Table 3. *First- and basic second-level graph set descriptors involving hydrogen bonds designated a–h in order as given in Table 2*

	a	b	c	d	e	f	g	h
a	D	$D_2^2(6)$	$D_2^2(9)$	$C_1^1(9)$	$D_3^3(10)$	$D_2^2(10)$	$D_2^2(4)$	$D_2^2(4)$
b		S(6)	$D_1^1(3)$	$D_2^2(10)$	$D_2^2(9)$	$D_2^2(10)$	–	–
c			D	$D_2^2(10)$	$C_1^1(9)$	$C_1^1(9)$	$D_3^3(4)$	$D_3^3(4)$
d				D	$D_2^2(5)$	$D_2^2(5)$	$D_3^3(4)$	$D_3^3(4)$
e					D	$R_4^2(8)$	$D_2^1(3)$	$D_2^1(3)$
f						D	$D_2^1(3)$	$D_2^1(3)$
g							D	$R_4^2(8)$
h								D

Scan widths were $(1.50 + 0.35\tan\theta)°$ in ω, with a background/scan time-ratio of 0.5. The data were corrected for Lorentz and polarization effects. The Laue group assignment, systematic absences and centrosymmetric intensity statistics indicated space group $P2_1/a$ (No. 14); since refinement proceeded well it was adopted, but subsequently was transformed to the standard setting, $P2_1/c$. Fourier difference methods were used to locate the initial H-atom positions and the H atoms were then refined isotropically. The refined C—H distances range from 0.93 (2) to 0.98 (2) Å, with a mean value of 0.96 (1) Å; refined N—H and O—H distances are given in Table 2. Hydrogen-bond angles were recalculated, with H atoms fixed at 0.98 Å from the donors along the D—H direction determined in the final least-squares fit; these values, in square brackets, are shown in Table 2 after the best-fit values obtained with the refined H atom positions. The maximum effect of extinction is 12.4% of F_o for 0$\overline{1}$2. The maximum positive residual peak is located ~ 1.0 Å from O2; the maximum negative peak is located ~ 1.3 Å from N1.

Data collection: *MSC/AFC Diffractometer Control Software* (Molecular Structure Corporation, 1988). Cell refinement: *MSC/AFC Diffractometer Control Software*. Data reduction: *TEXSAN* (Molecular Structure Corporation, 1995). Program(s) used to solve structure: *SHELXS86* (Sheldrick, 1985). Program(s) used to refine structure: *TEXSAN*. Molecular graphics: *ORTEP*II (Johnson, 1976). Software used to prepare material for publication: *TEXSAN* and *PLATON* (Spek, 1990).

Supplementary data for this paper are available from the IUCr electronic archives (Reference: FR1127). Services for accessing these data are described at the back of the journal.

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(4R)-(−)-2-Thioxothiazolidine-4-carboxylic Acid (Raphanusamic Acid)

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Abstract

The title acid, $C_4H_5NO_2S_2$, crystallized in the non-centrosymmetric space group $P2_12_12_1$ with one molecule as the asymmetric unit. Two hydrogen bonds occur, namely, N—H···O, with a donor–acceptor distance of 2.850 (2) Å, and O—H···S (resonance induced), with a donor–acceptor distance of 3.318 (2) Å; both H atoms involved are ordered. These two types of bonds link a given molecule to four neighbors, the molecules linked being of space-group symmetry types 1 and 3, or 2 and 4. These two subsets of molecules alternate in layers along c. Three significant C—H···O interactions occur, one of which crosslinks the subsets just described to produce a three-dimensional network of linked molecules. The absolute structure is determined.

Comment

This report is one of a series on hydrogen bonding in heterocyclic carboxylic acids. It follows reports on 2-aminonicotinic acid and 3-aminopyrazole-4-carboxylic acid (Dobson & Gerkin, 1997, 1998). The title acid, (I), crystallized in the non-centrosymmetric space group $P2_12_12_1$ with a single molecule as the asymmetric unit.

