5—S6—C6—C7—C8 planes are 33.8 (2)° for the disulfide and 28.89 (11)° for the diselenide. Here, a smaller torsion angle around the dichalcogenide bridge is accompanied by a smaller angle between the two planes of the 1,3-ene-dithiol-2-one moieties.

3. Supramolecular features

In the crystals, molecules are linked by C—H···O, C—H···S, and C—H···Se non-classical hydrogen-bonding interactions, some of which being comparably weak (Tables 1 and 2). One carbonyl oxygen but not the other participates in C4—H4*B*···O1ⁱ interactions zigzagging along the *b* axis, forming infinite chains (Fig. 4, left). The respective *D*···*A* distances are

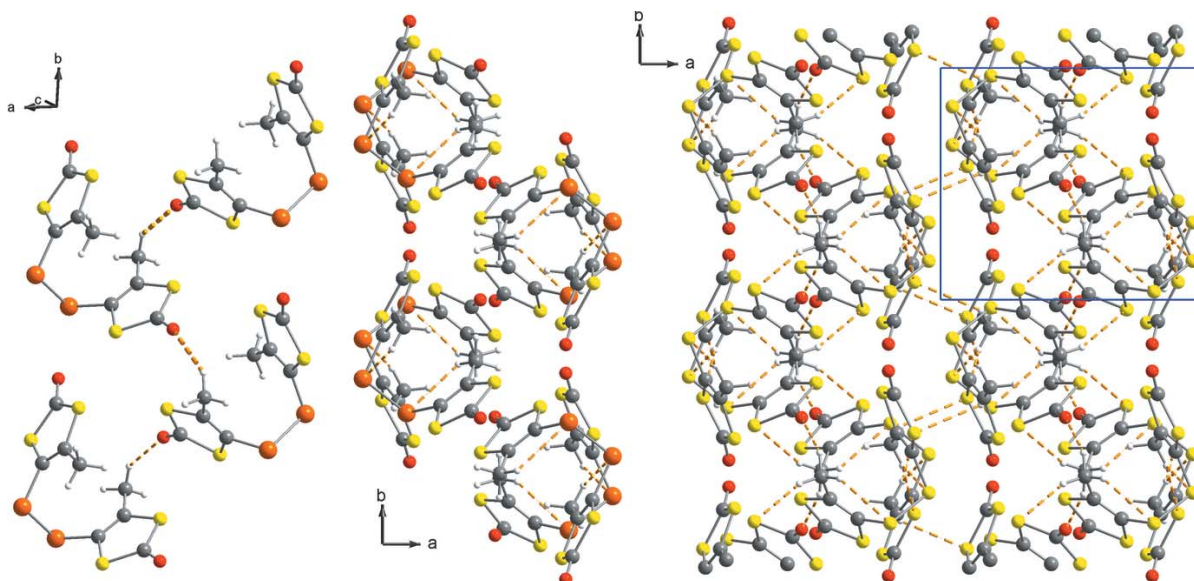


Figure 4
Packing and non-classical hydrogen-bonding motifs for the crystal structures of bis[4-methyl-1,3-ene-dithiol-2-one] disulfide and bis[4-methyl-1,3-ene-dithiol-2-one] diselenide. Left: C4—H4*B*···O1ⁱ interactions zigzagging along the *b* axis shown for the diselenide; center: hydrogen-bonding interactions of the diselenide bridge C5—H5*C*···Se1ⁱⁱ protruding along the *c* axis; right: additional symmetric hydrogen-bonding interactions between coplanar 1,3-ene-dithiol-2-one moieties connecting adjacent chains shown for the disulfide (C4—H4*C*···S2^{iv} and C5—H5*C*···S5ⁱⁱⁱ). For symmetry codes, see Tables 1 and 2.

