

# (4-Nitrophenylsulfinyl)acetic acid, a three-dimensional hydrogen-bonded framework built from a combination of two-centre O—H···O and C—H···O hydrogen bonds and a three-centre C—H···(O)<sub>2</sub> hydrogen bond

Christopher Glidewell,<sup>a\*</sup> John N. Low,<sup>b</sup> Janet M. S. Skakle<sup>b</sup> and James L. Wardell<sup>c</sup>

<sup>a</sup>School of Chemistry, University of St Andrews, St Andrews, Fife KY16 9ST, Scotland, <sup>b</sup>Department of Chemistry, University of Aberdeen, Meston Walk, Old Aberdeen AB24 3UE, Scotland, and <sup>c</sup>Instituto de Química, Departamento de Química Inorgânica, Universidade Federal do Rio de Janeiro, 21945-970 Rio de Janeiro, RJ, Brazil

Correspondence e-mail: cg@st-andrews.ac.uk

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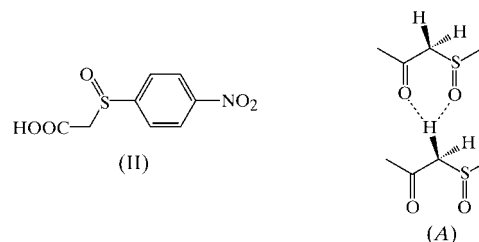
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Molecules of the title compound, C<sub>8</sub>H<sub>7</sub>NO<sub>5</sub>S, are linked into sheets by a combination of two-centre hydrogen bonds, one of type O—H···O [H···O = 1.81 Å, O···O = 2.648 (2) Å and O—H···O = 173°] and three of type C—H···O [H···O = 2.40–2.48 Å, C···O = 3.206 (3)–3.391 (3) Å and C—H···O = 131–160°]. These sheets are linked by an unusual three-centre C—H···(O)<sub>2</sub> hydrogen bond [H···O = 2.46 and 2.56 Å, C···O = 3.289 (3) and 3.351 (3) Å, and C—H···O = 141 and 137°], in which the two acceptors are carboxyl and sulfoxide O atoms.

## Comment

In (4-nitrophenylsulfonyl)acetic acid, O<sub>2</sub>NC<sub>6</sub>H<sub>4</sub>SCH<sub>2</sub>COOH, (I), the molecules are linked by paired O—H···O hydrogen bonds into dimers. These are further linked by C—H···O hydrogen bonds to form molecular ladders, which are themselves weakly linked into sheets by aromatic  $\pi$ - $\pi$ -stacking interactions (Glidewell *et al.*, 2002). Oxidation of this acid at the S atom to give (4-nitrophenylsulfinyl)acetic acid, O<sub>2</sub>NC<sub>6</sub>H<sub>4</sub>S(O)CH<sub>2</sub>COOH, (II), which contains three potential acceptors of hydrogen bonds (O=C, O=S and O=N), provides many other possibilities for the supramolecular aggregation, including the possible formation of O—H···O=S and C—H···O=S hydrogen bonds. We report here the molecular and supramolecular structure of (II) (Fig. 1), which contains, in addition to an O—H···O=S hydrogen

bond, a rather unusual three-centre C—H···(O)<sub>2</sub> hydrogen bond in which the two O-atom acceptors are bonded to C and S, respectively.