HOOC—NH / S=S

(I)
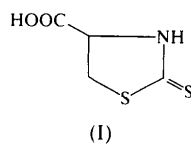
The refined molecule is shown in Fig. 1, together with the numbering scheme. In this structure, each molecule is linked with four neighbors by two types of hydrogen bond: N—H···O, with a donor–acceptor distance of 2.850 (2) Å, and O—H···S (resonance induced), with a donor–acceptor distance of 3.318 (2) Å. Further geometric details of these bonds are given in Table 2; they show that the H atoms involved in these hydrogen bonds (H1 and H3) are ordered. Hydrogen-bond graph-set analysis (Bernstein *et al.*, 1995) involving these two hydrogen bonds (for this purpose designated *a* and *b*, in the order given in Table 2) gives as descriptors for the first-level graph sets $C(7)$ for *a* and $C(5)$ for *b*, and for the basic second-level graph, $C_2^2(8)$. Thus, only chains occur; these propagate along **a** (2) or **b** (1). These hydrogen bonds link molecules into two distinct subsets consisting of space-group symmetry types 1 and 3, or 2 and 4. These subsets occur in alternating layers along **c**, as shown in the packing diagram (Fig. 2). These subsets are, however, crosslinked by one of the significant C—H···O interactions which occur in this structure and are delineated in Table 2. Thus, a three-dimensional network of linked molecules is formed.

For 38 examples of resonance-induced hydrogen bonding in $R_1R_2C=S\cdots H—(O$ or $N)$ systems, in which R_1 represents a three-bonded N atom [N3 in (I)] and R_2 represents a two-bonded S or O atom [S1 in (I)], Allen *et al.* (1997*a*) give the mean value of C=S as 1.674 (1) Å and of N—C as 1.327 (1) Å. In (I), these values are 1.661 (2) Å for C2=S2 and 1.322 (2) Å for N3—C2, in very good agreement with the cited means. Moreover, Allen *et al.* (1997*a*) give a mean value of 156 (2)° for the S···H—O angle in 71 cases of $R_1R_2C=S\cdots H—O$ (in which R_1 and R_2 are somewhat less restricted than above); in (I), this value is 160 (2)°.

For C_{sp^2}—S—C_{sp^2} systems [in (I), C2—S1—C5], Allen *et al.* (1997*b*) observe that, with N—H or O—H as potential hydrogen-bond donors, in only 2.8% of 372 such cases is hydrogen-bond formation observed. Considering that in (I), the nearest (N3—)H3 or (O1—)H1 atom lies 3.87 (2) Å from S1, hydrogen bonding involving S1 is not significant in this structure.

For further structural comparisons, the oxo analog, (4*R*)-oxothiazolidine-4-carboxylic acid (Keszler *et al.*, 1991) is of particular interest. Excluding the C2—S2 distance in (I) and its C—O analog in the oxo compound, the greatest difference in corresponding bond lengths for bonds listed in Table 1 is 0.023 Å, while the average difference is 0.008 Å. Similarly, the greatest difference in corresponding angles is 3.2°, while the average difference is 1.4°. Thus, the molecular
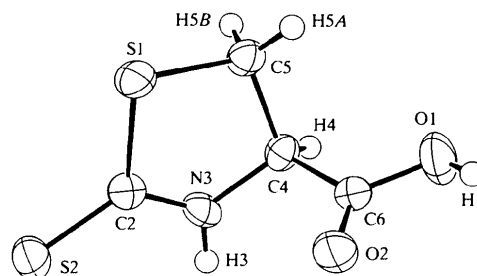