3.345 (2) Å for the disulfide and 3.369 (5) Å for the diselenide. This is complemented by two intramolecular interactions between the two chalcogens of the dichalcogenide bridges and the adjacent methyl substituents (C4—H4A···S3/Se1 and C5—H5A···S4/Se2) with *D*···*A* distances of 3.244 (2) for S3, of 3.234 (2) for S4, of 3.354 (4) for Se1, and of 3.341 (4) for Se2. Further intermolecular C—H···S and C—H···Se interactions contribute to the formation of a three-dimensional network. The interactions involving the bridging chalcogenides form chains protruding along the *c* axis (Fig. 4, center and right). The closest 3-methyl-1,3-ene-dithiol-2-one moieties of two adjacent molecules are perfectly coplanar with the carbonyl oxygen atoms pointing into opposite directions. The respective distances between the planes are 3.55 and 3.58 Å for pairs of S1—S2—C1—C2—C3 heterocycles for the disulfide and diselenide, and 3.64 and 3.66 Å for pairs of S5—S6—C6—C7—C8 heterocycles. This arrangement fosters weak symmetric bidirectional C5—H5C···S5ⁱⁱⁱ and C4—H4C···S2^{iv} hydrogen-bonding interactions between methyl hydrogen atoms and S2 and S5 ring atoms, connecting adjacent chains and forming a three-dimensional network (Fig. 4, right).

4. Database survey

In the literature to date, only S—S-bridged 1,3-ene-dithiol-2-thione compounds have been reported but no analogous 1,3-ene-dithiol-2-one compounds (excluding those in which the 'link' is part of a heterocycle). The first such thione crystal structure was reported in 1999 by Cerrada *et al.*, which comprises an S—S-linked [C₃S₅—C₃S₅]²⁻ dianion (Cerrada *et al.*, 1999). Ten years later, Cerrada *et al.* described the S—S coupling *via* dithiolate transfer from tin to nickel complexes where they isolated an S—S-bridged 1,3-dithiol-2-thione with different substituents as a crystalline byproduct (Cerrada *et al.*, 2009). Rauchfuss and co-workers described the isolation and structural characterization of an S—S-linked dianion [C₆S₁₀]²⁻ as the tetramethylammonium salt (Breitzer *et al.*, 2001). In 2002, Matsubayashi *et al.* reported the formation of an S—S-linked [C₃S₅—C₃S₅]²⁻ system bridging two Fe(CO)₂Cp complexes by coordination of thiolate sulfur to iron (Matsubayashi *et al.*, 2002). Wardell and coworkers carried out the controlled oxidation of cesium 4-benzoylthio-1,3-dithiole-2-thione-5-thiolate using iodine as oxidant and obtained bis(4-benzoylthio-1,3-dithiole-2-thione)-5,5-disulfide, in two polymorphic forms (Comerlato *et al.*, 2010). Recently the formation of a disulfide with a 4-(methylsulfanyl)-2*H*-1,3-dithiole-2-thione unit was reported from the reaction of a Cs complex with MCl₂ (*M* = Pt, Pd) by Kumar *et al.* (2017). Notably, such compounds predominantly constitute unanticipated side products and the focus of the respective characterization lies in crystallographic analyses with respect to solid-state intermolecular interactions and packing motifs. More in-depth studies have focused predominantly on their interesting redox properties (Breitzer *et al.*, 2001; Matsubayashi *et al.*, 2002).

Only two analogous diselenide compounds with Se—Se moieties linking two 1,3-ene-dithiol-2-thione moieties are reported in the literature, albeit without crystallographic data (Cerrada *et al.*, 1999; Takimiya *et al.*, 2002). To date, no such compounds are known with 1,3-ene-dithiol-2-one moieties. A few examples are available for distantly related compounds in which cyclic alkenes are bridged by a diselenide moiety. Already in 1981, the synthesis, characterization and crystal structure of such a diselenide was described by Ruban *et al.*: bis[4-(2-thienyl)selenolo[3,4-*b*]thiophen-6-yl]diselenide was formed unexpectedly by the reaction of 2-[(triphenylphosphonio)methyl] thiophene chloride with sodium hydrogen selenite (Ruban *et al.*, 1981). In 2000, Oilunkaniemi *et al.* published a procedure for the synthesis of thienyl- and furyl diselenide compounds, which was confirmed by respective crystal structures and selenium NMR spectra (Oilunkaniemi *et al.*, 2000). Kumar & Nangia (2000) published the crystal structure of 2,2'-diselenobis(4,4-diphenylcyclohexa-2,5-dienone). In 2003, Thaler *et al.* synthesized cyclopentadienyl selenium compounds as multifunctional ligand systems with a varied number of selenium atoms in the Se_{*n*} bridge (Thaler *et al.*, 2003). Recently, the formation of a diselenide as a byproduct during the synthesis of heliannuol C (as confirmed by X-ray diffraction) was described by Biswas *et al.* (2017). The crystal structures of bis[4-methyl-1,3-dithiol-2-one] disulfide and diselenide described in the current work are the first in which two 1,3-ene-dithiol-2-one moieties are linked by an S—S and an Se—Se bridge, respectively. For the latter, even the chemical structure is entirely unprecedented.

