

## Hydrogen-bonded molecular ladders in *S*-(4-nitrophenyl)thioglycolic acid

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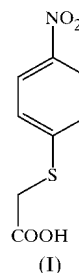
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Molecules of the title compound, [(4-nitrophenyl)sulfanyl]acetic acid, C<sub>8</sub>H<sub>7</sub>NO<sub>4</sub>S, are linked by paired O—H...O hydrogen bonds [H...O 1.81 Å, O...O 2.6456 (15) Å and O—H...O 178°] into centrosymmetric dimers containing an  $R_2^2(8)$  motif. A single C—H...O hydrogen bond having a nitro O atom as acceptor [H...O 2.47 Å, 3.3018 (19) Å and C—H...O 147°] links the dimers into a molecular ladder, and neighbouring ladders are weakly linked into sheets by aromatic  $\pi$ – $\pi$ -stacking interactions.

### Comment

Simple carboxylic acids containing the 4-nitrophenyl group exhibit a variety of supramolecular aggregation patterns. The simplest such acid, 4-nitrobenzoic acid, crystallizes in two polymorphic forms. In the  $P2_1/c$  polymorph (Groth, 1980), the molecules are linked by paired O—H...O hydrogen bonds into the dimeric unit so characteristic of carboxylic acids, and these dimers are linked into molecular ladders, or chains of fused  $R_2^2(8)$  and  $R_4^4(14)$  rings, generated by translation using a single C—H...O hydrogen bond in which the hydroxyl O atom of the carboxyl group is the acceptor. In the  $A2/a$  polymorph (Sakore & Pant, 1966; Tavale & Pant, 1971; Colapietro & Domenicano, 1977; Tonogaki *et al.*, 1993), the linking of the  $R_2^2(8)$  dimers is entirely different. The unique C—H...O hydrogen bond utilizes one of the nitro O atoms as acceptor, and the supramolecular structure consists of chains of alternating  $R_2^2(8)$  and  $R_2^2(10)$  rings, both types being centrosymmetric. In 4-nitrophenylacetic acid (Grabowski *et al.*, 1990), where there is an additional degree of conformational freedom, there are no significant C—H...O hydrogen bonds linking the carboxylic acid dimers, but instead these dimer units are weakly linked into sheets by aromatic  $\pi$ – $\pi$ -

stacking interactions. By contrast, neither polymorph of 4-nitrobenzoic acid exhibits any  $\pi$ – $\pi$ -stacking interactions. Seeking to introduce a further degree of conformational freedom, we have now investigated the supramolecular structure of *S*-(4-nitrophenyl)thioglycolic acid, O<sub>2</sub>NC<sub>6</sub>H<sub>4</sub>S-CH<sub>2</sub>COOH, (I), where both C—H...O hydrogen bonds and aromatic  $\pi$ – $\pi$ -stacking interactions occur.



The molecules of (I) (Fig. 1) are linked *via* a strong O—H...O hydrogen bond (Table 2) into the usual centrosymmetric dimer, characterized by an  $R_2^2(8)$  motif (Fig. 2) and located, for the sake of convenience, across the inversion centre at  $(\frac{1}{2}, \frac{1}{2}, \frac{1}{2})$ . The hydroxyl H atoms within the  $R_2^2(8)$  ring are fully localized, and this is reflected in the two independent C—O distances (Table 1), which are characteristic of double and single bonds, respectively.

The dimer units are linked by a single C—H...O hydrogen bond into molecular ladders. The aromatic C3 atom at  $(x, y, z)$  acts as a hydrogen-bond donor to the nitro O2 atom at  $(x, y - 1, z)$ , so generating by translation a  $C(6)$  chain running parallel to the [010] direction. Propagation of the two hydrogen bonds (Table 2) thus generates a molecular ladder along [010]. An antiparallel pair of  $C(6)$  chains form the uprights of the ladder, with the rungs being formed by the hydrogen-bonded  $(-SCH_2COOH)_2$  units. Within the ladder, there are  $R_2^2(8)$  rings centred at  $(\frac{1}{2}, n + \frac{1}{2}, \frac{1}{2})$  ( $n = \text{zero or integer}$ ) and  $R_4^4(36)$  rings centred at  $(\frac{1}{2}, n, \frac{1}{2})$  ( $n = \text{zero or integer}$ ). It is interesting to note that only one of the nitro O atoms acts as a hydrogen-bond acceptor, despite the excess of aromatic C—H bonds as potential donors.