The single O—H···O hydrogen bond in (II) generates continuous chains, rather than the usual  $R_2^2(8)$  dimer so characteristic of carboxylic acids. Carboxyl atom O4 in the molecule at  $(x, y, z)$  acts as hydrogen-bond donor to sulfoxide atom O5 in the molecule at  $(-x, \frac{1}{2} + y, \frac{3}{2} - z)$ , so producing a  $C(6)$  chain running parallel to the [010] direction and generated by the  $2_1$  screw axis along  $(0, y, \frac{3}{4})$ . Three C—H···O hydrogen bonds link these  $C(6)$  chains into sheets. Atom C5 at  $(x, y, z)$  acts as hydrogen-bond donor to nitro atom O1 at  $(1 - x, \frac{1}{2} + y, \frac{1}{2} - z)$ , so producing a  $C(5)$  chain that is also parallel to [010] but this time is generated by the  $2_1$  screw axis along  $(\frac{1}{2}, y, \frac{1}{4})$ . The combination of these two chain motifs suffices to generate a sheet parallel to (101) that is reinforced by a second C—H···O hydrogen bond. Atom C6 at  $(x, y, z)$  acts as donor to nitro atom O2 at  $(x, 1 + y, z)$ , so generating by translation a  $C(6)$  chain that is again parallel to [010]. The (101) sheet thus consists of alternating strips of edge-fused  $R_3^3(12)$  rings, which are generated by screw axes at  $(\frac{1}{2}, y, \frac{1}{4})$  and translation-related sites, and similar strips of edge-fused  $R_3^3(22)$  rings, which are generated by screw axes along  $(0, y, \frac{3}{4})$  and translation-related sites (Fig. 2). Further reinforcement of the sheets is provided by another type of C—H···O hydrogen bond, in which the methylene C atom acts as the donor. Atom C7 in molecule at  $(x, y, z)$  acts as donor, *via* H72, to carboxyl atom O3 in the molecule at  $(-x, -\frac{1}{2} + y, \frac{3}{2} - z)$ , so producing a  $C(4)$  chain generated by the  $2_1$  screw axis along  $(0, y, \frac{3}{4})$  (Fig. 3).

Two (101) sheets pass through each unit cell, and adjacent sheets are linked by a chain along [001] that is generated by a nearly planar three-centre C—H···(O)<sub>2</sub> hydrogen bond; the sum of the angles at the H atom is 357°. Atom C7 in the molecule at  $(x, y, z)$  acts, *via* H71, as hydrogen-bond donor to both carboxyl atom O3 and sulfoxide atom O5, which are both

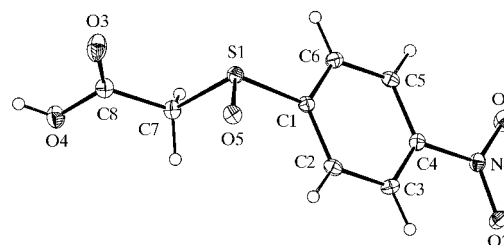
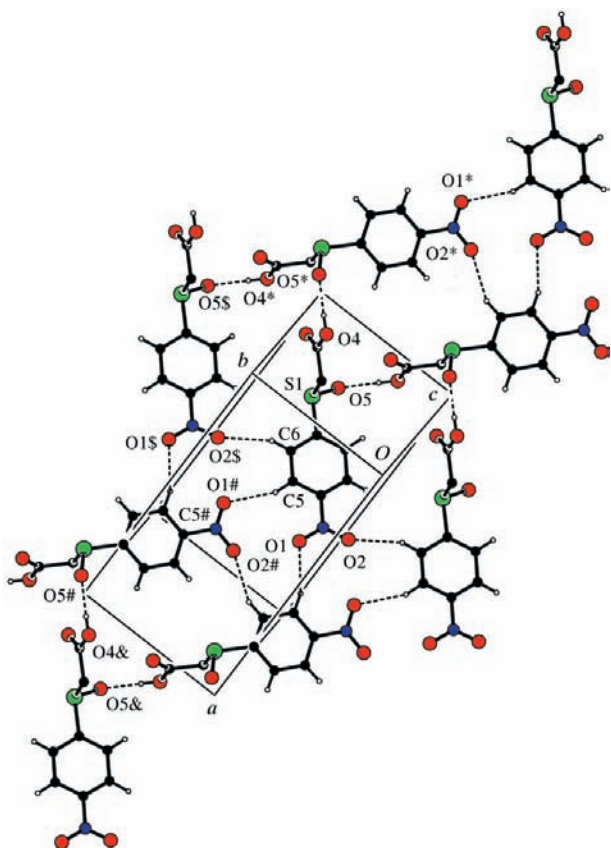