5. Synthesis and crystallization

Preparation of bis[4-methyl-1,3-dithiol-2-one] disulfide: This was undertaken by a modification of a published procedure (Dinsmore *et al.*, 1998). 4-Methyl-1,3-dithiol-2-one (0.95 g, 7.2 mmol) and tributyltin chloride (2.92 ml, 8.63 mmol) in dry THF (10 ml) under nitrogen were cooled to 169 K (N₂/MeOH:Et₂O or dry ice/Et₂O), and LDA (9.8 ml, 7.9 mmol, 10% solution in hexane) was added dropwise over 5 min. The mixture was allowed to stand for 35 min, warmed to ice-bath temperature and after a further 10 minutes quenched with a saturated aqueous solution of NH₄Cl (around 20 ml). The organic phase was diluted with EtOAc, separated and the aqueous phase re-extracted with Et₂O (2 × 15 ml). The combined organic phases were washed with brine, dried and the solvent evaporated *in vacuo* to give a yellowish oil as crude product. This was purified by chromatography (silica gel), eluting with EtOAc/petroleum ether (40/60) 3:97 *v/v* to give 4-methyl-5-tri-*n*-butylstannyl-1,3-dithiol-2-one as the major product. During purification, a yellowish oily fraction was isolated and subsequently stored at 253 K, forming large yellow crystals. Crystallographic evaluation of these crystals reveals the formation of the side product bis[4-methyl-1,3-dithiol-2-one] disulfide.

Preparation of bis[4-methyl-1,3-dithiol-2-one] diselenide: The synthesis was carried out under an inert gas atmosphere of nitrogen, whereas the purification steps were carried out in

Table 3
Experimental details.

	C ₈ H ₆ O ₂ S ₆	C ₈ H ₆ O ₂ S ₄ Se ₂
Crystal data		
<i>M_r</i>	326.49	420.29
Crystal system, space group	Monoclinic, <i>P</i> ₂ / <i>c</i>	Monoclinic, <i>P</i> ₂ / <i>c</i>
Temperature (K)	170	170
<i>a</i> , <i>b</i> , <i>c</i> (Å)	10.845 (2), 9.0387 (18), 13.370 (3)	10.960 (2), 9.1348 (18), 13.495 (3)
β (°)	108.95 (3)	108.29 (3)
<i>V</i> (Å ³)	1239.6 (4)	1282.8 (5)
<i>Z</i>	4	4
Radiation type	Mo <i>K</i> α	Mo <i>K</i> α
μ (mm ⁻¹)	1.08	6.40
Crystal size (mm)	0.50 × 0.20 × 0.001	0.48 × 0.43 × 0.41
Data collection		
Diffractometer	STOE IPDS2T	Stoe IPDS2T
Absorption correction	Numerical face indexed	Numerical face indexed
<i>T</i> _{min} , <i>T</i> _{max}	0.771, 0.942	0.393, 0.786
No. of measured, independent and observed [<i>I</i> > 2σ(<i>I</i>)] reflections	13324, 3344, 2636	10805, 2733, 2009
<i>R</i> _{int}	0.034	0.063
(sin θ/λ) _{max} (Å ⁻¹)	0.687	0.636
Refinement		
<i>R</i> [<i>F</i> ² > 2σ(<i>F</i> ²)], <i>wR</i> (<i>F</i> ²), <i>S</i>	0.027, 0.064, 1.03	0.029, 0.058, 0.97
No. of reflections	3344	2733
No. of parameters	147	147
H-atom treatment	H-atom parameters constrained	H-atom parameters constrained
Δρ _{max} , Δρ _{min} (e Å ⁻³)	0.36, -0.34	0.41, -0.51

Computer programs: *X-AREA* (Stoe & Cie, 2010), *SIR92* (Altomare *et al.*, 1994), *SHELXS2016/6* (Sheldrick, 2008), *SHELXL2016/6* (Sheldrick, 2015), *XP* (Bruker, 1998), *DIAMOND* (Brandenburg, 2001), *Mercury* (Macrae *et al.*, 2006) and *CIFTAB* (Sheldrick, 2015).

air. To a solution of 4-methyl-5-tri-*n*-butylstannyl-1,3-dithiol-2-one (352.5 mg, 0.84 mmol) in freshly distilled dioxane (5 ml) was added freshly sublimed selenium dioxide (134.2 mg, 1.21 mmol). The reaction mixture was heated at reflux temperature for 6 h. After cooling, the solution was filtered through celite. Solvent removal gave an orange solid (188.0 mg, 0.38 mmol, 45%). Yellow crystals suitable for crystallographic analysis were obtained by recrystallization from acetone.

