2-{[(Dodecylsulfanyl)carbonothioyl]sulfanyl}-2-methylpropanoic acid: a chain of edge-fused $R_2^2(8)$ and $R_4^4(20)$ rings built from O—H⋯O and C—H⋯O hydrogen bonds

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In the title compound, $C_{17}H_{32}O_2S_3$, the dodecyl chain and the trithiocarbonate unit adopt a nearly planar all-*trans* conformation, while the carboxyl group is synclinal to this chain direction. The molecules are linked by pairs of inversion-related O—H⋯O hydrogen bonds to form centrosymmetric dimers of $R_2^2(8)$ type, and dimers related by translation are linked by C—H⋯O hydrogen bonds to form a chain of edge-fused rings, or a molecular ladder, containing alternating $R_2^2(8)$ and $R_4^4(20)$ rings.

Comment

The strong affinity of gold for sulfur makes sulfur derivatives attractive possibilities for use as reagents for the production of gold nanoparticles, which themselves have wide-ranging potential applications in areas as diverse as biology, catalysis and nanotechnology (Daniel & Astruc, 2004). We report here the molecular and supramolecular structure of 2-{[(dodecylsulfanyl)carbonothioyl]sulfanyl}-2-methylpropanoic acid, (I), which was synthesized for use in this way.

The dodecyl chain in (I) (Fig. 1) adopts an almost planar all-*trans* conformation, as shown by the leading torsion angles (Table 1). For the chain fragment between atoms S5 and C17, the maximum deviation of the skeletal torsion angles from 180° is less than 1.5°, and the maximum deviation from the mean plane through the non-H atoms between S5 and C17 is only 0.038 (3)°, for atom C6. In addition, the chain fragment between atoms S5 and C22 also adopts a nearly planar all-*trans* conformation, with the torsion angles along this chain all within 12° of 180°. It is interesting to note the asymmetric orientation of the –CMe₂COOH fragment relative to the trithiocarbonate unit and the hydrocarbon chain, with the

carboxyl group synclinal (*gauche*) to the extended chain; this can probably be attributed to the intermolecular hydrogen bonding (see below).

(I)

(II), ROGHOL

(III), ZENTAN
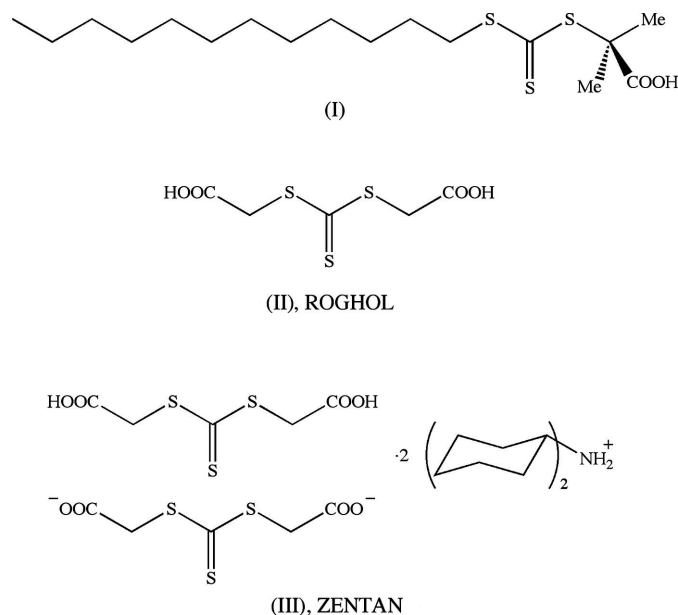
The bond distances and angles (Table 1) in the trithiocarbonate fragment are very similar to those found in compound (II) [Cambridge Structural Database (CSD; Allen, 2002) refcode ROGHOL; Zeng *et al.*, 2008], where the molecules lie across a twofold rotation axis in the space group $C2/c$, with distances C=S = 1.634 (3) Å and C—S = 1.7438 (18) Å, and angles S—C=S = 125.75 (7)° and S—C—S^i 108.50 (15)° [symmetry code: (i) $1 - x, y, \frac{1}{2} - z$]. The C—O

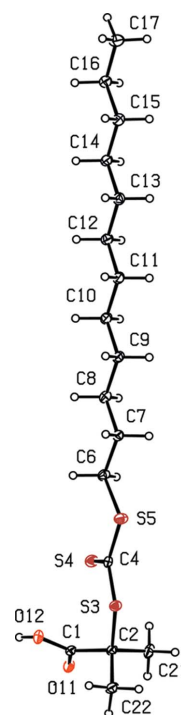**Figure 1**
The molecular structure of (I), showing the atom-labelling scheme. Displacement ellipsoids are drawn at the 30% probability level.