Overall, the molecules of (I) are almost planar, as shown by the torsion angles (Table 1). Possibly associated with this, the aryl rings of neighbouring molecules are weakly linked by aromatic  $\pi$ – $\pi$ -stacking interactions. The aryl rings at  $(x, y, z)$

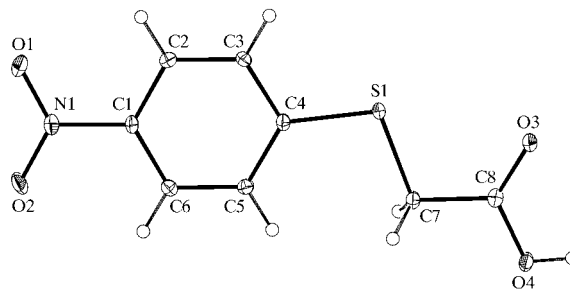
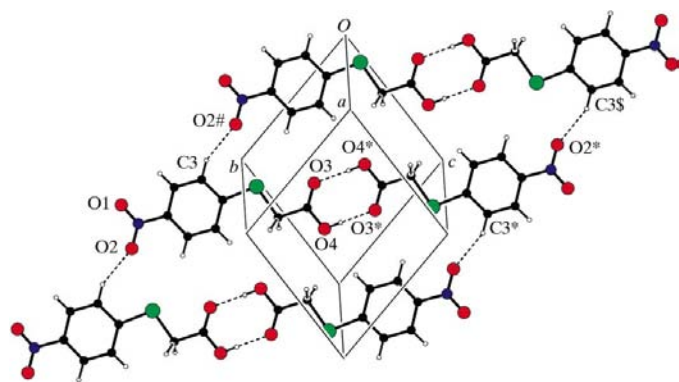


Figure 1

A view of the molecule of (I) showing the atom-labelling scheme. Displacement ellipsoids are drawn at the 30% probability level and H atoms are shown as small spheres of arbitrary radii.

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**Figure 2**

Part of the crystal structure of (I), showing the formation of a molecular ladder running along [010] and containing  $R_2^2(8)$  and  $R_4^4(36)$  rings. Atoms marked with an asterisk (\*), hash (#) or dollar sign (\$) are at the symmetry positions  $(1-x, 1-y, 1-z)$ ,  $(x, y-1, z)$  and  $(1-x, -y, 1-z)$ , respectively.

and at  $(-x, 3-y, -z)$  have an interplanar separation of 3.370 (2) Å and a centroid separation of 3.7992 (9) Å, corresponding to a centroid offset of 1.754 (2) Å. These two rings lie in the dimers centred at  $(\frac{1}{2}, \frac{1}{2}, \frac{1}{2})$  and  $(-\frac{1}{2}, \frac{5}{2}, -\frac{1}{2})$ , respectively, so giving rise to a  $\pi$ - $\pi$  chain along  $[\bar{1}2\bar{1}]$ . In combination with the [010] ladders, this interaction thus generates a sheet parallel to  $(10\bar{1})$ , so that the overall supramolecular structure is two-dimensional.

Within the molecule of (I), the S-C<sub>aryl</sub> distance is significantly less than the S-C<sub>methylene</sub> distance (Table 1), and the O-C-O and O-N-O angles are both significantly greater than 120°. The least expected feature of the internal molecular dimensions is found in the two exocyclic C-C-S angles, which differ by more than 10° (Table 1 and Fig. 1). However, the magnitude of the C-S-C angles is unexceptional. If the exocyclic C-C-S angles were dominated by the non-bonded H...H interactions between C5 and C7, it might be expected either that the C-S-C angle would be larger than normal or, more probably, that the aryl ring would simply rotate out of the C-S-C plane. The observed C-C-S angles thus have no simple interpretation.