6. Refinement

Crystal data, data collection and structure refinement details are summarized in Table 3. The six methyl hydrogen atoms of each structure were included in calculated positions and treated as riding with C–H = 0.98 Å and *U*_{iso}(H) = 1.5*U*_{eq}(C).

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supporting information

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Crystal structures of 4,4'-(disulfane-1,2-diyl)bis(5-methyl-2*H*-1,3-dithiol-2-one) and 4,4'-(diselanane-1,2-diyl)bis(5-methyl-2*H*-1,3-dithiol-2-one)

Ivan Trentin, Claudia Schindler and Carola Schulzke

Computing details

For both structures, data collection: *X-AREA* (Stoe & Cie, 2010); cell refinement: *X-AREA* (Stoe & Cie, 2010); data reduction: *X-AREA* (Stoe & Cie, 2010); program(s) used to solve structure: *SIR92* (Altomare *et al.*, 1994), *SHELXS2016/6* (Sheldrick, 2008); program(s) used to refine structure: *SHELXL2016/6* (Sheldrick, 2015); molecular graphics: *XP* (Bruker, 1998), *DIAMOND* (Brandenburg, 2001), *Mercury* (Macrae *et al.*, 2006); software used to prepare material for publication: *CIFTAB* (Sheldrick, 2015).

4,4'-(Disulfane-1,2-diyl)bis(5-methyl-2*H*-1,3-dithiol-2-one) (CSV72a12)

Crystal data

$C_8H_6O_2S_4Se_2$

$M_r = 420.29$

Monoclinic, $P2_1/c$

$a = 10.960$ (2) Å

$b = 9.1348$ (18) Å

$c = 13.495$ (3) Å

$\beta = 108.29$ (3)°

$V = 1282.8$ (5) Å³

$Z = 4$

$F(000) = 808$

$D_x = 2.176$ Mg m⁻³

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

Cell parameters from 11124 reflections

$\theta = 3.2$ – 53.8 °

$\mu = 6.40$ mm⁻¹

$T = 170$ K

Block, yellow

$0.48 \times 0.43 \times 0.41$ mm

Data collection

Stoe IPDS2T

diffractometer

Radiation source: fine-focus sealed tube

Detector resolution: 6.67 pixels mm⁻¹

ω scans

Absorption correction: numerical

face indexed

$T_{\min} = 0.393$, $T_{\max} = 0.786$

10805 measured reflections

2733 independent reflections

2009 reflections with $I > 2\sigma(I)$

$R_{\text{int}} = 0.063$

$\theta_{\max} = 26.9$ °, $\theta_{\min} = 2.0$ °

$h = -13 \rightarrow 13$

$k = -11 \rightarrow 11$

$l = -17 \rightarrow 17$

Refinement

Refinement on F^2

Least-squares matrix: full

$R[F^2 > 2\sigma(F^2)] = 0.029$

$wR(F^2) = 0.058$

$S = 0.97$

2733 reflections

147 parameters

0 restraints

Hydrogen site location: inferred from neighbouring sites

H-atom parameters constrained

$w = 1/[\sigma^2(F_o^2) + (0.0249P)^2]$

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

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

$\Delta\rho_{\max} = 0.41$ e Å⁻³

$\Delta\rho_{\min} = -0.51$ e Å⁻³

Special details

Experimental. (*X-RED32* and *X-SHAPE*; Stoe, 2010)