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distances in (I) are consistent with the position of the fully ordered hydroxy H atom as located in a difference map. Very similar geometries but at slightly lower precision were found for the corresponding fragments in both the neutral and the anionic components of compound (III) (CSD refcode ZENTAN; Ng, 1995). In (III), which was reported in the nonstandard $P2/a$ setting of the space group $P2/c$, the neutral and anionic components in the selected asymmetric unit lie across the twofold rotation axes along $(\frac{3}{4}, y, 0)$ and $(\frac{3}{4}, y, \frac{1}{2})$, respectively, so that the asymmetric unit comprises one-half of each of the S-containing components together with one cation, although the original report does not specify the imposed symmetry and its scheme implies the presence of two independent cations.

The supramolecular aggregation in (I) is determined by one O—H···O hydrogen bond and one rather weak C—H···O hydrogen bond (Table 2). The only other short intermolecular contacts all involve C—H bonds from the two methyl groups containing atoms C21 and C22. These bonds are of low acidity and the methyl groups are likely to be undergoing very fast rotation about the C2—C21 and C2—C22 bonds, respectively. Hence, the intermolecular contacts involving these methyl groups are not regarded as structurally significant.

The O—H···O hydrogen bond links pairs of inversion-related molecules to form cyclic centrosymmetric dimers containing the $R_2^2(8)$ motif (Bernstein *et al.*, 1995) so characteristic of simple carboxylic acids (Fig. 2). Dimers of this type, related to one another by translation, are linked by the C—H···O hydrogen bond to form a chain of edge-fused rings running parallel to the [100] direction, which can alternatively be regarded as a molecular ladder, and in which $R_2^2(8)$ rings centred at $(n + \frac{1}{2}, \frac{1}{2}, \frac{1}{2})$, where n represents an integer, alternate with $R_4^4(20)$ rings centred at $(n, \frac{1}{2}, \frac{1}{2})$, where n again represents an integer (Fig. 2). One ladder of this type passes through each unit cell, but there are no direction-specific interactions between adjacent chains.

The formation of the ladder in (I), containing two types of ring motif, may be contrasted with that in (II), where the unique O—H···O hydrogen bond generates a ladder containing a single type of $R_2^2(20)$ ring (Zeng *et al.*, 2008). The hydrogen bonding in (III), on the other hand, is rather more problematic, in terms of both the location of one of the H atoms and the overall action of the hydrogen bonds.

Although the coordinates of the H atom bonded to an O atom in (III) were refined, and although the structure was described (Ng, 1995) in terms of a neutral acid component and a dianionic component, the interatomic distances do not readily sustain such a description. In the component described as anionic, the two independent C—O distances are 1.224 (4) and 1.266 (4) Å, while in the component described as neutral these distances are 1.225 (4) and 1.283 (4) Å. However, for a fully ionized carboxylate anion, the two C—O distances are expected to be essentially identical, while in an un-ionized carboxylic acid the C—O distances typically differ by *ca* 0.10 Å, as found here for (I). By contrast, in (III), the corresponding distances in the two independent components are remarkably similar. In addition, the refined O—H distance is
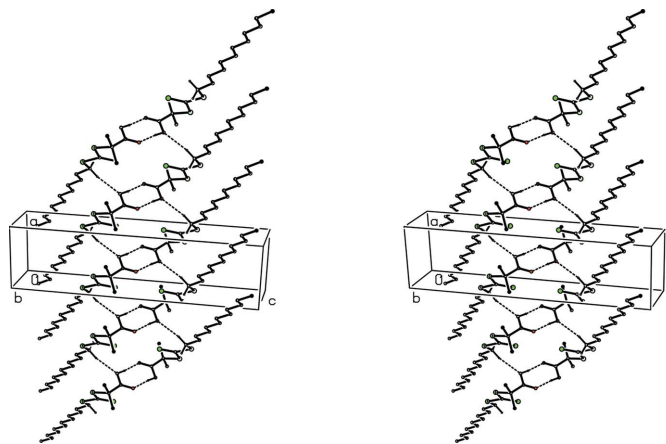

Figure 2
A stereoview of part of the crystal structure of (I), showing the formation of a hydrogen-bonded ladder along [100] containing alternating $R_2^2(8)$ and $R_4^4(20)$ rings. For the sake of clarity, H atoms bonded to C atoms which are not involved in the motifs shown have been omitted.