Fig. 1. *ORTEP*II (Johnson, 1976) drawing of (I) showing the atomic numbering scheme. Displacement ellipsoids are drawn at 50% probability for all atoms except H, which are shown as spheres of arbitrary radii.
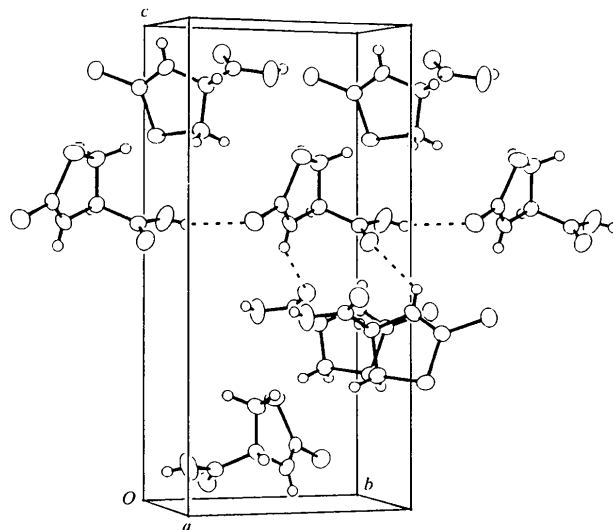

Fig. 2. *ORTEP*II (Johnson, 1976) packing diagram of (I) including a central acid molecule and the four molecules to which it is directly hydrogen bonded. Displacement ellipsoids are drawn at 50% probability for all atoms except H, which are shown as spheres of arbitrary radii. The four intermolecular hydrogen bonds are shown as dashed lines.

geometries are in close accord. Moreover, the hydrogen bonding is also quite similar, though the orthorhombic unit cells are apparently not related in a simple fashion, the unit-cell edges for the oxo compound being a = 5.968 (3), b = 17.945 (3) and c = 5.387 (3) Å. As in (I), there are two hydrogen bonds: an O—H···O(carbonyl) bond with an O···O distance of 2.62 Å, the analog of the O1—H1···S2^i bond in (I), and an N—H···O(carboxyl) bond, the analog of N3—H3···O2^{ii}, with an N···O distance of 2.96 Å [*versus* 2.850 (2) Å in (I)] (symmetry codes as in Table 2). As in (I), these hydrogen bonds form first-level $C(7)$ and $C(5)$ chains which, however, propagate along [10$\bar{1}$] and **a**, respectively. Also as in (I), the hydrogen bonds link molecules of space-group symmetry types 1 and 3, or 2 and 4.

Distances and angles of special interest in the title molecule are given in Table 1. The closest intermolecular approaches in this structure, excluding pairs of atoms in groups hydrogen bonded to each other, are between O2 and C4^v [symmetry code: (v) $\frac{1}{2} + x$, $\frac{3}{2} - y$, $1 - z$], and are 0.20 Å less than the corresponding van der Waals radius sum (Bondi, 1964). The molecules in which these atoms occur are, however, hydrogen bonded to each other.

Experimental

The title acid was obtained as a pale ecru powder of stated purity 99% from the Aldrich Chemical Company. Optical polarimetric measurements gave $[\alpha]_D^{16}$ $-88.7\,(8)^\circ$ (c = 0.25, H_2O), in good agreement with the stated value $[\alpha]_D^{29}$ -86° (c = 2.5, 0.5 N HCl). A portion of this solid was dissolved in water at room temperature and the solution was filtered. Room-temperature evaporation of the filtrate produced chunks, one of which was cut and coated with Apiezon grease to provide the experimental sample.

Crystal data

$C_4H_5NO_2S_2$	Mo $K\alpha$ radiation
M_r = 163.21	λ = 0.71073 Å
Orthorhombic	Cell parameters from 25
$P2_12_12_1$	reflections
a = 5.0309 (6) Å	θ = 15.8–17.3°
b = 7.7455 (6) Å	μ = 0.725 mm^{-1}
c = 16.276 (1) Å	T = 296 K
V = 634.2 (1) Å^3	Cut chunk
Z = 4	0.35 × 0.35 × 0.19 mm
D_x = 1.709 Mg m^{-3}	Colorless
D_m not measured	