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>	$U_{\text{iso}}^*/U_{\text{eq}}$
C1	0.5603 (4)	0.9723 (4)	0.2588 (3)	0.0330 (8)
C2	0.6767 (3)	0.9491 (4)	0.4583 (3)	0.0283 (7)
C3	0.5772 (3)	0.8578 (4)	0.4418 (3)	0.0292 (7)
C4	0.5451 (4)	0.7610 (4)	0.5199 (3)	0.0407 (9)
H4A	0.610175	0.773264	0.588334	0.061*
H4B	0.543631	0.658702	0.497773	0.061*
H4C	0.460552	0.787918	0.524643	0.061*
C5	0.8143 (4)	0.6153 (5)	0.3661 (3)	0.0430 (10)
H5A	0.857954	0.708541	0.364796	0.064*
H5B	0.722081	0.626480	0.330068	0.064*
H5C	0.849415	0.539960	0.331030	0.064*
C6	0.8349 (3)	0.5707 (4)	0.4771 (3)	0.0300 (7)
C7	0.8914 (3)	0.6483 (4)	0.5642 (3)	0.0288 (7)
C8	0.8162 (4)	0.4074 (4)	0.6323 (3)	0.0333 (8)
O1	0.5276 (3)	1.0021 (3)	0.16730 (19)	0.0441 (7)
O2	0.7920 (3)	0.3109 (3)	0.6837 (2)	0.0445 (7)
S1	0.47447 (9)	0.85051 (10)	0.31380 (8)	0.0387 (2)
S2	0.69642 (9)	1.04502 (9)	0.35303 (6)	0.02911 (19)
S5	0.89572 (10)	0.57233 (10)	0.68357 (7)	0.0345 (2)
S6	0.77748 (10)	0.39942 (10)	0.49537 (7)	0.0368 (2)
Se1	0.80328 (4)	0.98085 (4)	0.58945 (3)	0.03435 (11)
Se2	0.96657 (4)	0.83504 (4)	0.56427 (3)	0.03646 (11)

Atomic displacement parameters (\AA^2)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
C1	0.039 (2)	0.0238 (17)	0.0322 (19)	0.0044 (15)	0.0063 (16)	-0.0015 (14)
C2	0.0338 (19)	0.0256 (16)	0.0271 (17)	0.0018 (14)	0.0116 (15)	-0.0010 (13)
C3	0.0321 (19)	0.0247 (17)	0.0331 (18)	0.0017 (14)	0.0135 (16)	-0.0005 (13)
C4	0.045 (2)	0.036 (2)	0.048 (2)	-0.0067 (17)	0.026 (2)	0.0043 (17)
C5	0.050 (3)	0.049 (2)	0.032 (2)	0.0010 (19)	0.0172 (19)	-0.0009 (16)
C6	0.0266 (18)	0.0348 (18)	0.0300 (18)	0.0022 (15)	0.0108 (15)	-0.0002 (14)
C7	0.0258 (18)	0.0295 (17)	0.0308 (18)	0.0004 (14)	0.0085 (15)	0.0014 (14)
C8	0.037 (2)	0.0308 (18)	0.0375 (19)	0.0024 (16)	0.0188 (17)	-0.0044 (16)
O1	0.0597 (18)	0.0337 (14)	0.0289 (13)	-0.0022 (13)	-0.0007 (13)	-0.0016 (11)
O2	0.0629 (19)	0.0320 (14)	0.0475 (15)	-0.0064 (13)	0.0303 (15)	-0.0005 (12)
S1	0.0328 (5)	0.0319 (5)	0.0450 (5)	-0.0072 (4)	0.0030 (4)	0.0015 (4)
S2	0.0334 (5)	0.0295 (4)	0.0240 (4)	-0.0052 (4)	0.0082 (4)	-0.0003 (3)

S5	0.0448 (6)	0.0306 (4)	0.0256 (4)	-0.0044 (4)	0.0075 (4)	-0.0008 (3)
S6	0.0432 (6)	0.0337 (5)	0.0331 (5)	-0.0064 (4)	0.0116 (4)	-0.0095 (4)
Se1	0.0484 (2)	0.02951 (19)	0.02304 (17)	-0.00266 (16)	0.00823 (15)	-0.00313 (14)
Se2	0.0296 (2)	0.0350 (2)	0.0410 (2)	-0.00724 (16)	0.00564 (16)	0.00402 (16)

Geometric parameters (Å, °)