## Experimental

Compound (I) was prepared by reaction of 4-nitrobenzenethiol with chloroacetic acid in the presence of triethylamine. Crystals of (I) suitable for single-crystal X-ray diffraction were grown by slow evaporation of a solution in ethanol.

### Crystal data

$C_8H_7NO_4S$	$Z = 2$
$M_r = 213.21$	$D_x = 1.649 \text{ Mg m}^{-3}$
Triclinic, $P\bar{1}$	Mo $K\alpha$ radiation
$a = 7.1540$ (3) Å	Cell parameters from 1902 reflections
$b = 7.8750$ (2) Å	$\theta = 3.2$ – $27.5^\circ$
$c = 8.0352$ (3) Å	$\mu = 0.36 \text{ mm}^{-1}$
$\alpha = 73.8820$ (16)°	$T = 150$ (2) K
$\beta = 85.7214$ (13)°	Block, yellow
$\gamma = 80.9841$ (15)°	$0.4 \times 0.2 \times 0.1 \text{ mm}$
$V = 429.29$ (3) Å <sup>3</sup>	

**Table 1**

Selected geometric parameters (Å, °).

S1—C4	1.7502 (14)	C8—O3	1.2203 (18)
S1—C7	1.7987 (15)	C8—O4	1.3144 (17)
S1—C4—C3	114.32 (11)	O3—C8—O4	123.84 (13)
S1—C4—C5	125.93 (11)	O1—N1—O2	123.40 (13)
C4—S1—C7	103.67 (7)		
O1—N1—C1—C2	6.7 (2)	C4—S1—C7—C8	−174.84 (10)
O2—N1—C1—C6	7.8 (2)	S1—C7—C8—O3	−3.79 (18)
C3—C4—S1—C7	179.23 (11)	S1—C7—C8—O4	176.42 (10)

**Table 2**

Hydrogen-bonding geometry (Å, °).

$D-H\cdots A$	$D-H$	$H\cdots A$	$D\cdots A$	$D-H\cdots A$
O4—H4 <sup>i</sup> ...O3 <sup>i</sup>	0.84	1.81	2.6456 (15)	178
C3—H3 <sup>i</sup> ...O2 <sup>ii</sup>	0.95	2.47	3.3018 (19)	147

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

### Data collection

Nonius KappaCCD area-detector diffractometer	1902 independent reflections
$\varphi$ scans, and $\omega$ scans with $\kappa$ offsets	1701 reflections with $I > 2\sigma(I)$
Absorption correction: multi-scan (DENZO-SMN; Otwinowski & Minor, 1997)	$R_{\text{int}} = 0.039$
$T_{\text{min}} = 0.869$ , $T_{\text{max}} = 0.965$	$\theta_{\text{max}} = 27.5^\circ$
5562 measured reflections	$h = -9 \rightarrow 9$
	$k = -10 \rightarrow 9$
	$l = -10 \rightarrow 10$

### Refinement

Refinement on $F^2$	$w = 1/[\sigma^2(F_o^2) + (0.0409P)^2 + 0.1827P]$
$R[F^2 > 2\sigma(F^2)] = 0.032$	where $P = (F_o^2 + 2F_c^2)/3$
$wR(F^2) = 0.089$	$(\Delta/\sigma)_{\text{max}} < 0.001$
$S = 1.08$	$\Delta\rho_{\text{max}} = 0.39 \text{ e \AA}^{-3}$
1902 reflections	$\Delta\rho_{\text{min}} = -0.28 \text{ e \AA}^{-3}$
128 parameters	
H-atom parameters constrained	

Compound (I) crystallized in the triclinic system; space group  $P\bar{1}$  was assumed and confirmed by the analysis. H atoms were treated as riding, with C—H distances of 0.95 (aromatic) or 0.99 Å (CH<sub>2</sub>), and an O—H distance of 0.84 Å.

Data collection: *KappaCCD Server Software* (Nonius, 1997); cell refinement: *DENZO-SMN* (Otwinowski & Minor, 1997); data reduction: *DENZO-SMN*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 1997); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *PLATON* (Spek, 2002); software used to prepare material for publication: *SHELXL97* and *PRPKAPPA* (Ferguson, 1999).

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: SK1535). Services for accessing these data are described at the back of the journal.

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