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S—H···S hydrogen-bond chain in thiosalicylic acid

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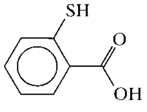
In crystalline thiosalicylic acid (2-mercaptobenzoic acid), $C_7H_6O_2S$, the carboxylic acid groups form hydrogen-bonded dimers, whereas the S—H groups form an infinite S—H···S—H···S—H hydrogen-bond chain, with an S···S distance of 3.986 (3) Å.

Comment

Although S—H is a classical hydrogen-bonding functional group, there is surprisingly little structural information on S—H···*X* hydrogen bonds. Even for the most common variant, S—H···O, the published material is scarce (Allen *et al.*, 1997). For all the other cases, like S—H···S, S—H···N, S—H···Cl$^-$, S—H···Ph *etc.*, there are only a handful of relevant crystal structures (surveyed by Desiraju & Steiner, 1999; see also Steiner, 1998; Rozenberg *et al.*, 1999). In this context, the crystal structure of thiosalicylic acid, (I), was determined. Initially, it was unclear which kind of hydrogen bond the S—H group would form (inter- or intramolecular; S—H···O or S—H···S).



(I)

The molecular structure of (I) in the crystal is shown in Fig. 1. The mercapto and carboxyl groups have normal geometries [C2—S1 = 1.766 (3), S1—H1 = 1.30 (5) Å and C2—S1—H1 = 95 (2)°; O1=C7 = 1.219 (4) and O2—C7 = 1.306 (4) Å]. No intramolecular S—H···O hydrogen bond is formed, but the S—H group is oriented away from the carboxylic acid moiety [torsion angle C1—C2—S1—H1 = 178 (2)°]. This contrasts with the oxygen analogue salicylic acid, where an intramolecular O—H···O=C hydrogen bond is formed with O···O = 2.62 Å (Sundaralingam & Jensen, 1965). The molecule of (I) is significantly non-planar, with the carboxylic acid group rotated 10.0 (2)° out of the aromatic plane. This way, the O1 atom is displaced by 0.131 (5) Å from the ring plane. Atom S1 is displaced from that plane in the opposite direction by −0.016 (4) Å. The angle C1—C2—S1 is widened to 122.1 (2)°. These distortions indicate significant steric repulsion between O1 and S1 [distance 2.752 (3) Å]. In order to understand why no intramolecular hydrogen bond is formed, one must consider that S···O distances in S—H···O hydrogen bonds have only been found longer than 3.2 Å (Desiraju & Steiner, 1999). A hypothetical S—H···O interaction with an S···O separation of around 2.75 Å would (if relatively linear) have an H···O distance so short that it is deep in the repulsive regime of the hydrogen-bond potential.

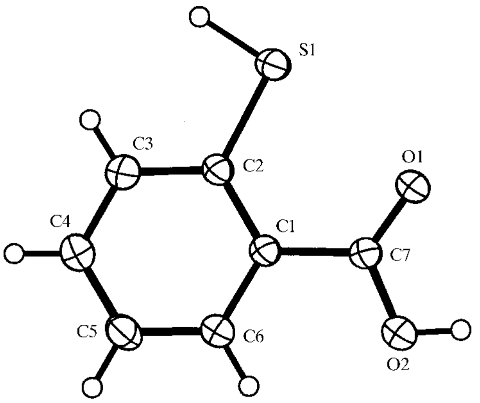


Figure 1
The molecular structure of (I) with displacement ellipsoids drawn at the 30% probability level.

The hydrogen-bond scheme that is actually formed in (I) is shown in Fig. 2 and geometrical parameters are listed in Table 1. The carboxylic acid groups form dimers with standard geometry [O···O = 2.657 (4) Å]. The S—H groups form an infinite S—H···S—H···S—H hydrogen-bond chain in the direction of the *y* axis, with distances S···S = 3.986 (3) Å and H···S = 2.72 (5) Å. Since the C—S—H group has refined almost to typical neutron diffraction geometry [*e.g.* S—H = 1.338 (2) Å and C—S—H = 96.9 (2)° in the neutron diffraction