C1—O1	1.203 (4)	C5—H5A	0.9800
C1—S2	1.759 (4)	C5—H5B	0.9800
C1—S1	1.765 (4)	C5—H5C	0.9800
C2—C3	1.335 (5)	C6—C7	1.346 (5)
C2—S2	1.739 (3)	C6—S6	1.733 (4)
C2—Se1	1.898 (4)	C7—S5	1.741 (3)
C3—C4	1.499 (5)	C7—Se2	1.895 (3)
C3—S1	1.742 (4)	C8—O2	1.202 (4)
C4—H4A	0.9800	C8—S6	1.763 (4)
C4—H4B	0.9800	C8—S5	1.769 (4)
C4—H4C	0.9800	Se1—Se2	2.3397 (7)
C5—C6	1.498 (5)		
O1—C1—S2	124.6 (3)	C6—C5—H5C	109.5
O1—C1—S1	123.2 (3)	H5A—C5—H5C	109.5
S2—C1—S1	112.15 (19)	H5B—C5—H5C	109.5
C3—C2—S2	118.9 (3)	C7—C6—C5	127.9 (3)
C3—C2—Se1	124.8 (3)	C7—C6—S6	116.0 (3)
S2—C2—Se1	116.29 (19)	C5—C6—S6	116.1 (3)
C2—C3—C4	127.6 (3)	C6—C7—S5	118.1 (3)
C2—C3—S1	115.4 (3)	C6—C7—Se2	123.7 (3)
C4—C3—S1	117.0 (3)	S5—C7—Se2	118.23 (18)
C3—C4—H4A	109.5	O2—C8—S6	123.4 (3)
C3—C4—H4B	109.5	O2—C8—S5	124.7 (3)
H4A—C4—H4B	109.5	S6—C8—S5	111.8 (2)
C3—C4—H4C	109.5	C3—S1—C1	97.42 (17)
H4A—C4—H4C	109.5	C2—S2—C1	96.07 (17)
H4B—C4—H4C	109.5	C7—S5—C8	96.36 (17)
C6—C5—H5A	109.5	C6—S6—C8	97.68 (17)
C6—C5—H5B	109.5	C7—Se2—Se1	99.23 (10)
H5A—C5—H5B	109.5	C2—Se1—Se2	98.40 (10)

Hydrogen-bond geometry (Å, °)

<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>
C4—H4A \cdots Se1	0.98	2.84	3.354 (4)	114
C5—H5A \cdots Se2	0.98	2.83	3.341 (4)	114
C4—H4B \cdots O1 ⁱ	0.98	2.55	3.369 (5)	141
C5—H5C \cdots Se1 ⁱⁱ	0.98	3.14	3.801 (4)	126

C5—H5C···S5 ⁱⁱⁱ	0.98	3.04	3.850 (4)	141
C4—H4C···S2 ^{iv}	0.98	3.13	3.992 (4)	148

Symmetry codes: (i) $-x+1, y-1/2, -z+1/2$; (ii) $x, -y+3/2, z-1/2$; (iii) $-x+2, -y+1, -z+1$; (iv) $-x+1, -y+2, -z+1$.

4,4'-(Diselanane-1,2-diyl)bis(5-methyl-2H-1,3-dithiol-2-one) (it14ii)

Crystal data

$C_8H_6O_2S_6$	$F(000) = 664$
$M_r = 326.49$	$D_x = 1.749 \text{ Mg m}^{-3}$
Monoclinic, $P2_1/c$	Mo $K\alpha$ radiation, $\lambda = 0.71073 \text{ \AA}$
Hall symbol: $-P 2ybc$	Cell parameters from 13753 reflections
$a = 10.845 (2) \text{ \AA}$	$\theta = 6.4\text{--}58.5^\circ$
$b = 9.0387 (18) \text{ \AA}$	$\mu = 1.08 \text{ mm}^{-1}$
$c = 13.370 (3) \text{ \AA}$	$T = 170 \text{ K}$
$\beta = 108.95 (3)^\circ$	Plate, yellow
$V = 1239.6 (4) \text{ \AA}^3$	$0.50 \times 0.20 \times 0.001 \text{ mm}$
$Z = 4$	

Data collection

STOE IPDS2T diffractometer	13324 measured reflections
Radiation source: fine-focus sealed tube	3344 independent reflections
Detector resolution: $6.67 \text{ pixels mm}^{-1}$	2636 reflections with $I > 2\sigma(I)$
ω scans	$R_{\text{int}} = 0.034$
Absorption correction: numerical face indexed	$\theta_{\text{max}} = 29.2^\circ, \theta_{\text{min}} = 3.2^\circ$
$T_{\text{min}} = 0.771, T_{\text{max}} = 0.942$	$h = -14 \rightarrow 11$
	$k = -12 \rightarrow 12$
	$l = -18 \rightarrow 18$