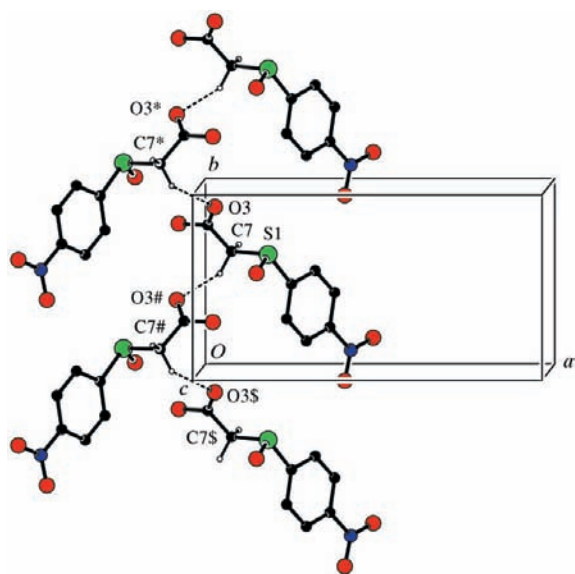
Figure 1

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



**Figure 2**

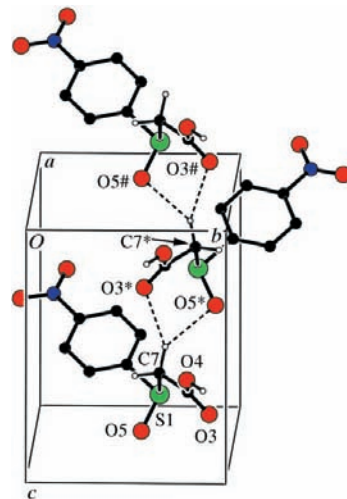
Part of the crystal structure of (II), showing the formation of a (101) hydrogen-bonded sheet built from  $R_3^3(12)$  and  $R_3^3(22)$  rings. Atoms marked with an asterisk (\*), hash (#), dollar sign (\$) or ampersand (&) are at the symmetry positions  $(-x, \frac{1}{2} + y, \frac{3}{2} - z)$ ,  $(1 - x, \frac{1}{2} + y, \frac{1}{2} - z)$ ,  $(x, 1 + y, z)$  and  $(1 + x, y, -1 + z)$ , respectively.



**Figure 3**

Part of the crystal structure of (II), showing the formation of a  $C(4)$  chain along [010]. Atoms marked with an asterisk (\*), hash (#) or dollar sign (\$) are at the symmetry positions  $(-x, \frac{1}{2} + y, \frac{3}{2} - z)$ ,  $(-x, -\frac{1}{2} + y, \frac{3}{2} - z)$  and  $(x, -1 + y, z)$ , respectively.

in the molecule at  $(x, \frac{3}{2} - y, -\frac{1}{2} + z)$ , so producing a  $C(4)C(4)[R_3^3(6)]$  chain of rings (Fig. 3) running parallel to [001] and generated by the  $c$ -glide plane at  $y = \frac{3}{4}$  (Fig. 4). This chain contains the uncommon supramolecular synthon (A) (see Scheme), in which a C—H bond acts as donor concurrently to carboxyl and sulfoxide O atoms.



**Figure 4**

Part of the crystal structure of (II), showing the formation of a chain of rings along [001]. Atoms marked with an asterisk (\*) or hash (#) are at the symmetry positions  $(x, \frac{3}{2} - y, -\frac{1}{2} + z)$  and  $(x, y, -1 + z)$ , respectively.

The combination of the (101) sheets and the [001] chains is sufficient to generate a single three-dimensional framework. However, in contrast to the supramolecular structure of (I), there are no  $\pi$ - $\pi$ -stacking interactions in (II). Note that while the sulfoxide O atom in (II) participates in an O—H $\cdots$ O hydrogen bond in preference to the other potential acceptors in the carboxyl and nitro groups, the C—H $\cdots$ O hydrogen bonds utilize all three types of O acceptor (Table 2).

Within the molecule of (II), the lengths of the three bonds to the S atom (Table 1) are all typical of their types (Allen *et al.*, 1987). The two C—O distances in the carboxyl group are entirely consistent with the location of the acid H atom as deduced from a difference map. Although the coordination around the S atom is sharply pyramidal, torsion angles C1—S1—C7—C8 and S1—C7—C8—O3/4 indicate that the molecular fragment running from C1 to the carboxyl O atoms O3 and O4 is nearly planar. By contrast, torsion angle C7—S1—C1—C2 indicates that the aryl ring is nearly orthogonal to the plane of the side chain, while the dihedral angle between the nitro group and the aryl ring is only 5.2 (2) Å.

## Experimental

Compound (I) was prepared by the reaction of 4-nitrobenzenethiol with chloroacetic acid in the presence of triethylamine. Compound (I) was then oxidized using 30% aqueous hydrogen peroxide in a two-phase water/dichloromethane system, thus producing a mixture of (II) and (4-nitrophenylsulfinyl)acetic acid, (III). Compound (II) was readily separable from this mixture by fractional crystallization from ethanol.