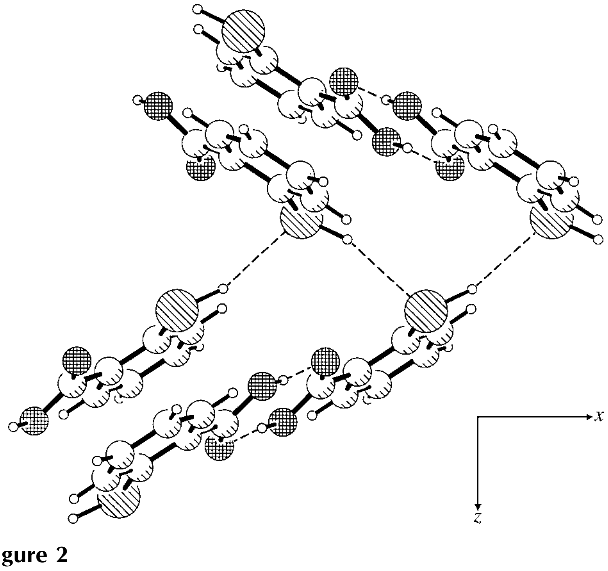


Figure 2
Section of the crystal packing illustrating the system of O—H···O and S—H···S hydrogen bonds. The S—H···S chain runs in the direction of the *y* axis, which is horizontal here. The projection plane is rotated by 10° around the *x* axis from the orientation shown.

study of *N*-acetyl-L-cysteine; Takusagawa *et al.*, 1981], the geometry in Table 1 is already realistic and normalization is unnecessary. The distances are similar to those in other S—H···S hydrogen bonds between poorly activated S—H groups, like in thiols and thiophenols (they can be considerably shorter between more polar S—H groups). The acceptor directionality is described by the angle H···S1—C2 of 76.1 (9)° and the torsion angle H···S1—C2—C1 of −81 (1)°, showing that the hydrogen bonds are directed at the 'sides' of the C—S—H acceptors. Two weak C—H···O hydrogen bonds are also formed (Table 1).

Experimental

Thiosalicylic acid, (I), was obtained from Aldrich and was recrystallized from MeOH by slow evaporation of the solvent.

Crystal data

$C_7H_6O_2S$
$M_r = 154.18$
Monoclinic, $P2_1/c$
$a = 7.856$ (7) Å
$b = 5.963$ (5) Å
$c = 14.940$ (11) Å
$\beta = 100.69$ (7)°
$V = 687.7$ (10) Å^3
$Z = 4$

$D_x = 1.489$ Mg m^{-3}
Mo $K\alpha$ radiation
Cell parameters from 34 reflections
$\theta = 7.2$–16.2°
$\mu = 0.396$ mm^{-1}
$T = 293$ (2) K
Plate, yellow
0.25 × 0.20 × 0.03 mm

Data collection

Stoe four-circle diffractometer
ω scans
1692 measured reflections
1580 independent reflections
1188 reflections with $I > 2\sigma(I)$
$R_{\rm int} = 0.043$
$\theta_{\rm max} = 27.50°$

$h = -10 \rightarrow 7$
$k = -7 \rightarrow 7$
$l = -19 \rightarrow 14$
3 standard reflections
frequency: 90 min
intensity decay: 5%

Table 1

Hydrogen-bonding geometry (Å, °).

D—H···A	D—H	H···A	D···A	D—H···A
O2—H2···O1$^{\rm i}$	0.91 (6)	1.75 (6)	2.657 (4)	174 (5)
S1—H1···S1$^{\rm ii}$	1.30 (5)	2.72 (5)	3.986 (3)	164 (3)
C5—H5···O1$^{\rm iii}$	0.93	2.66	3.584 (5)	171
C6—H6···O2$^{\rm iv}$	0.93	2.62	3.362 (5)	137

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

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.057$
$wR(F^2) = 0.171$
$S = 1.026$
1580 reflections
103 parameters
H atoms treated by a mixture of independent and constrained refinement

$w = 1/[\sigma^2(F_o^2) + (0.1042P)^2 + 0.1754P]$
where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{\rm max} < 0.001$
$\Delta\rho_{\rm max} = 0.53$ e Å^{-3}
$\Delta\rho_{\rm min} = -0.30$ e Å^{-3}

H atoms bonded to C atoms were treated in the default riding model; the H atoms bonded to O2 and S1 were located in difference Fourier calculations and refined isotropically. All H-atom displacement parameters refined to realistic values [H atoms bonded to C: 0.056–0.072 Å^2; H atoms bonded to O and S: 0.11 (1) and 0.09 (1) Å^2, respectively].

Program(s) used to solve structure: *SHELXS*86 (Sheldrick, 1985); program(s) used to refine structure: *SHELXL*97 (Sheldrick, 1997); molecular graphics: *PLATON* (Spek, 1990) and *ORTEP*II (Johnson, 1976); software used to prepare material for publication: *SHELXL*97.

Dr D. Lentz is thanked for providing access to the single-crystal diffractometer.

Supplementary data for this paper are available from the IUCr electronic archives (Reference: DE1138). Services for accessing these data are described at the back of the journal.

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