Refinement

Refinement on F^2	Secondary atom site location: difference Fourier map
Least-squares matrix: full	Hydrogen site location: inferred from neighbouring sites
$R[F^2 > 2\sigma(F^2)] = 0.027$	H-atom parameters constrained
$wR(F^2) = 0.064$	$w = 1/[\sigma^2(F_o^2) + (0.031P)^2 + 0.2272P]$
$S = 1.03$	where $P = (F_o^2 + 2F_c^2)/3$
3344 reflections	$(\Delta/\sigma)_{\text{max}} = 0.001$
147 parameters	$\Delta\rho_{\text{max}} = 0.36 \text{ e \AA}^{-3}$
0 restraints	$\Delta\rho_{\text{min}} = -0.34 \text{ e \AA}^{-3}$
Primary atom site location: structure-invariant direct methods	

Special details

Experimental. (*X-RED32* and *X-SHAPE*; Stoe, 2010)

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.

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 $F^2 > 2\sigma(F^2)$ 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 (\AA^2)

	<i>x</i>	<i>y</i>	<i>z</i>	$U_{\text{iso}}^*/U_{\text{eq}}$
C1	0.56140 (18)	0.97691 (18)	0.25987 (13)	0.0303 (3)
C2	0.68624 (16)	0.94540 (18)	0.46161 (11)	0.0264 (3)
C3	0.58060 (16)	0.85986 (19)	0.44516 (12)	0.0283 (3)
C4	0.54816 (19)	0.7632 (2)	0.52398 (15)	0.0377 (4)
H4A	0.616846	0.771796	0.592700	0.057*
H4B	0.541661	0.660179	0.500052	0.057*
H4C	0.464737	0.794436	0.530838	0.057*
C5	0.8123 (2)	0.6221 (2)	0.36279 (14)	0.0432 (4)
H5A	0.856072	0.716664	0.361746	0.065*
H5B	0.718458	0.633249	0.326446	0.065*
H5C	0.847281	0.546622	0.326768	0.065*
C6	0.83515 (16)	0.5762 (2)	0.47454 (13)	0.0310 (3)
C7	0.89133 (16)	0.6551 (2)	0.56261 (13)	0.0298 (3)
C8	0.82334 (18)	0.4069 (2)	0.63253 (14)	0.0345 (4)
O1	0.52663 (15)	1.00821 (15)	0.16765 (9)	0.0419 (3)
O2	0.80246 (16)	0.30792 (16)	0.68404 (11)	0.0476 (3)
S1	0.47149 (4)	0.85968 (5)	0.31651 (4)	0.03579 (11)
S2	0.70545 (4)	1.04272 (5)	0.35471 (3)	0.02809 (9)
S3	0.80927 (5)	0.96538 (5)	0.58353 (3)	0.03365 (10)
S4	0.95479 (4)	0.83296 (5)	0.56233 (4)	0.03649 (11)
S5	0.89988 (5)	0.57621 (5)	0.68428 (3)	0.03564 (11)
S6	0.78190 (5)	0.40033 (5)	0.49318 (3)	0.03672 (11)