Data collection

Rigaku AFC-5S diffractom-	1742 reflections with
eter	$I > 2\sigma_I$
ω scans	R_{int} = 0.008
Absorption correction:	θ_{max} = 30.06°
empirical ψ scan (North	$h = 0 \rightarrow 7$
et al., 1968)	$k = 0 \rightarrow 10$
T_{min} = 0.821, T_{max} = 0.871	$l = -22 \rightarrow 22$
2180 measured reflections	6 standard reflections
1848 independent reflections	every 150 reflections
	intensity variation:$\pm 1.2\%$

Refinement

Refinement on F^2	Extinction correction:
$R(F)$ = 0.025	Zachariasen (1963, 1968)
$wR(F^2)$ = 0.033	Extinction coefficient:
S = 2.15	31.2 (19) × 10^{-7}
1848 reflections	Scattering factors from
103 parameters	Stewart et al. (1965) (H)
All H atoms refined	and Creagh & McAuley
$w = 1/\sigma^2(F^2)$	(1992) (C, N, O, S)
$(\Delta/\sigma)_{max} < 0.01$	Absolute structure:
$\Delta\rho_{max}$ = 0.19 e Å^{-3}	Flack (1983)
$\Delta\rho_{min}$ = −0.18 e Å^{-3}	Flack parameter = −0.07 (9)

Table 1. Selected geometric parameters (Å, °)

S1—C2	1.747 (1)	N3—C2	1.322 (2)
S1—C5	1.814 (2)	N3—C4	1.451 (2)
S2—C2	1.661 (2)	C4—C5	1.539 (2)
O1—C6	1.323 (2)	C4—C6	1.513 (2)
O2—C6	1.205 (2)		
C2—S1—C5	93.01 (7)	N3—C4—C6	110.2 (1)
C2—N3—C4	118.4 (1)	C5—C4—C6	110.8 (1)
S1—C2—S2	122.00 (8)	S1—C5—C4	105.46 (10)
S1—C2—N3	110.8 (1)	O1—C6—O2	124.6 (1)
S2—C2—N3	127.2 (1)	O1—C6—C4	111.1 (1)
N3—C4—C5	105.7 (1)	O2—C6—C4	124.3 (1)

Table 2. Intermolecular hydrogen bonds and C—H⋯O interactions (Å, °)

D—H⋯A	D—H	H⋯A	D⋯A	D—H⋯A
O1—H1⋯S2^i	0.77 (2)	2.58 (2)	3.318 (2)	160 (2)
N3—H3⋯O2^{ii}	0.82 (2)	2.28 (2)	2.850 (2)	127 (2)
C4—H4⋯O2^{iii}	0.98 (1)	2.69 (1)	3.613 (2)	157 (1)
C4—H4⋯O2^{ii}	0.98 (1)	2.76 (1)	3.004 (2)	95 (1)
C5—H5B⋯O1^{iv}	0.92 (2)	2.80 (1)	3.434 (2)	127 (1)

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

Scan widths were $(1.50 + 0.35\tan\theta)^\circ$ in ω, with a background/scan time-ratio of 0.5. The data were corrected for Lorentz and polarization effects. The Laue group assignment, systematic absences and non-centrosymmetric intensity statistics indicated uniquely space group $P2_12_12_1$ (No. 19); since refinement proceeded well, it was adopted. Fourier difference methods were used to locate the initial H-atom positions. The H atoms were then refined isotropically. The refined C—H distances ranged from 0.92 (2) to 1.01 (1) Å, with a mean value of 0.97 (4) Å; refined O—H and N—H distances are given in Table 2. The maximum effect of extinction is 7.3% of F_o for 006. The maximum positive residual peak is located $\sim$1.0 Å from S1 and C2, and the maximum negative peak is located $\sim$0.6 Å from S2.