1.17 (6) Å, while the H···O and O···O distances in the hydrogen bond linking the neutral and anionic components are 1.28 (6) and 2.448 (3) Å, respectively, with no significant difference between the reported O—H and H···O distances. The overall geometry suggests two possibilities other than the fully ordered structure actually reported: either the acidic H atom could be disordered over two sites, or, more plausibly in view of the short O···O distance, the H atom is located at the mid-point of the O···O vector within the hydrogen bond. In this latter case, no chemical distinction could be made between the two independent carboxyl components. Without the reflection data (the FCF data are deposited in printed-journal format rather than in CIF format), it is not possible to establish which of the various possibilities provides the best model, but the ambiguities need to be borne in mind in the following discussion, which is based upon the reported atomic coordinates using a description in terms of neutral and dianionic S-containing components.

In the original report on (III) (Ng, 1995), no details of the hydrogen bonds were provided, and no description or analysis of their actions was provided beyond the statement that the hydrogen-bonded network was three-dimensional. Analysis of the structure of (III) using the reported atomic coordinates shows that the hydrogen-bonded structure is, in fact, two-dimensional, not three-dimensional. A single O—H···O hydrogen bond links the neutral and anionic components into chains running parallel to the [001] direction. The chain containing the reference components is propagated by means of the twofold rotation axes at $x = \frac{3}{4}$, and this chain is linked by the cations to the two analogous chains which are propagated by the twofold rotation axes at $x = \frac{1}{4}$ and $x = \frac{5}{4}$, respectively, so forming a sheet built from two types of $R_6^6(32)$ ring, both of them centrosymmetric, and lying parallel to (010) (Fig. 3). Within this sheet, each neutral component acts as a twofold donor to anions *via* O—H···O hydrogen bonds and as a twofold acceptor from cations *via* N—H···O hydrogen bonds. Each anion acts as a fourfold acceptor, from two neutral acid units *via* O—H···O hydrogen bonds and from two cations *via*
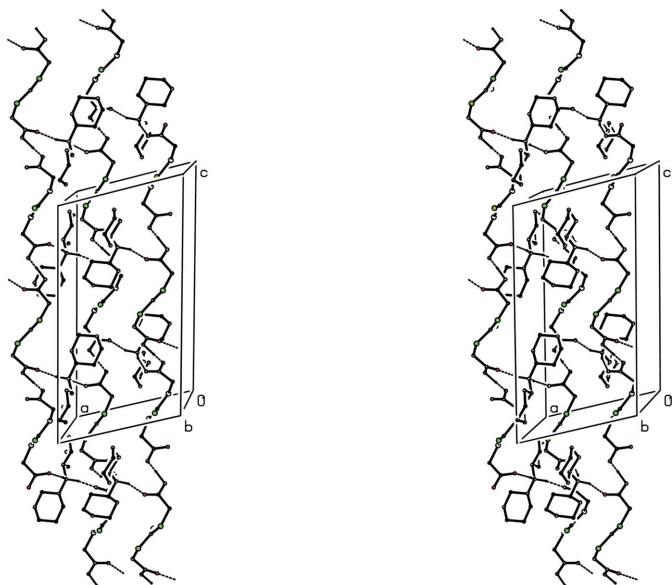
Figure 3
A stereoview of part of the crystal structure of (III) (CSD refcode ZENTAN; Ng, 1995), showing the formation of a hydrogen-bonded sheet containing $R_6^6(32)$ rings and lying parallel to (010). The original atomic coordinates have been used and, for the sake of clarity, H atoms not involved in the motifs shown have been omitted.

Table 1
Selected geometric parameters (Å, °).

C1—O11	1.210 (3)	C4—S4	1.624 (3)
C1—O12	1.310 (3)	C4—S5	1.736 (3)
C2—S3	1.822 (3)	S5—C6	1.796 (3)
S3—C4	1.737 (3)		
S3—C4—S4	126.53 (18)	S3—C4—S5	107.25 (16)
S4—C4—S5	126.22 (18)		
O11—C1—C2—S3	150.7 (2)	S5—C6—C7—C8	179.6 (2)
O12—C1—C2—S3	−34.9 (3)	C6—C7—C8—C9	178.8 (2)
C21—C2—S3—C4	69.2 (2)	C7—C8—C9—C10	179.7 (2)
C1—C2—S3—C4	−55.9 (2)	C8—C9—C10—C11	179.1 (2)
C22—C2—S3—C4	−172.00 (19)	C9—C10—C11—C12	179.0 (2)
C2—S3—C4—S4	11.7 (2)	C10—C11—C12—C13	179.5 (2)
C2—S3—C4—S5	−168.94 (14)	C11—C12—C13—C14	−179.2 (2)
S4—C4—S5—C6	8.9 (2)	C12—C13—C14—C15	−179.6 (3)
S3—C4—S5—C6	−170.49 (14)	C13—C14—C15—C16	−179.6 (3)
C4—S5—C6—C7	−173.8 (2)	C14—C15—C16—C17	179.3 (2)