Atomic displacement parameters (\AA^2)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
C1	0.0363 (9)	0.0215 (8)	0.0301 (7)	0.0009 (6)	0.0065 (6)	-0.0033 (6)
C2	0.0309 (8)	0.0246 (8)	0.0253 (7)	0.0014 (6)	0.0113 (6)	-0.0017 (6)
C3	0.0306 (8)	0.0246 (8)	0.0321 (7)	0.0016 (6)	0.0136 (6)	-0.0012 (6)
C4	0.0428 (10)	0.0325 (9)	0.0453 (9)	-0.0018 (8)	0.0247 (8)	0.0031 (7)
C5	0.0495 (11)	0.0536 (12)	0.0298 (8)	0.0029 (9)	0.0174 (8)	-0.0026 (8)
C6	0.0253 (8)	0.0377 (9)	0.0321 (7)	0.0022 (7)	0.0125 (6)	-0.0032 (7)
C7	0.0232 (7)	0.0338 (9)	0.0313 (7)	0.0011 (6)	0.0075 (6)	-0.0001 (6)
C8	0.0353 (9)	0.0333 (9)	0.0383 (8)	0.0016 (7)	0.0164 (7)	-0.0036 (7)
O1	0.0567 (9)	0.0324 (7)	0.0277 (6)	-0.0020 (6)	0.0014 (6)	-0.0005 (5)
O2	0.0646 (10)	0.0338 (7)	0.0514 (8)	-0.0031 (7)	0.0285 (7)	0.0010 (6)
S1	0.0296 (2)	0.0294 (2)	0.0422 (2)	-0.00548 (17)	0.00317 (17)	0.00138 (17)
S2	0.0311 (2)	0.0284 (2)	0.02544 (17)	-0.00528 (16)	0.01009 (15)	-0.00122 (14)
S3	0.0417 (2)	0.0317 (2)	0.02435 (17)	-0.00303 (18)	0.00641 (16)	-0.00476 (15)
S4	0.0255 (2)	0.0372 (2)	0.0426 (2)	-0.00639 (17)	0.00532 (17)	0.00179 (18)
S5	0.0422 (2)	0.0332 (2)	0.02811 (18)	-0.00173 (18)	0.00668 (16)	-0.00185 (16)
S6	0.0386 (2)	0.0352 (2)	0.0367 (2)	-0.00491 (18)	0.01269 (18)	-0.01011 (17)

Geometric parameters (Å, °)

C1—O1	1.200 (2)	C5—H5A	0.9800
C1—S2	1.7652 (19)	C5—H5B	0.9800
C1—S1	1.7682 (19)	C5—H5C	0.9800
C2—C3	1.340 (2)	C6—C7	1.342 (2)
C2—S2	1.7473 (16)	C6—S6	1.7363 (19)
C2—S3	1.7486 (17)	C7—S4	1.7494 (18)
C3—C4	1.496 (2)	C7—S5	1.7507 (17)
C3—S1	1.7426 (18)	C8—O2	1.195 (2)
C4—H4A	0.9800	C8—S6	1.7700 (18)
C4—H4B	0.9800	C8—S5	1.7710 (19)
C4—H4C	0.9800	S3—S4	2.0723 (7)
C5—C6	1.492 (2)		
O1—C1—S2	124.61 (15)	C6—C5—H5C	109.5
O1—C1—S1	123.25 (15)	H5A—C5—H5C	109.5
S2—C1—S1	112.13 (9)	H5B—C5—H5C	109.5
C3—C2—S2	118.62 (12)	C7—C6—C5	127.68 (18)
C3—C2—S3	124.44 (12)	C7—C6—S6	115.98 (13)
S2—C2—S3	116.93 (10)	C5—C6—S6	116.34 (14)
C2—C3—C4	127.26 (16)	C6—C7—S4	123.61 (14)
C2—C3—S1	115.65 (12)	C6—C7—S5	118.09 (14)
C4—C3—S1	117.07 (13)	S4—C7—S5	118.30 (10)
C3—C4—H4A	109.5	O2—C8—S6	123.42 (15)
C3—C4—H4B	109.5	O2—C8—S5	125.06 (15)
H4A—C4—H4B	109.5	S6—C8—S5	111.52 (10)
C3—C4—H4C	109.5	C3—S1—C1	97.47 (8)
H4A—C4—H4C	109.5	C2—S2—C1	96.03 (8)
H4B—C4—H4C	109.5	C2—S3—S4	101.38 (6)
C6—C5—H5A	109.5	C7—S4—S3	102.29 (6)
C6—C5—H5B	109.5	C7—S5—C8	96.44 (8)
H5A—C5—H5B	109.5	C6—S6—C8	97.92 (8)

Hydrogen-bond geometry (Å, °)

<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>
C4—H4A \cdots S3	0.98	2.76	3.244 (2)	111
C5—H5A \cdots S4	0.98	2.75	3.234 (2)	111
C4—H4B \cdots O1 ⁱ	0.98	2.53	3.345 (2)	141
C5—H5C \cdots S3 ⁱⁱ	0.98	3.14	3.8063 (19)	126
C5—H5C \cdots S5 ⁱⁱⁱ	0.98	3.01	3.825 (2)	142
C4—H4C \cdots S2 ^{iv}	0.98	3.12	4.021 (2)	153

Symmetry codes: (i) $-x+1, y-1/2, -z+1/2$; (ii) $x, -y+3/2, z-1/2$; (iii) $-x+2, -y+1, -z+1$; (iv) $-x+1, -y+2, -z+1$.