Crystal data

$C_8H_7NO_5S$	$D_x = 1.628 \text{ Mg m}^{-3}$
$M_r = 229.22$	Mo $K\alpha$ radiation
Monoclinic, $P2_1/c$	Cell parameters from 2124 reflections
$a = 13.7110 (7) \text{ \AA}$	$\theta = 3.2\text{--}27.5^\circ$
$b = 7.3037 (3) \text{ \AA}$	$\mu = 0.35 \text{ mm}^{-1}$
$c = 9.3537 (4) \text{ \AA}$	$T = 120 (2) \text{ K}$
$\beta = 93.088 (2)^\circ$	Plate, colourless
$V = 935.33 (7) \text{ \AA}^3$	$0.20 \times 0.15 \times 0.02 \text{ mm}$
$Z = 4$	

Data collection

Nonius KappaCCD diffractometer	2124 independent reflections
$\varphi$ scans, and $\omega$ scans with $\kappa$ offsets	1588 reflections with $I > 2\sigma(I)$
Absorption correction: multi-scan ( <i>DENZO-SMN</i> ; Otwinowski & Minor, 1997)	$R_{\text{int}} = 0.056$
$T_{\text{min}} = 0.923$ , $T_{\text{max}} = 0.993$	$\theta_{\text{max}} = 27.5^\circ$
7061 measured reflections	$h = -15 \rightarrow 17$
	$k = -9 \rightarrow 8$
	$l = -11 \rightarrow 12$

Refinement

Refinement on $F^2$	$w = 1/[\sigma^2(F_o^2) + (0.0526P)^2 + 0.33P]$
$R[F^2 > 2\sigma(F^2)] = 0.043$	where $P = (F_o^2 + 2F_c^2)/3$
$wR(F^2) = 0.110$	$(\Delta/\sigma)_{\text{max}} < 0.001$
$S = 1.02$	$\Delta\rho_{\text{max}} = 0.79 \text{ e \AA}^{-3}$
2124 reflections	$\Delta\rho_{\text{min}} = -0.35 \text{ e \AA}^{-3}$
144 parameters	
H-atom parameters constrained	

Compound (II) is monoclinic and the space group  $P2_1/c$  was uniquely assigned from the systematic absences. H atoms were treated as riding, with O—H distances of 0.84 Å and C—H distances of 0.95 (aromatic) or 0.99 Å (CH<sub>2</sub>).

Table 1

Selected geometric parameters (Å, °).

S1—C1	1.789 (2)	C8—O3	1.212 (3)
S1—C7	1.809 (2)	C8—O4	1.320 (3)
S1—O5	1.5045 (16)		
O5—S1—C1	107.08 (10)	S1—C1—C2	121.26 (17)
O5—S1—C7	106.57 (10)	S1—C1—C6	116.79 (16)
C1—S1—C7	96.54 (10)	O1—N4—O2	123.77 (18)
C1—S1—C7—C8	−175.84 (16)	C5—C4—N4—O1	5.6 (3)
C7—S1—C1—C2	−87.3 (2)	S1—C7—C8—O3	7.3 (3)
C3—C4—N4—O1	−175.0 (2)	S1—C7—C8—O4	−174.0 (2)

Table 2

Hydrogen-bonding geometry (Å, °).

$D-H \cdots A$	$D-H$	$H \cdots A$	$D \cdots A$	$D-H \cdots A$
O4—H4 $\cdots$ O5 <sup>i</sup>	0.84	1.81	2.648 (2)	173
C5—H5 $\cdots$ O1 <sup>ii</sup>	0.95	2.48	3.391 (3)	160
C6—H6 $\cdots$ O2 <sup>iii</sup>	0.95	2.40	3.286 (3)	155
C7—H71 $\cdots$ O3 <sup>iv</sup>	0.99	2.56	3.351 (3)	137
C7—H71 $\cdots$ O5 <sup>iv</sup>	0.99	2.46	3.289 (3)	141
C7—H72 $\cdots$ O3 <sup>v</sup>	0.99	2.47	3.206 (3)	131

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

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, 2003); 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: SK1614). Services for accessing these data are described at the back of the journal.

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