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

D—H$\cdots A$	D—H	H$\cdots A$	$D\cdots A$	D—H$\cdots A$
O12—H12$\cdots$O11^i	0.82	1.82	2.638 (3)	173
C6—H6$A\cdots$O12^{ii}	0.99	2.53	3.486 (4)	162

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

N—H$\cdots$O hydrogen bonds. Each cation acts as a twofold donor in N—H$\cdots$O hydrogen bonds, one each to a neutral component and to an anion. It must be emphasized here that, while the details of the donor/acceptor behaviour of the individual carboxyl units will change if the model of the O—H$\cdots$O interactions is changed, the overall two-dimensional nature of the hydrogen-bonded structure will not change.

Thus, despite the much greater complexity in terms of the chemical constitution of (III) compared with (II), in each of them the hydrogen-bonded structure is two-dimensional. In (I), on the other hand, where the molecular units contain only a single carboxyl group, the hydrogen-bonded structure is only one-dimensional.

Experimental

Compound (I) was prepared by an adaptation of a reported procedure (Lai *et al.*, 2002). 1-Dodecanethiol (0.02 mol), acetone (0.166 mol) and tricaprylylmethylammonium chloride (0.0008 mol) were mixed under an N$_2$ atmosphere and cooled to 283 K. An aqueous solution (50%) of sodium hydroxide (0.021 mol) was added dropwise over a period of 20 min. The reaction was stirred for an additional 15 min, before a solution of carbon disulfide (0.020 mol) in acetone (0.034 mol) was added over a period of 20 min until the colour turned red. After 10 min, chloroform (0.030 mol) was added in one portion, followed by dropwise addition of a 50% aqueous solution of NaOH (0.1 mol) over a period of 30 min. The mixture was then stirred overnight. After this, water (30 ml) was added, followed by concentrated hydrochloric acid (5 ml) to acidify the solution. The resulting solid was collected by filtration and then stirred in propan-2-ol (50 ml). The resultant solution was concentrated under reduced pressure and the resulting solid product, (I), was recrystallized from hexane to afford pale-yellow crystals (yield 59%, m.p. 335–337 K).

Crystal data

C$_{17}$H$_{32}$O$_2$S$_3$	$\gamma = 68.34\ (4)°$
$M_r = 364.64$	$V = 988.5\ (9)$ Å^3
Triclinic, $P\bar{1}$	$Z = 2$
$a = 6.775\ (4)$ Å	Mo $K\alpha$ radiation
$b = 6.924\ (3)$ Å	$\mu = 0.38$ mm^{-1}
$c = 22.815\ (9)$ Å	$T = 120$ K
$\alpha = 84.69\ (3)°$	$0.40 \times 0.17 \times 0.10$ mm
$\beta = 84.73\ (5)°$	

Data collection

Bruker–Nonius KappaCCD area-detector diffractometer	22623 measured reflections
Absorption correction: multi-scan (*SADABS*; Sheldrick, 2003)	3689 independent reflections
$T_{min} = 0.839$, $T_{max} = 0.963$	2727 reflections with $I > 2\sigma(I)$
	$R_{int} = 0.076$

Refinement

$R[F^2 > 2\sigma(F^2)] = 0.051$	202 parameters
$wR(F^2) = 0.129$	H-atom parameters constrained
$S = 1.05$	$\Delta\rho_{max} = 0.55$ e Å^{-3}
3689 reflections	$\Delta\rho_{min} = -0.29$ e Å^{-3}

All H atoms were located in difference maps. H atoms bonded to C atoms were then treated as riding atoms in geometrically idealized positions, with C—H = 0.95 (aromatic), 0.98 (CH$_3$) or 0.99 Å (CH$_2$), and with U_{iso}(H) = kU_{eq}(C), where $k = 1.5$ for the methyl groups, which were permitted to rotate but not to tilt, and 1.2 otherwise. The O-bound H atom was permitted to ride at the location deduced from a difference map, with U_{iso}(H) = $1.5U_{eq}$(O), giving an O—H distance of 0.82 Å.

Data collection: *COLLECT* (Nonius, 1999); cell refinement: *DIRAX/LSQ* (Duisenberg *et al.*, 2000); data reduction: *EVALCCD* (Duisenberg *et al.*, 2003); program(s) used to solve structure: *SIR2004*

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: SK3394). Services for accessing these data are described at the back of the journal.

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