Data collection: MSC/AFC Diffractometer Control Software (Molecular Structure Corporation, 1988). Cell refinement: MSC/AFC Diffractometer Control Software. Data reduction: TEXSAN (Molecular Structure Corporation, 1995). Program(s) used to solve structure: SHELXS86 (Sheldrick, 1985). Program(s) used to refine structure: TEXSAN and SHELXL93 (Sheldrick, 1993). Molecular graphics: ORTEPII (Johnson, 1976). Software used to prepare material for publication: TEXSAN.

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1,3,5-Trihydroxybenzene–2,2'-Bipyridyl (1/2): a Hydrogen-Bonded Structure Based on a Stem-and-Leaves Motif

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Abstract

In the 1:2 adduct formed between 1,3,5-trihydroxybenzene (phloroglucinol) and 2,2'-bipyridyl, $C_6H_6O_3 \cdot 2C_{10}H_8N_2$, the triol molecules and half of the bipyridyl molecules are linked into chains by means of O—H$\cdots$N hydrogen bonds, forming a stem, while the other half of the bipyridyl molecules are pendent from this stem, *via* O—H$\cdots$N hydrogen bonds.

Comment

1,3,5-Trihydroxybenzene (phloroglucinol) forms a 2:3 hydrogen-bonded adduct with 4,4'-bipyridyl, with stoi-

chiometry $[C_6H_3(OH)_3]_2 \cdot [C_{10}H_8N_2]_3$ (Coupar *et al.*, 1996). In this adduct, each molecule of the triol component acts as a triple donor in O—H$\cdots$N hydrogen bonds and each molecule of the bipyridyl acts as a double acceptor. Two molecules of each component are linked by hydrogen bonds to form $R_4^4(30)$ rings (Bernstein *et al.*, 1995), and these rings are linked by the third independent bipyridyl unit into a $C_4^4(30)[R_4^4(30)]$ chain-of-rings.

In contrast, cocrystallization of 1,3,5-trihydroxybenzene with 2,2'-bipyridyl yields the 1:2 adduct $C_6H_3(OH)_3 \cdot [C_{10}H_8N_2]_2$, (I). In adduct (I) (Fig. 1), the

(I)
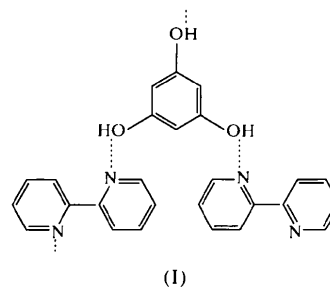
triol molecules all act as triple donors in O—H$\cdots$N hydrogen bonds, but the two independent bipyridyl units behave differently; half of the bipyridyl molecules act as double acceptors in O—H$\cdots$N hydrogen bonds, forming a chain motif with the triol molecules, while the other half of the bipyridyl molecules act as single acceptors of O—H$\cdots$N hydrogen bonds and are pendent from this chain, so forming a stem-and-
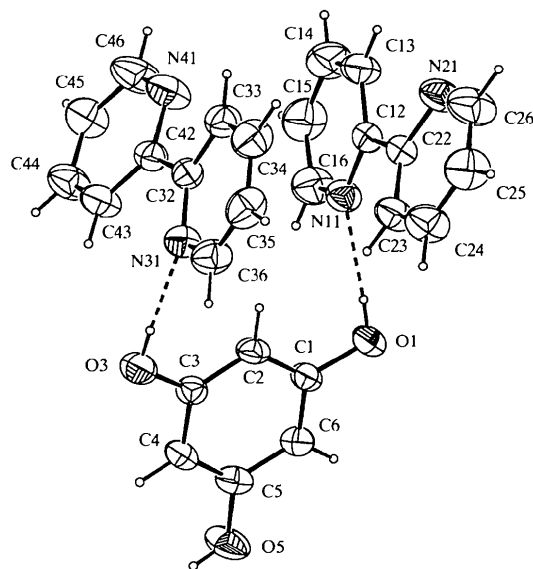

Fig. 1. The asymmetric unit of compound (I), showing the atom-numbering scheme. Displacement ellipsoids are drawn at the 30% probability level.